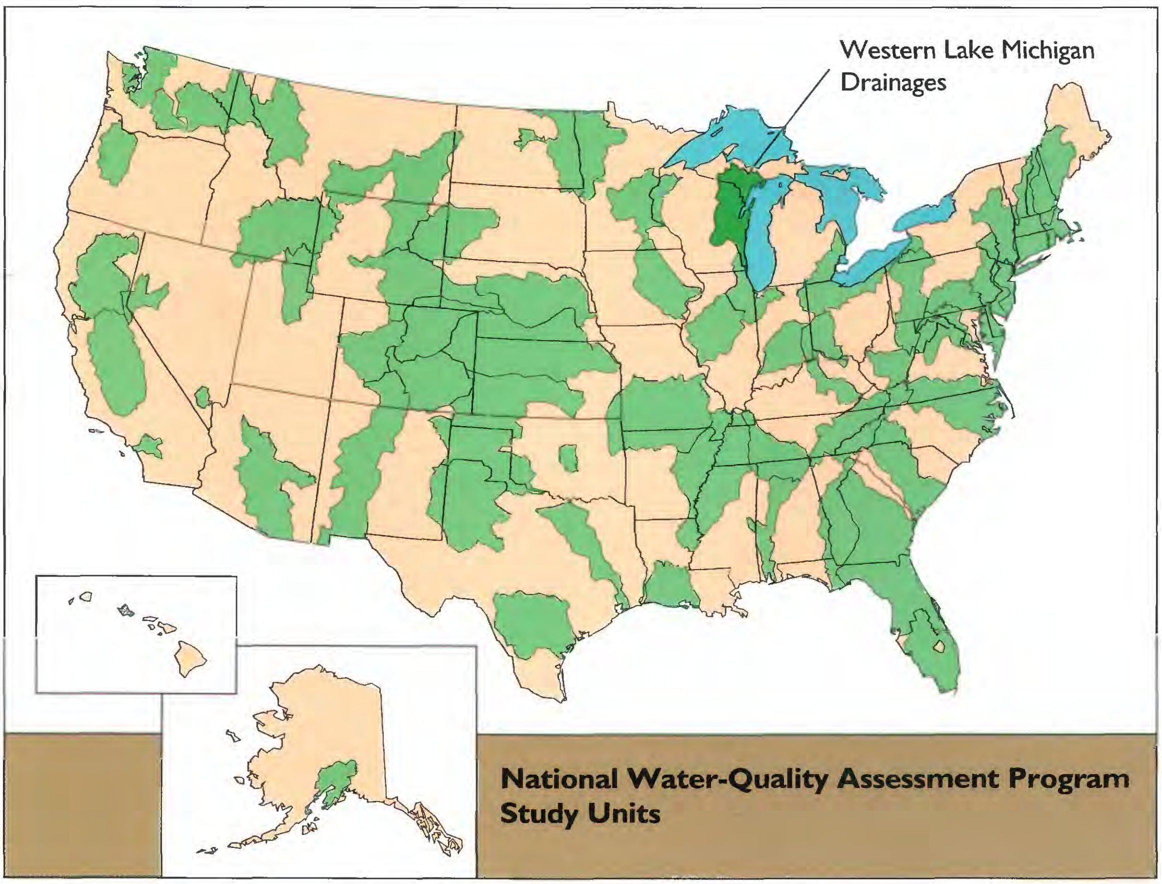
U.S. GEOLOGICAL SURVEY
Water-Resources Investigations Report 96-4012

Water Quality Assessment of the Western Lake Michigan Drainages — Analysis of Available Information on Nutrients and Suspended Sediment, Water Years 1971–90



WATER-QUALITY ASSESSMENT OF THE WESTERN LAKE MICHIGAN DRAINAGES—ANALYSIS OF AVAILABLE INFORMATION ON NUTRIENTS AND SUSPENDED SEDIMENT, WATER YEARS 1971–90

By Dale M. Robertson and David A. Saad

U.S. GEOLOGICAL SURVEY
Water-Resources Investigations Report 96-4012

NATIONAL WATER-QUALITY ASSESSMENT PROGRAM

Madison, Wisconsin
1996

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FOREWORD

The mission of the U.S. Geological Survey (USGS) is to assess the quantity and quality of the earth resources of the Nation and to provide information that will assist resource managers and policymakers at Federal, State, and local levels in making sound decisions. Assessment of water-quality conditions and trends is an important part of this overall mission.

One of the greatest challenges faced by water-resources scientists is acquiring reliable information that will guide the use and protection of the Nation's water resources. That challenge is being addressed by Federal, State, interstate, and local water-resource agencies and by many academic institutions. These organizations are collecting water-quality data for a host of purposes that include: compliance with permits and water-supply standards; development of remediation plans for specific contamination problems; operational decisions on industrial, wastewater, or water-supply facilities; and research on factors that affect water quality. An additional need for water-quality information is to provide a basis on which regional- and national-level policy decisions can be based. Wise decisions must be based on sound information. As a society we need to know whether certain types of water-quality problems are isolated or ubiquitous, whether there are significant differences in conditions among regions, whether the conditions are changing over time, and why these conditions change from place to place and over time. The information can be used to help determine the efficacy of existing water-quality policies and to help analysts determine the need for and likely consequences of new policies.

To address these needs, the U.S. Congress appropriated funds in 1986 for the USGS to begin a pilot program in seven project areas to develop and refine the National Water-Quality Assessment (NAWQA) Program. In 1991, the USGS began full implementation of the program. The NAWQA Program builds upon an existing base of water-quality studies of the USGS, as well as those of other Federal, State, and local agencies. The objectives of the NAWQA Program are to:

- Describe current water-quality conditions for a large part of the Nation's freshwater streams, rivers, and aquifers.
- Describe how water quality is changing over time.
- Improve understanding of the primary natural and human factors that affect water-quality conditions.

This information will help support the development and evaluation of management, regulatory, and monitoring decisions by other Federal, State, and local agencies to protect, use, and enhance water resources.

The goals of the NAWQA Program are being achieved through ongoing and proposed investigations of 60 of the Nation's most important river basins and aquifer systems, which are referred to as study units. These study units are distributed throughout the Nation and cover a diversity of hydrogeologic settings. More than two-thirds of the Nation's freshwater use occurs within the 60 study units and more than two-thirds of the people served by public water-supply systems live within their boundaries.

National synthesis of data analysis, based on aggregation of comparable information obtained from the study units, is a major component of the program. This effort focuses on selected water-quality topics using nationally consistent information. Comparative studies will explain differences and similarities in observed water-quality conditions among study areas and will identify changes and trends and their causes. The first topics addressed by the national synthesis are pesticides, nutrients, volatile organic compounds, and aquatic biology. Discussions on these and other water-quality topics will be published in periodic summaries of the quality of the Nation's ground and surface water as the information becomes available.

This report is an element of the comprehensive body of information developed as part of the NAWQA Program. The program depends heavily on the advice, cooperation, and information from many Federal, State, interstate, Tribal, and local agencies and the public. The assistance and suggestions of all are greatly appreciated.

Robert M. Hirsch

Robert M. Hirsch
Chief Hydrologist

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CONVERSION FACTORS AND ABBREVIATED WATER-QUALITY UNITS

Multiply	By	To Obtain
millimeter (mm)	0.03937	inch
centimeter (cm)	0.3937	inch
meter (m)	3.281	foot
hectare (ha)	2.471	acre
kilometer (km)	.6214	mile
square kilometer (km^2)	.3861	square mile
cubic meter per second (m^3/s)	35.3107	cubic foot per second
kilogram (kg)	2.2045	pound
liter (L)	.2642	gallon
milligram (mg)	.000002205	pound
kilogram per hectare (kg/ha)	.89218	pound per acre
liters per second (L/s)	.0353	cubic feet per second
cubic meter per day (m^3/d)	.1834	gallon per minute
centimeter per year (cm/yr)	0.3937	inch per year

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

°F = 1.8 (°C) + 32.

Abbreviated water-quality units: Chemical concentrations and water temperature are given in metric units. Chemical concentration is given in milligrams per liter (mg/L) or micrograms per liter (µg/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.

MISCELLANEOUS ABBREVIATIONS

Ag	Agriculture (where followed by number, denotes a particular RHU)
AF	Agriculture/forest (where followed by number, denotes a particular RHU)
BFS	Basic Fixed Sites
F	Forest (where followed by number, denotes a particular RHU)
GBMSD	Green Bay Metropolitan Sewerage District
GIN	Groundwater Information Network
MCL	Maximum Contaminant Level
MDL	Highest reported Minimum Detection Limit
MMSD	Milwaukee Metropolitan Sewerage District
as N	as quantified as measured nitrogen
NAC	"National average" surface-water concentration
NADP	National Atmospheric Deposition Program
NASQAN	National Stream-Quality Accounting Network
NAWQA	National Water-Quality Assessment
as NO_3	as quantified as measured nitrate
NWIS	National Water-Information System
NWQL	National Water-Quality Laboratory
as P	as quantified as measured phosphorus
PCB's	Polychlorinated biphenyls
as PO_4	as quantified as measured phosphate
RHU	Relatively Homogenous Unit
Q	Stream discharge
QA/QC	Quality Assurance/Quality Control
STORET	Storage and Retrieval System
T	Time of the year in radians
U	Urban (where followed by number, denotes a particular RHU)
USEPA	United States Environmental Protection Agency
USGS	U.S. Geological Survey
VOC's	Volatile organic compounds
WATSTORE	Water Storage and Retrieval System
WDNR	Wisconsin Department of Natural Resources
WMIC	Western Lake Michigan Drainages
WSLOH	Wisconsin State Laboratory of Hygiene
WUDS	Water-Use Data System

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Water-Quality Assessment of the Western Lake Michigan Drainages—Analysis of Available Information on Nutrients and Suspended Sediment, Water Years 1971–90

By Dale M. Robertson *and* David A. Saad

EXECUTIVE SUMMARY

In 1986, Congress appropriated funds for the U.S. Geological Survey (USGS) to develop the pilot phase of the National Water-Quality Assessment (NAWQA) Program. The long-term goals of this program are to (1) provide a nationally consistent description of current water-quality conditions for a large part of the Nation's water resources; (2) define long-term trends (or lack of trends) in water quality; and (3) identify, describe, and explain, as possible, the major factors that affect the observed water-quality conditions and trends.

To fulfill the goals of the NAWQA program, the USGS plans to examine 60 areas (study units) across the United States during full implementation of the program. In 1991, the NAWQA program went into full implementation with the intensive investigation of 20 of these study units; one of these study units is the Western Lake Michigan Drainages (WMIC) study unit.

The Western Lake Michigan Drainages Study Unit

The WMIC study unit drains 51,500 km^2 (square kilometers) of Wisconsin and part of the Upper Peninsula of Michigan (Upper Michigan) emptying into Lake Michigan and Green Bay. The study unit is bounded on the south by the Illinois State line and extends north through Wisconsin and Upper Michigan to approximately 50 km (kilometers) north of Escanaba, Mich. Drainage basins of nine major rivers and numerous smaller tributaries are contained in the WMIC study unit. The northern half of this area is dominated by forests, and the southern half is dominated by agriculture, primarily dairy-farm operations.

Staff from each of the NAWQA study units, during the early years of investigation, examine, assemble, and summarize available water-quality and ancillary information in retrospective reports. The purposes of this report are to (1) provide information that will assist in designing the sampling components of the intensive phase of the WMIC study unit; (2) propose preliminary conclusions and hypotheses that can be further tested using data collected during the intensive phase; (3) describe the spatial and temporal distribution and the availability of nutrient and suspended-sediment data collected within the study unit (and the gaps in the available data); (4) describe the natural and anthropogenic factors affecting the spatial patterns in concentrations and loads within the study unit; (5) describe long-term trends (or lack of trends) in water quality and provide data for future examinations for trends; and (6) provide data to the NAWQA national synthesis team, who will assemble data from the individual study units and interpret this information from a national perspective.

Amount and Geographical Distribution of Data

This retrospective report summarizes the nutrient (phosphorus and nitrogen species) and suspended-sediment data collected in the surface water and ground water of the WMIC study unit during the 1971–90 water years[1]. Surface-water samples were collected at 712 sites; total phosphorus was the constituent sampled at the most sites (561 sites). Surface-water samples

[1]Water year is the period from October 1 of a given year through September 30 of the succeeding year and is designated by the calender year in which it ends.

were collected relatively uniformly throughout the year and range of streamflows; however, most samples were collected in areas integrating the effects of various environmental and anthropogenic factors. Few surface-water samples were collected in headwater areas with relatively uniform land use, surficial deposits, and bedrock types, and in the southwest and northwest parts of the study unit. Ground-water samples were collected from 919 wells; dissolved nitrite plus nitrate was the constituent sampled at the most wells (789 wells). Ground-water samples were collected primarily in the southern two-thirds of the study unit; however, samples analyzed for total ammonia, total phosphorus, and total orthophosphate were collected mostly in Upper Michigan. Ground-water sites were generally sampled only once during the entire period.

Water-Quality Conditions

Land use was the primary factor affecting the distribution of nutrient and suspended-sediment concentrations and total export in surface water. Total nitrogen and total phosphorus concentrations were directly related to the input of nutrients associated with the specific land use in the drainage basins, especially from fertilizers, manure, and additional fixation (not accounted for in manure inputs); concentrations decreased from agricultural to urban to forested areas. Nutrient concentrations in ground water were also related to land use; however, well depth and texture of surficial deposits also were important. Nutrient concentrations were inversely related to well depth; generally higher in clayey surficial deposits than in sand and gravel deposits, with the exception of dissolved nitrite plus nitrate, for which the opposite was true.

The total export of phosphorus, nitrogen, and suspended sediment was directly related to land use: the agricultural areas in the southern half of the study unit contributed approximately 80 percent of the total load of phosphorus, 70 percent of the total load of nitrogen, and 75 to 90 percent of the total load of suspended sediment. Although point sources of nutrients have been significantly controlled, point sources of phosphorus may still contribute a significant proportion of the total export, especially during dry years in the Fox and Milwaukee River Basins.

Concentrations of nitrite plus nitrate in agricultural and urban areas (median concentrations of 0.92 and 0.44 mg/L, respectively) in the surface water of the WMIC study unit were similar to the "national average" surface-water concentrations (NAC) (median concentrations of 0.72 and 0.47 mg/L, respectively); however, the concentrations in forested areas (median concentration of 0.09 mg/L) were lower than the NAC (0.21 mg/L). Concentrations exceeding the U.S. Environmental Protection Agency (USEPA) 10-mg/L Maximum Contamination Level (MCL) for dissolved nitrite plus nitrate were found only in agricultural areas. Only two samples from mixed (downstream, integrator) land-use areas exceeded the 1-mg/L MCL for dissolved nitrite.

Total phosphorus concentrations were less than the NAC for their respective land uses. Median concentrations were 0.13 mg/L for agricultural areas (0.23 mg/L, NAC), 0.11 mg/L for urban areas (0.20 mg/L, NAC), and 0.02 mg/L for forested areas (0.05 mg/L, NAC). Concentrations exceeding the 0.1-mg/L suggested limit by the USEPA for total phosphorus were commonly found in all land-use categories, except forested areas, where this limit was sporadically exceeded.

Suspended-sediment concentrations in surface water were highest in urban areas, moderate in agricultural areas, and lowest in forested areas. These concentrations were quite different from the NAC. Median concentrations were 148 mg/L (25 mg/L, NAC) in urban areas, 25 mg/L (131 mg/L, NAC) in agricultural areas, and 4 mg/L (19 mg/L, NAC) in forested areas. The differences in the concentrations from the forested and agricultural areas of the WMIC study unit and those from the NAC may have been a result of upstream dams on many of the major rivers through these areas within the WMIC.

Dissolved nitrate and organic nitrogen were the primary forms of nitrogen in surface water for all land-use categories, except urban, where ammonia was also an important fraction. Concentrations of dissolved nitrate and organic nitrogen were highest in agricultural areas, moderate in urban areas, and lowest in forested areas. Concentrations of total and dissolved ammonia and dissolved nitrite were highest in urban areas, moderate in agricultural areas, and lowest in forested areas. Dissolved nitrate was the primary form of nitrogen found in ground water in forested and agricultural/forested areas; however, dissolved ammonia was also important in urban and agricultural areas. Forested areas also had significant fractions as organic nitrogen and particulate ammonia.

Dissolved inorganic (dissolved reactive) phosphorus and particulate phosphorus were the primary forms of phosphorus in surface water for all land-use categories, except agriculture, where dissolved organic phosphorus also was important. Concentrations of dissolved phosphorus, and total orthophosphate and dissolved orthophosphate were highest in agricultural areas, moderate in urban areas, and lowest in forested areas. The few phosphorus samples precluded the partitioning of phosphorus for each land-use category for ground water.

To determine how various environmental and anthropogenic factors affect the distribution of nutrients and suspended sediment, samples were subdivided into areas of similar land use, which were further subdivided into areas of similar texture of surficial deposit and bedrock type. Therefore, samples either represented specific indicator areas referred to as "relatively homogeneous units" (RHU's) or integrator areas representing several RHU's. Samples from specific RHU's indicated no significant difference in concentration caused by texture of surficial deposit and bedrock type for dissolved nitrite plus nitrate, Kjeldahl nitrogen, and total ammonia. Significantly higher dissolved nitrite concentrations were found in surface water surrounded by agriculture on sandy deposits than those surrounded by agriculture on clayey deposits. Significantly lower concentrations of dissolved ammonia were found in areas with clayey surficial deposits than in areas with sandy deposits, possibly caused by clayey deposits preferentially adsorbing ammonia, which is positively charged at most ambient pHs, and therefore, may be less readily transferred to streams than other nitrogen species.

No statistical differences were detected in surface water from RHU's of similar land use for concentrations of dissolved, dissolved inorganic, and total orthophosphate. Total phosphorus and dissolved orthophosphate concentrations were significantly higher in areas with sandy deposits than in areas with clayey deposits, possibly because of differences in the biological communities, which were not examined. Total phosphorus and dissolved orthophosphate concentrations were also higher in areas with carbonate bedrock than areas with sandstone bedrock, possibly because of the differences in the phosphorus content of the bedrock.

Trends in Water Quality

During 1971–90 water years, no significant ($\rho < 0.10$) trends were found in dissolved nitrate plus nitrate concentrations. In general, Kjeldahl nitrogen concentrations increased at almost all of the sites examined; however, this upward trend was significant ($\rho < 0.15$) only for the Ford, Fox, Manitowoc, and Milwaukee Rivers. The increase in Kjeldahl nitrogen concentrations in association with no change in dissolved nitrite plus nitrate concentrations indicates an increase in total-nitrogen concentrations in rivers draining these areas.

During 1980–90, few changes in total phosphorus concentrations were found across the study unit; however, when the 1971–79 data were included, significant ($\rho < 0.10$) downward trends in concentrations were found for the Popple and Milwaukee Rivers. Significant ($\rho < 0.01$) downward trends were also found in dissolved phosphorus concentrations for the Fox and Milwaukee Rivers. Similar downward trends were found in dissolved orthophosphate concentrations, but these were not statistically significant. The downward trend in phosphorus concentrations, which were most significant in the southern part of the study unit, may have been caused by the reduction in phosphorus in detergents and by improvements in sewage-treatment facilities.

During 1980–90, suspended-sediment concentrations increased or remained unchanged at all of the sites, except the Ford River; however, the only significant ($\rho < 0.10$) increase occurred in the Popple River. When the 1971–79 data were included, the increases in the southern half of the study unit (agricultural and urban areas) became more significant, but the increase in the Popple River was no longer apparent.

Implications for Future NAWQA Sampling

The results and preliminary conclusions from this study were used to assist in the initial selection of locations for future sampling to be done within the WMIC NAWQA study unit. Eight Basic Fixed Sites (BFS's) representing specific RHU's were chosen for further examination of the observed differences in surface-water nutrient concentrations caused by differences in land use and surficial-deposit texture. Three BFS's representing an integration of various factors were chosen to represent the diverse conditions throughout the study unit, as well as the major contributors of nutrients and suspended sediment. The location of two land-use surveys were chosen to examine how agricultural land use affects shallow ground-water quality. The location of a flow-path study was chosen to examine changes in nutrients and pesticides along a ground-water flow path in an agricultural setting.

INTRODUCTION

In 1986, Congress appropriated funds for the U.S. Geological Survey (USGS) to develop the pilot phase of the National Water-Quality Assessment (NAWQA) Program. In 1991, the NAWQA program went into full implementation. The long-term goals of this program are to (1) provide a nationally consistent description of current water-quality conditions for a large part of the Nation's water resources; (2) define long-term trends (or lack of trends) in water quality; and (3) identify, describe, and explain, as possible, the major factors that affect the observed water-quality conditions and trends (Hirsch and others, 1988).

In the pilot phase of the program, seven areas (study units) were selected to test and further develop assessment concepts: four study units concentrated on surface water (the Yakima River Basin in Washington, the Lower Kansas River Basin in Kansas and Nebraska, the Kentucky River Basin in Kentucky, and the Upper Illinois River Basin in Illinois, Indiana, and Wisconsin), and three concentrated on ground water (the Carson Basin in Nevada and California, the Central Oklahoma aquifer in Oklahoma, and the Delmarva Peninsula in Delaware, Maryland, and Virginia).

To fulfill the goals of the NAWQA program, the USGS plans to examine 60 areas (study units) across the United States during full implementation of the program (fig. 1). These study units represent approximately 60 to 70 percent of the Nation's water use and population. Assessment of surface- and ground-water quality in each of the study units is planned to be done on a rotational rather than a continuous basis. Only a subset of the study units will be intensively examined at any given time. Project teams in 20 of the study units began intensive investigations in 1991: one of these study units is the Western Lake Michigan Drainages (WMIC) study unit. During the first intensive phase (lasting about 5 years), each study unit is to examine, assemble, and summarize available water-quality and ancillary information in retrospective reports, one being a report describing nutrients and suspended sediments. Intensive data collection will be done for 3 years during this phase. After the intensive data-collection phase is completed, low-intensity data collection is planned to begin at a small subset of sampling sites while data collected during intensive sampling are interpreted and summarized in reports. Part of the interpretation will involve comparisons of the data presented in the retrospective reports with data collected during the intensive sampling. A second group of study units will begin during the intensive data-collection phase of the first group; therefore, only 20 study units will be in the intensive data-collection phase at a time.

The information collected and (or) assembled by the NAWQA program and interpretations of the data are to be made available to water managers, policymakers, and the general public. This information not only will provide a description of the water quality within individual study units and in a large area of the country, but also will help delineate the major factors that affect water quality. In addition, the data will give policy makers and resource managers a basis for evaluating the effectiveness of management programs and estimating the effects of contemplated changes in land use.

Purpose and Scope

The purposes of this report are to (1) provide information that will assist in designing the sampling components of the intensive phase of the WMIC study unit; (2) propose preliminary conclusions and hypotheses that can be further tested by means of data collected during the intensive phase; (3) describe the spatial and temporal distribution and the availability of nutrient and suspended-sediment data collected within the WMIC study unit (and the gaps in the available data); (4) describe the natural and anthropogenic factors affecting the spatial patterns in concentrations and loads within the study unit; (5) describe long-term trends (or lack of trends) in water quality and provide data for future examinations for trends; and (6) provide data to the NAWQA national synthesis team, who will assemble data from the individual study units and interpret this information from a national perspective.

The scope of this report includes (1) a compilation of the available surface- and ground-water data for dissolved nitrite plus nitrate, dissolved nitrite, total ammonia plus organic nitrogen, total and dissolved ammonia, total and dissolved phosphorus, total and

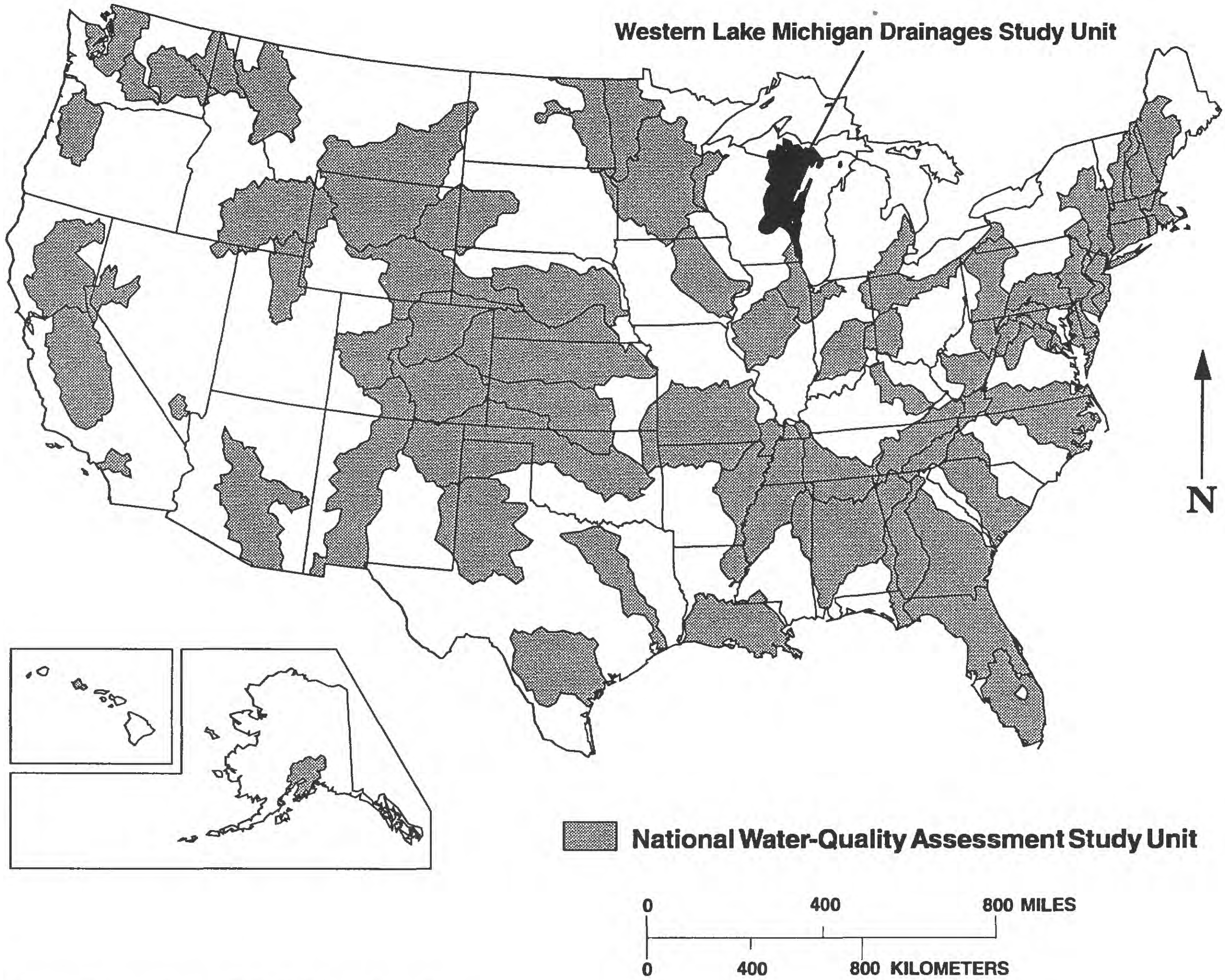


Figure 1. Locations of NAWQA study units.

dissolved orthophosphate, and suspended sediment collected within the WMIC study unit from water years 1971–90; (2) an assessment of the available data with respect to land use, texture of surficial deposits, bedrock type, and atmospheric and anthropogenic loading; (3) an assessment of trends in water quality and loads of nitrogen, phosphorus, and suspended sediment at selected sites; and (4) a discussion of the implications and suggestions for future sampling within the WMIC study unit.

DESCRIPTION OF THE WESTERN LAKE MICHIGAN DRAINAGES STUDY UNIT

Many factors potentially affect the distribution of nutrients and suspended sediments in surface water and ground water. Therefore, the general description of the WMIC study unit given in this section emphasizes the factors thought to be the most influential. In addition, the point and nonpoint sources of nutrients added onto the land and into the water are described and estimated. Finally, the water-quality problems are summarized.

Location and Surface-Water Features

The WMIC study unit is bounded on the south by the Illinois State line, and extends north through Wisconsin and Upper Peninsula of Michigan (Upper Michigan) to approximately 50 km north of Escanaba, Mich. (fig. 2). Nine major rivers and numerous smaller tributaries are contained in the study unit. These rivers drain 51,500 km^2 of Wisconsin and part of Upper Michigan

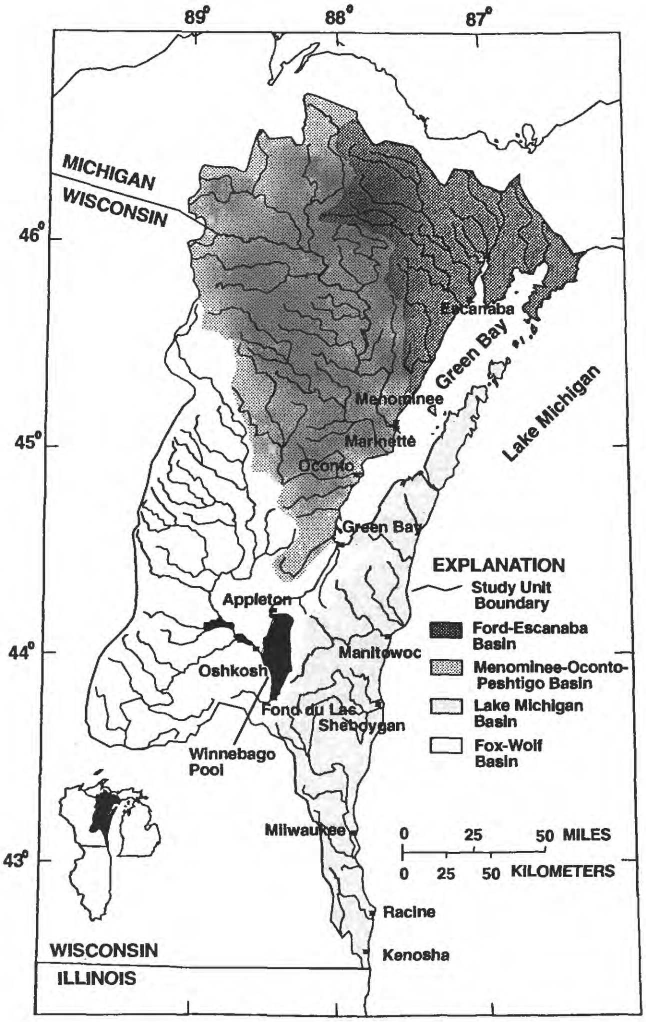


Figure 2. Location, major cities, hydrologic subunits, and watershed boundary of the Western Lake Michigan Drainages NAWQA study unit.

emptying into Lake Michigan and Green Bay. The study unit includes all of hydrologic subregion 0403 and part of hydrologic subregion 0404 as defined by the U.S. Water Resources Council (Seaber and others, 1984).

The nine major rivers that drain the study unit (from north to south) are the Escanaba and Ford Rivers in Upper Michigan; the Menominee River, which partly defines the state boundary that divides Wisconsin and Michigan; the Peshtigo and Oconto Rivers and the Fox/Wolf River system, which drain into Green Bay; and the Manitowoc, Sheboygan, and Milwaukee Rivers, which drain directly into Lake Michigan.

Several large natural lakes are present in the study unit. The largest lakes in the study unit are part of the Winnebago Pool [(Lake Winnebago (555 km^2), Lake Poygan (44 km^2) and Lake Butte des Morts (36 km^2)]. All three lakes are part of the Fox/Wolf River system.

Climate

Because the WMIC study unit is located in north-central United States, it has a temperate, continental climate associated with a large annual range in air temperature and little monthly variation in precipitation. The study unit is also in the mid-latitude belt, marked by large seasonal changes in the solar-zenith angle and day length that together produce a significant north-south air-temperature gradient (Wisconsin Agricultural Statistics Service, 1987). The north-south air-temperature gradient and the seasonal range in temperatures, however, are modified by the neighboring Great Lakes.

Air Temperature

Average annual and seasonal air temperatures differ widely across the study unit. Average annual temperature ranges from approximately 9°C in the southern tip of the study unit to approximately 4°C in the northern parts (Wisconsin Agricultural Statistics Service, 1987). January is usually the coldest month of the year; for the study unit as a whole, the average January air temperature is approximately -9.5°C, and the range is from about -6.5°C in the southern tip to about -12°C in the northwestern corner (Wendland and others, 1992). April is a month of transition from cold winter to warm summer air temperatures. The average temperature across the study unit in April is approximately 6°C, and the range is from about 8°C in the south to about 5.5°C in the north. July is usually the warmest month of the year; the average air temperature for the study unit as a whole is approximately 20°C, and the range is from 21.5°C in the south to 18.5°C in the north. October is a month of transition back to colder winter conditions. The average air temperature across the study unit in October is approximately 9°C, and the range is from approximately 11°C in the south to 7°C in the north.

Precipitation

Mean annual precipitation (for 1951–80) ranges from approximately 71cm (28 in.) in the central part of the study unit to more than 81 cm (32 in.) near Lake Superior and in the southernmost areas (fig. 3) (Wendland and others, 1985). Precipitation varies seasonally, and about 60 percent falls from May through September. In fig. 4, average total monthly precipitation is shown for three sites in the study unit: Escanaba (north), Green Bay (central) and Racine (south). During summer, approximately 8 to 10 cm of precipitation falls on average per month. Less precipitation falls in the winter, especially during January and February, when only about 2 to 4 cm falls per month, almost all as snow. Average total snowfall ranges from approximately 100 cm/yr in far southern areas to 300 cm/yr in the far northern areas (Wendland and others, 1992).

Annual precipitation is highly variable from year to year. Annual departures during 1971–90 ranged from about 40 percent more than the annual average in Racine in 1972 and 1986 to about 30 percent less than the annual average in Oconto in 1987 (fig. 5). During this period, two extended droughts occurred in the study unit. The first drought was in 1976–77 and affected the central and southern areas. The second drought was in 1987–89 and affected primarily the central area. Floods are of much shorter duration and are difficult to detect in annual summaries. During this period, extensive floods occurred in spring of 1973 (affecting the central area), summer of 1986 (affecting the southern area), and summer of 1990 (affecting the central area).

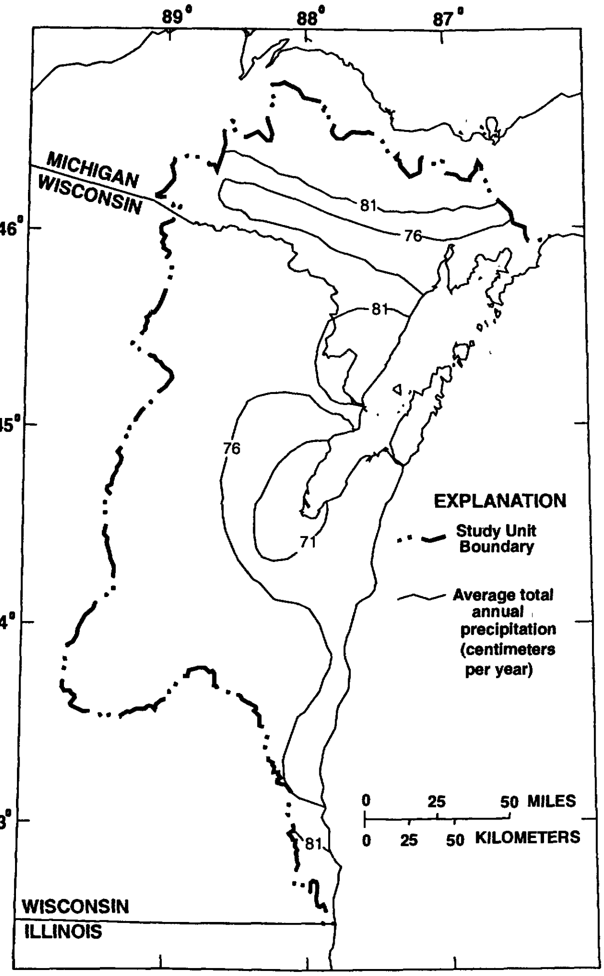


Figure 3. Average total annual precipitation (in centimeters) in the Western Lake Michigan Drainages study unit (from Wendland and others, 1985).

Physical Features

Surface-Water Hydrology

The study unit contains several individual drainage basins emptying into Green Bay or directly into Lake Michigan. These basins can be grouped into four main subunits: the Ford-Escanaba Basin, the Menominee-Oconto-Peshtigo Basin, the Fox-Wolf Basin, and the direct Lake Michigan Basin (fig. 2). Streamflow in most reaches of the rivers within the Ford-Escanaba and Menominee-Oconto-Peshtigo Basins is perennial, whereas streamflow ceases in many of the headwater areas of the Fox-Wolf and direct Lake Michigan Basins. The absence of flow in summer is primarily a result of minimal ground-water discharge from the tight, clay, surficial deposits that are found in these areas.

Annual runoff ranges from less than 20 cm (8 in.) south of Lake Winnebago to more than 38 cm (15 in.) in the far northern areas of the study unit (Hindall, 1976; Gebert and others, 1987) (fig. 6). The monthly and seasonal variabilities among sites are shown for one site from each of the four main subunits in fig. 7. Streamflow has a strong seasonal component. Most flow is associated with snowmelt in March and April. Lowest flow occurs in midwinter (January and February) and midsummer (July and August). The highest monthly variability occurs during high-flow periods. Average annual runoffs (computed by summing the mean monthly streamflows and dividing by drainage

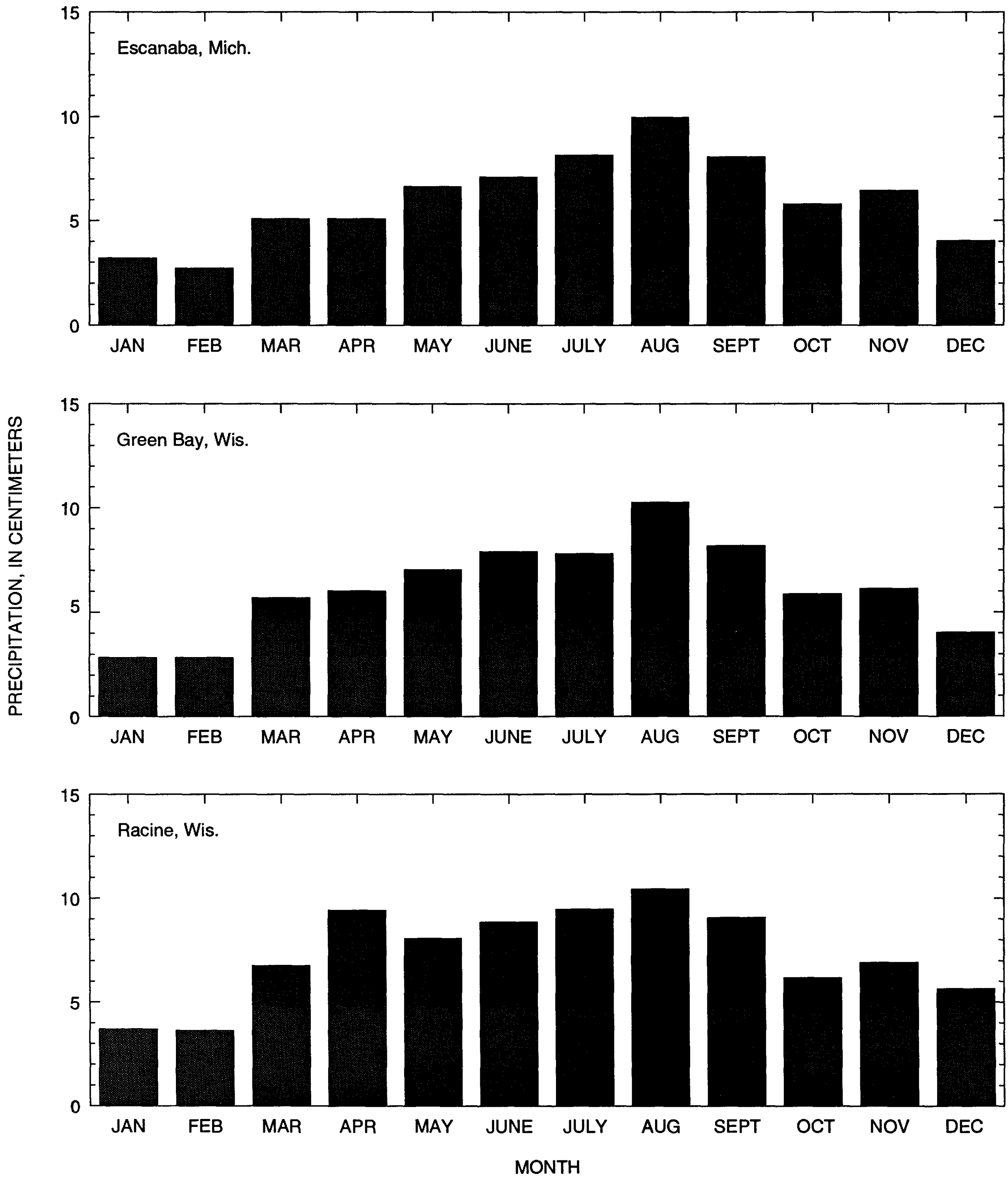


Figure 4. Average total-monthly precipitation for three locations in the Western Lake Michigan Drainages study unit. [Averages computed for water years 1971–90.]

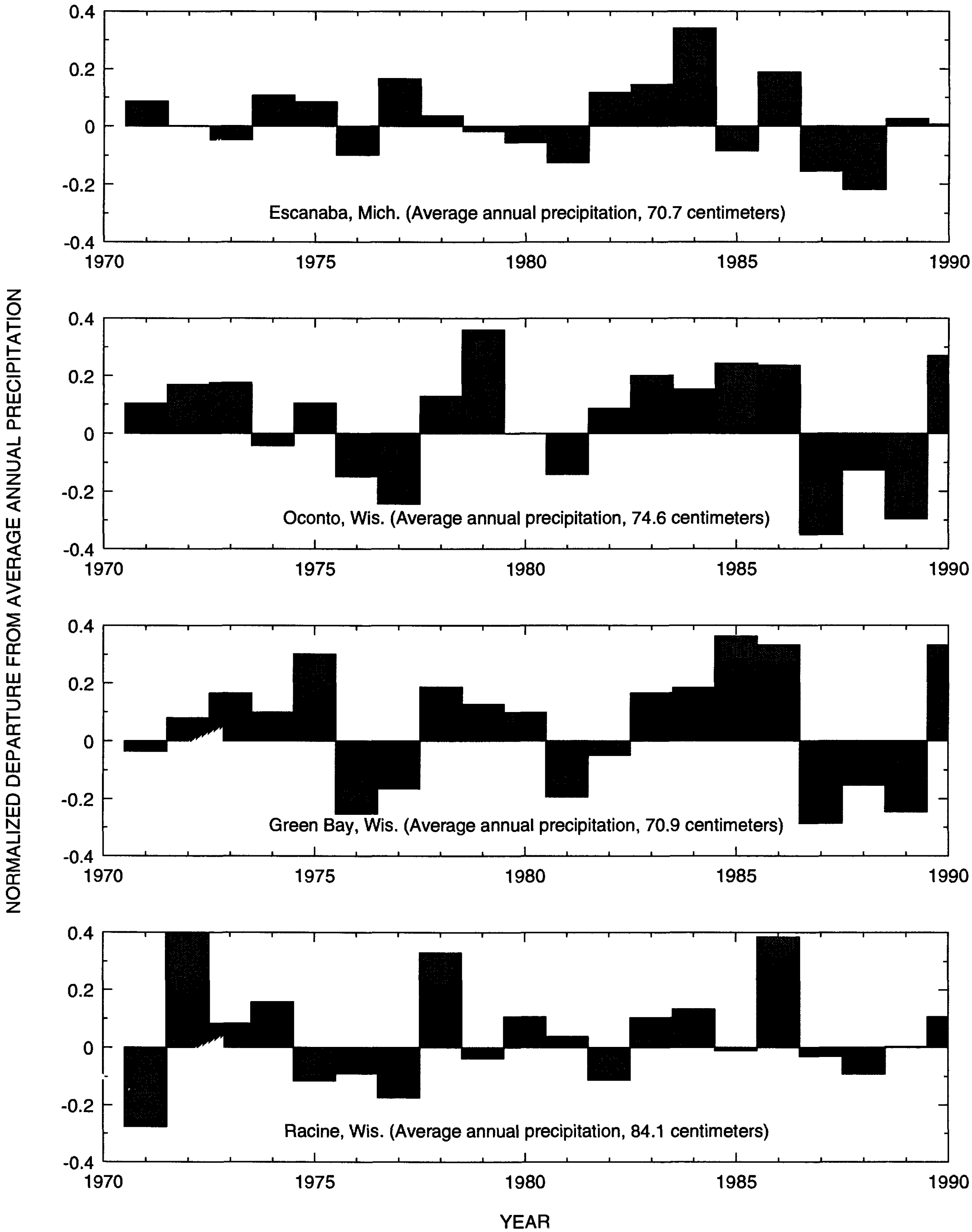


Figure 5. Normalized annual departures from the average annual precipitation computed from 1911–90 for four locations in the Western Lake Michigan Drainages study unit. [Normalized departures were calculated as annual total precipitation divided by the long-term average.]

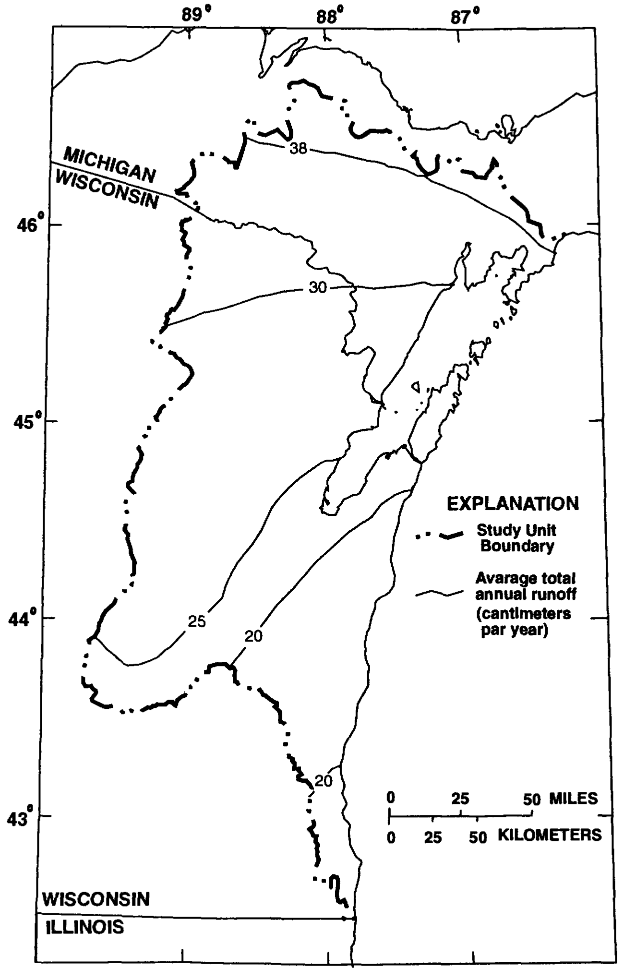


Figure 6. Average annual runoff (in centimeters) in the Western Lake Michigan Drainages study unit (from Gebert and others, 1987).

areas) for these four sites are the following: Escanaba, 34.0 cm; Oconto, 29.2 cm; Wolf, 29.5 cm; and Milwaukee, 27.7 cm. These averages agree closely with those estimated by Hindall (1976), and Gebert and others (1987).

Streamflows of many rivers are affected by dams associated with major or minor impoundments. The effect of dams is to dampen the seasonal variability in flow, especially by increasing the low flows that normally occur during winter. This effect can be seen by comparing sites on the Fox-Wolf River system, one of the most regulated rivers in the study unit. A comparison of flows at the Wolf River at New London (relatively unregulated above Lake Winnebago) with the Fox River at Wrightstown (highly regulated downstream from Lake Winnebago) demonstrates this reduction in seasonal variability downstream from Lake Winnebago because of increasing winter flow (fig. 8). Low summer flows, however, still occur downstream from Lake Winnebago.

Streamflow in rivers in areas within clay surficial deposits is more seasonally variable than in rivers in areas of coarser deposits, owing to very low flow in summer and winter. A comparison between the Wolf River at New London (sand and gravel surficial deposits) and the Manitowoc River at Manitowoc (clay surficial deposits) demonstrates this difference (fig. 8). Many of the upstream reaches of the Manitowoc River freeze solid in winter and dry up completely in summer.

Variability in annual streamflow is shown for one site in each of the subunits in figure 9. Fox River at Wrightstown is used for the Fox-Wolf River Basin. Normalized departure in annual streamflow is variable—perhaps more variable—than normalized departures in annual precipitation (fig. 5). Throughout the study unit, annual precipitation rarely was more than 30 percent different than the long-term annual mean; however, annual runoff occasionally was more than 50 percent different than the long-term mean. Only the Escanaba River did not have a year in which an annual departure during this period did not exceed 55 percent of the annual average. In general, changes in streamflow correspond to changes in precipitation; however, the responses of streamflows were delayed because of ground-water storage. For example, during the two extended droughts in 1976–77 and 1987–89, streamflows were primarily affected only in the second and third years of the drought.

Normalized departures (from the 1911–90 average) in the annual streamflow at Milwaukee during 1971–90 demonstrate the effects of a long-term change in streamflow. Despite many years of average or below-average precipitation during the period, deviations in streamflow were above average for all years except 1977 (a major drought). The increased urbanization around the Milwaukee River and the corresponding decreases in infiltration and ground-water storage may have resulted in the long-term trend, as well as more annual variability and a change in the rainfall-runoff relations. If normalized departures from the 1971–90 period were used for the Milwaukee River, several annual departures would still exceed 60 percent of the long-term mean.

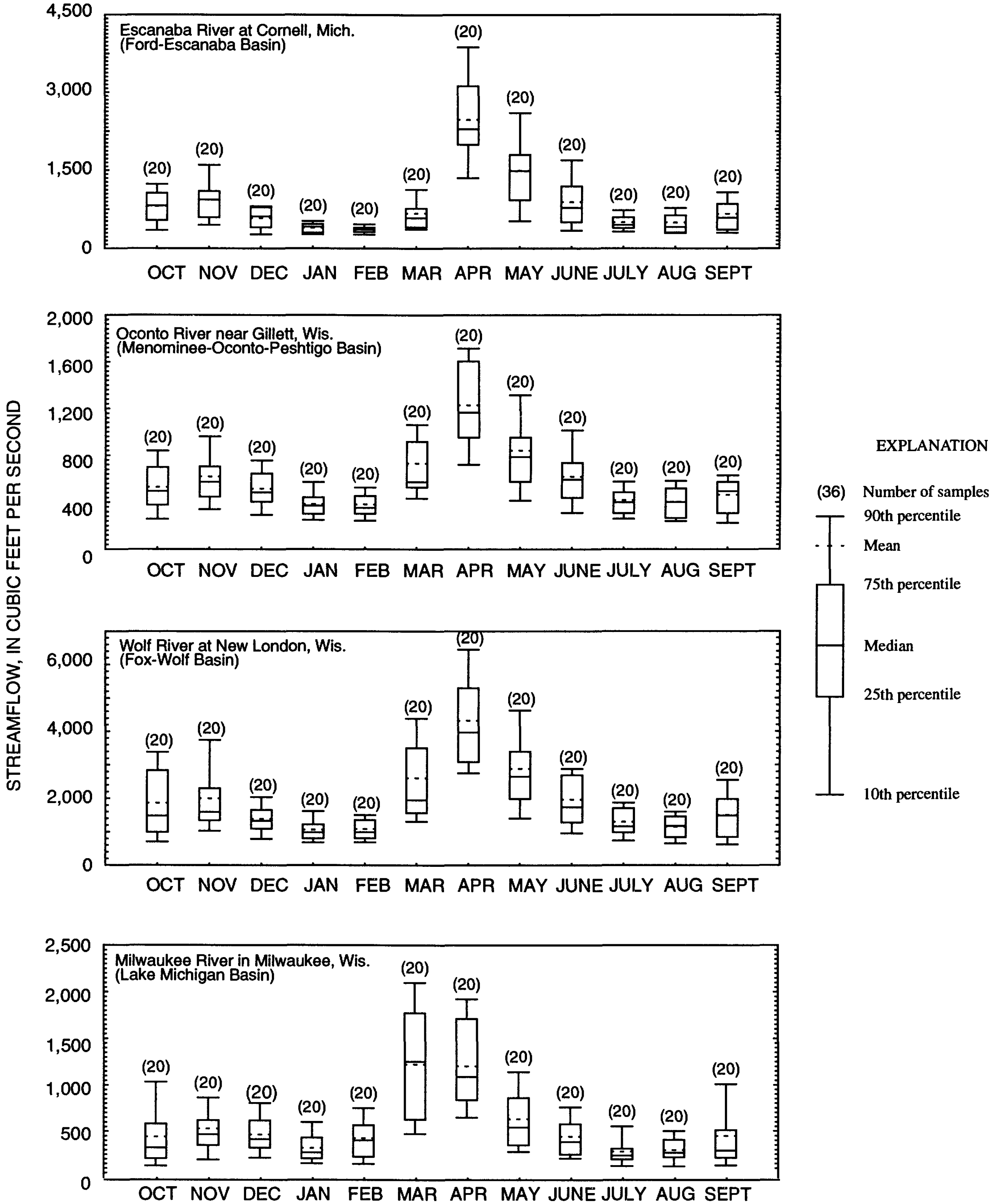


Figure 7. Boxplots of streamflow, by month, for four locations in the Western Lake Michigan Drainages study unit, water years 1971–90.

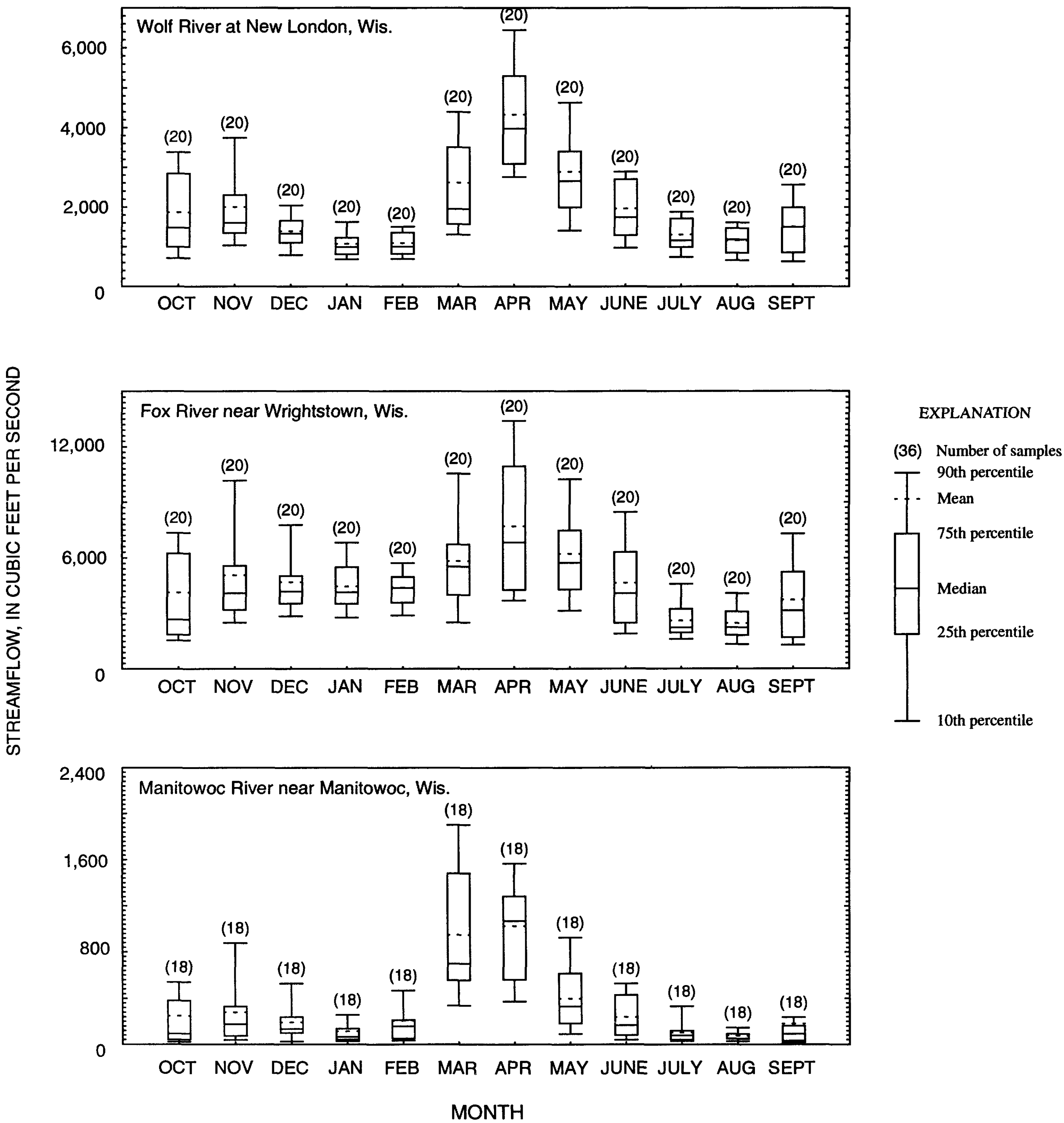


Figure 8. Boxplots of streamflow, by month, for three locations in the Western Lake Michigan Drainages study unit, water years 1971–90.

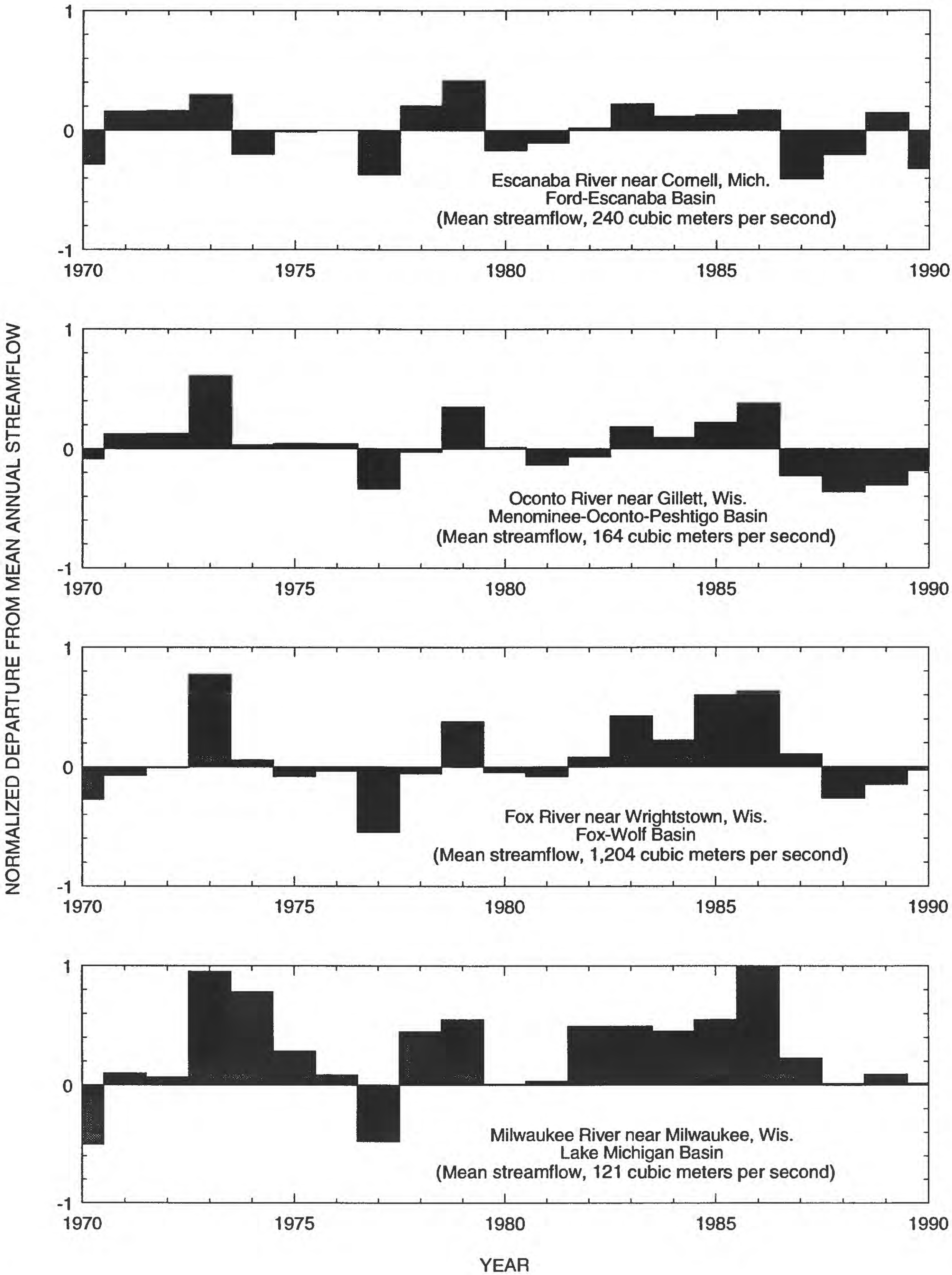


Figure 9. Normalized annual departures from the mean annual streamflow computed for 1911–90 at four sites in the Western Lake Michigan Drainages study unit. [Normalized departures were computed as annual mean discharge divided by the long-term annual mean discharge.]

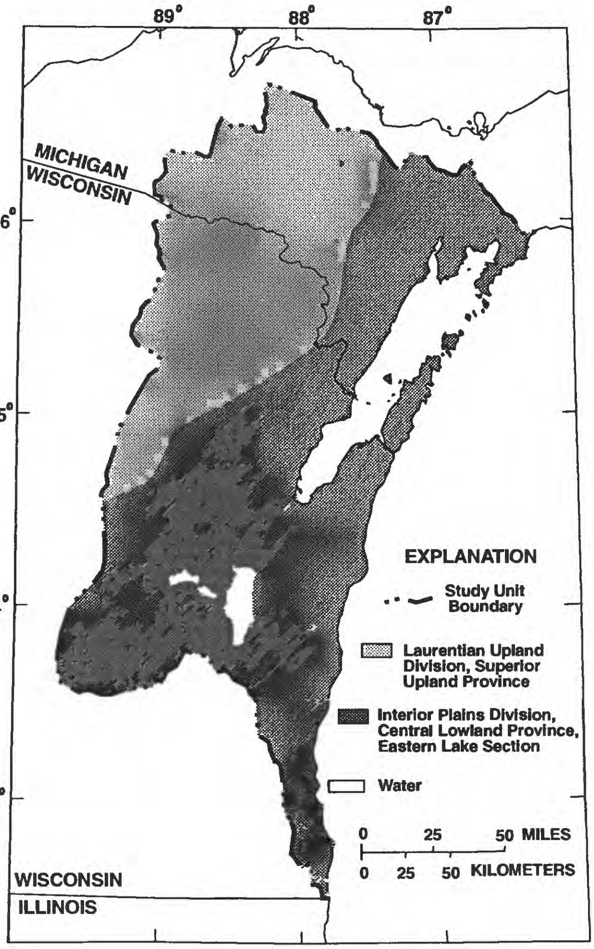


Figure 10. Physiographic provinces of the Western Lake Michigan Drainages study unit. [Based on Fenneman, 1938.]

Physiography

The study unit is part of two physiographic provinces: the Laurentian Upland Division, Superior Upland Province and the Interior Plains Division, Central Lowland Province, Eastern Lake Section (Fenneman, 1938) (fig. 10). The Laurentian Upland Division, Superior Upland Province is classified as the area underlain by Precambrian rocks, and it includes the northwestern one-third of the study unit. The topography of this area is variable and mainly controlled by bedrock lithology and structure. Lowlands are present where the bedrock is fairly erodible, and ridges are present where the bedrock is more resistent. Glacial drift that overlies the bedrock is varied in thickness and is absent in some areas. The Interior Plains Division, Central Lowland Province, Eastern Lake Section is underlain by Paleozoic rocks and includes the southeastern two-thirds of the study area. The topography of this area is mainly controlled by glacial depositional processes and bedrock geology. The area is characterized by relatively young glacial deposits with pitted outwash, drumlins, and extensive glaciolacustrine deposits.

Bedrock Geology

The bedrock underlying the study unit is primarily composed of Precambrian and Paleozoic rocks previously mentioned. These materials include Precambrian igneous and metamorphic rocks; Cambrian sandstones; Ordovician carbonates, sandstone, and shale; Silurian carbonates; and Devonian carbonates (fig. 11). The digital bedrock coverage was derived

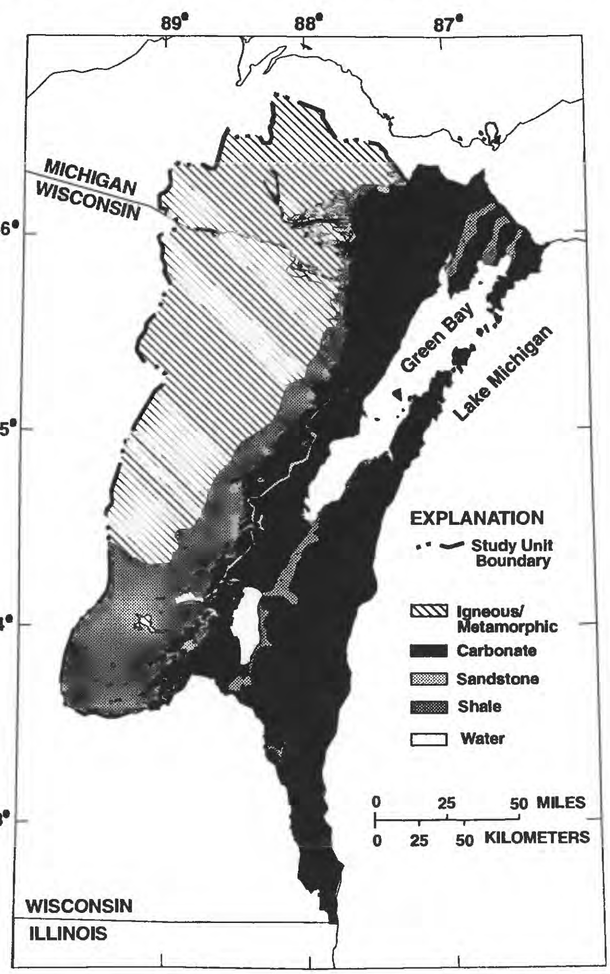


Figure 11. Bedrock types in the Western Lake Michigan Drainages study unit. [Modified from Mudrey and others, 1982, and Reed and Daniels, 1987.]

from maps for Wisconsin (Mudrey and others, 1982) and Michigan (Reed and Daniels, 1987). The bedrock units dip southeast toward Lake Michigan, the youngest rocks (Devonian) being found at the bedrock surface in the southeastern part of the study unit and the oldest rocks (Precambrian) being found at the bedrock surface in the northwestern part of the study unit.

Texture of Surficial Deposits

The bedrock in the study unit is overlain by unconsolidated deposits of Pleistocene age (glacial deposits, outwash, and glaciolacustrine deposits), and Holocene age (alluvium, colluvium, lacustrine, and aeolian deposits). These unconsolidated deposits can be divided into five texture types: sand and gravel, sand, loam, clay, and peat (fig. 12). A description of the texture of surficial deposits throughout the study unit was derived from Quaternary geologic maps as published in the "Quaternary Atlas of the United States" by the U.S. Geological Survey (Wisconsin portion) (Richmond and Fullerton, 1983) and "Quaternary Geological Maps of Northern Michigan" (Michigan portion) (Farrand and Bell, 1982). Clayey deposits predominate along Lake Michigan and in the central part of the study unit. Sandy deposits predominate south of Lake Winnebago; however, this area does have small regions of sand and gravel interspersed. Along the entire western side of the study unit, sandy deposits are mixed with sand and gravel deposits, except in the far north where sandy deposits again predominate. The northeastern one-third of the study unit is dominated by loamy deposits, except in the middle and far northeastern parts of this area which are interspersed with sand and gravel deposits.

Hydrogeology

Four aquifers underlie the study unit: the sand and gravel aquifer, the Silurian dolomite aquifer, the sandstone aquifer, and the basement complex (Kammerer, 1984) (fig. 13). The sand and gravel aquifer consists of permeable unconsolidated deposits that cover much of the study unit. This aquifer is generally 25 to 200 m thick, although in some parts of the study unit it is very thin or absent. Well yields from this aquifer are generally from 0.3 to 12.5 L/s. The Silurian dolomite aquifer is located in the eastern part of the study unit and consists of Silurian and Devonian rocks. This aquifer is overlain by the sand and gravel aquifer and underlain by the Maquoketa Shale, a confining unit that separates it from the sandstone aquifer. Well yields depend on how many fractures and solution openings a well intersects; generally, yields range from 0.3 to 19 L/s. The sandstone aquifer is composed of Cambrian and Ordovician rocks and underlies all but the northwestern part of the study unit. Well yields from this aquifer are generally between 0.6 and 31.5 L/s. Yields are highest where this aquifer is overlain only by the sand and gravel aquifer. The basement complex underlies the entire study unit and is composed of the Precambrian igneous and metamorphic rocks. Wells drilled into the basement complex generally yield little or no water unless they are completed in fractured or weathered zones.

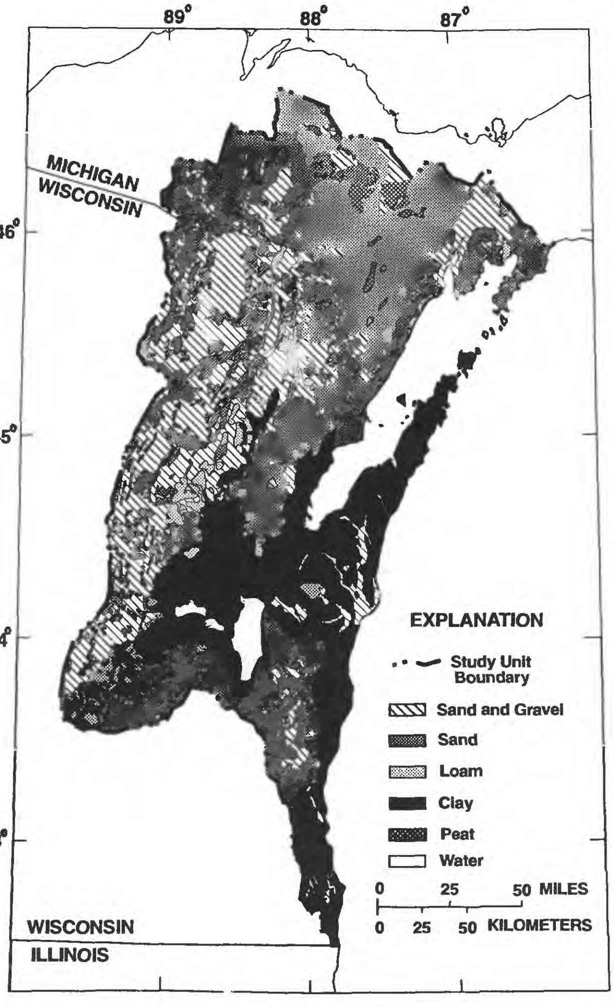


Figure 12. Texture of surficial deposits in the Western Lake Michigan Drainages study unit. [Based on Farrand and Bell, 1982, and Richmond and Fullerton, 1983.]

Geologic age	Geologic unit	Dominant lithology	Aquifer
Quaternary	Holocene alluvial and Pleistocene glacial deposits	Unconsolidated sand and gravel; variable amounts of silt, clay, and organic material	 Sand and gravel (thin or absent in parts of the study unit)
Devonian-Silurian	Undifferentiated	Dolomite	 Silurian dolomite
Ordovician-Cambrian	Undifferentiated	Sandstone and dolomite	 Sandstone
Precambrian	Igneous and metamorphic rocks	Granite and metamorphic rocks	 Basement complex

Figure 13. Aquifers in the Western Lake Michigan Drainages study unit. [Modified from Kammerer, 1984.]

Land Use/Land Cover and Population

Land-use/land-cover information for the study unit was obtained from high-altitude aerial photographs taken by the USGS between 1971 and 1981 (Feagus and others, 1983) and interpreted manually based on the land-use/land-cover classification system of Anderson and others (1976). Land-use/land-cover maps (1:250,000 scale) were produced from these data and digitized into a Geographic Information System (GIS). Ten of these digitized maps (Escanaba, Green Bay, Iron Mountain, Iron River, Madison, Manitowoc, Marquette, Milwaukee, Racine, and Rockford) covering the entire study area were joined together with a GIS and analyzed for land-use/land-cover distributions. The distribution of level I land-use/land-cover categories is shown in figure 14.

Forest land is the largest level I category, and accounts for approximately 40 percent (20,760 km^2) of the study area. Forest land is mainly in the northern part of the study unit, and is composed of three level II classifications: deciduous-forest land, evergreen-forest land, and mixed. Deciduous-forest and mixed-forest lands are mainly in the north-central and northwestern parts of the study area. Evergreen-forest land is mainly in the north-central and northeastern parts of the study area.

Agricultural land is the second largest level I category and accounts for approximately 37 percent (19,200 km^2) of the study unit. Large areas of agricultural land are mainly in the southern and central parts of the study area. More than 99 percent of this land is classified as cropland and pasture, but small areas of orchards, groves, vineyards, and so forth are found on the eastern side of Green Bay.

Wetlands account for approximately 15 percent (8,000 km^2) of the study unit. Wetlands are divided into the level II classifications of forested wetland (wetlands dominated by woody vegetation) and nonforested wetland (wetlands dominated by herbaceous vegetation or open water). Eighty-nine percent of the wetlands are classified as forested and are dispersed over much of the northern part of the study area. Large contiguous areas of forested wetland are in the northeastern part of the study unit and along the northwestern shore of Green Bay. Non-forested wetlands are mainly in the central part of the study unit, west of Lake Winnebago along the Upper Fox and Wolf Rivers, but small areas are also in the northeast part of the study unit.

Table 1. Populations of some of the major cities in the Western Lake Michigan Drainages study unit in 1990

[Data from U.S. Department of Commerce, 1991]

City	Population
Appleton, Wis.	65,695
Escanaba, Mich.	13,659
Fond du Lac, Wis.	37,757
Green Bay, Wis.	96,466
Kenosha, Wis.	80,352
Manitowoc, Wis.	32,520
Marinette, Wis.	11,843
Menominee, Mich.	9,398
Milwaukee, Wis.	628,088
Oshkosh, Wis.	55,006
Racine, Wis.	84,298
Sheboygan, Wis.	49,676

Large areas of urban or developed land surround the major cities found along Lake Michigan in the southeastern part of the study area and around and north of Lake Winnebago. Some of these major cities include Menominee and Escanaba, Mich. and Marinette, Oconto, Green Bay, Appleton, Manitowoc, Oshkosh, Fond du Lac, Sheboygan, Kenosha, Milwaukee, and Racine, Wis. (fig. 2). Smaller urban areas are also in the northeastern part of the study area along Green Bay. The urban areas of the study unit account for about 3 percent (1,670 km^2) of the level I land-use classification. Most of the people in the study area (2,435,120 in 1990, U.S. Department of Commerce, 1991) live in and around these urban areas. The 1990 populations for some of the major cities in the study unit are listed in table 1.

Approximately 3 percent (1,670 km^2) of the study unit is classified as open water, which includes lakes, streams, and reservoirs. The most notable water feature is the Winnebago Pool Lakes in the south-central portion of the study unit. Many smaller lakes are also in the northwestern portion of the study unit. Less than 1 percent (175 km^2) of the study unit is classified as barren land and includes strip mines, quarries, and gravel pits (not shown on fig. 14). Areas of barren land, predominantly iron mines, are in the northern portion of the study unit.

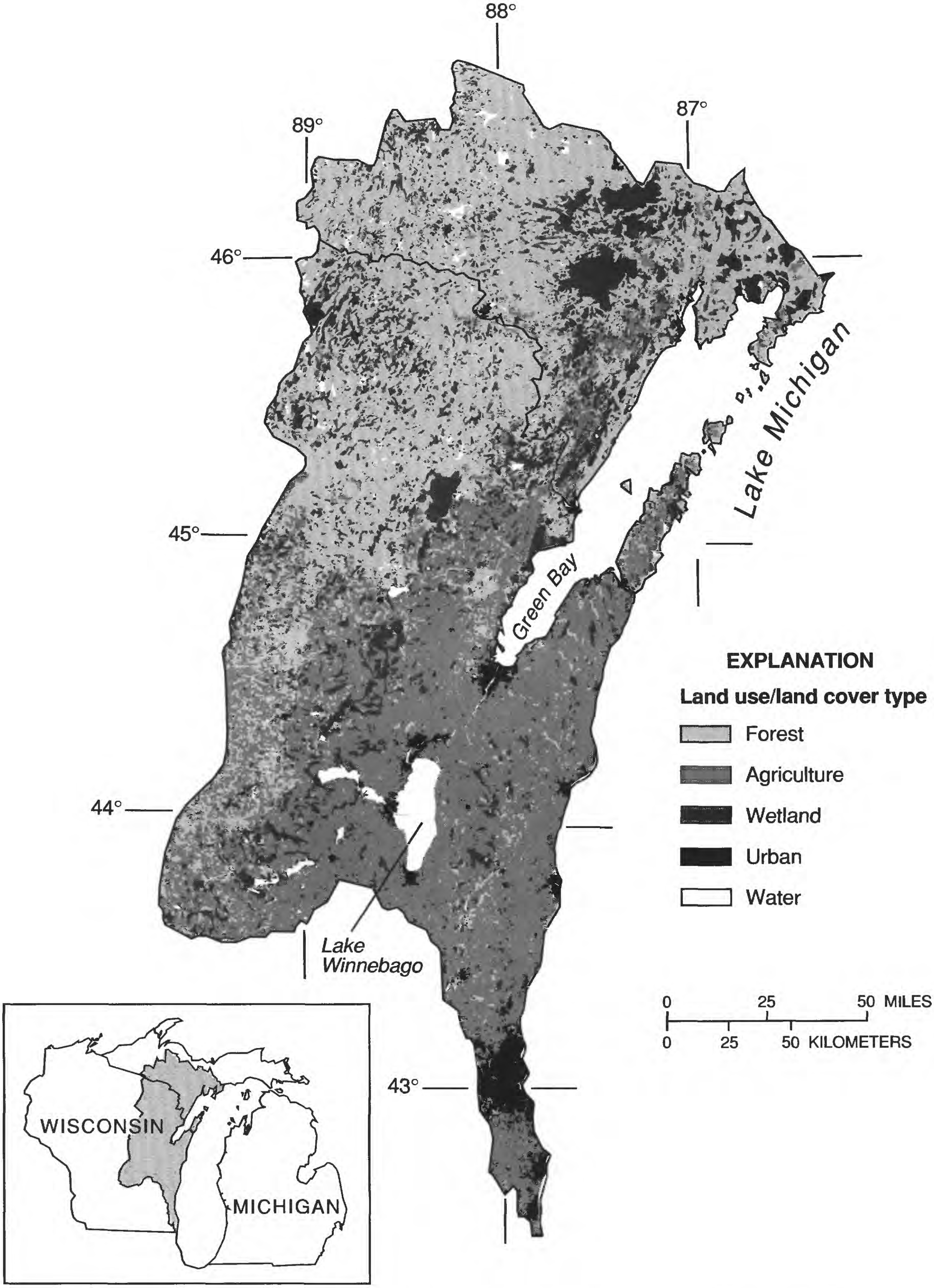


Figure 14. Distribution of Andersons Level I land-use/land-cover categories in the Western Lake Michigan Drainages study unit.

Table 2. Water use for the Western Lake Michigan Drainages study unit in 1990
[m^3/d, cubic meters per day]

Water-use category	Surface-water use (m^3/d)	Ground-water use (m^3/d)	Percentage of total water use
Animal specialties	46,600	4,100	0.28
Commercial	300	128,800	.71
Domestic	0	122,500	.67
Industrial	849,400	48,300	4.93
Irrigation	2,800	67,600	.39
Livestock	8,700	68,400	.42
Mining	16,600	74,300	.11
Public supply	1,150,000	263,000	7.77
Thermoelectric, fossil fuel	9,332,100	0	51.29
Thermoelectric, nuclear	6,081,100	300	33.42
Total	17,487,600	707,300	100.00

Water Use

Water-use information for the study unit was obtained from the USGS Water-Use Data System (WUDS) for the year 1990. The data were compiled by hydrologic unit code and water-use category for the parts of Michigan and Wisconsin contained within the study unit, then aggregated by water-use category for the entire study unit. Only water withdrawn from its source and pumped to a different location is included in this discussion. Also in the study unit are significant nonwithdrawal water uses, such as navigation, recreation, and hydroelectric power generation; these are considered instream (or inlake) uses and are not included in this discussion.

The major water-use categories for surface water are thermoelectric (fossil fuel and nuclear), public supply, and industrial (table 2). Most of this surface water is withdrawn from Lakes Michigan and Winnebago. The major water-use categories for ground water are public supply, commercial, domestic, agricultural (watering livestock and crop irrigation) and industrial (table 2). Ground-water withdrawals from the four principal aquifers in the study unit—sandstone, sand and gravel, Silurian dolomite, and basement complex—is estimated to be 40, 31, 27, and <1.0 percent, respectively, of the total ground-water use in the study unit.

The largest use of water in the study unit was for the generation of thermoelectric power by means of fossil fuels (largest single use) and nuclear energy (second largest single use); collectively these accounted for about 85 percent of all water use. Most water used in thermoelectric power generation is for cooling. Approximately 99 percent of this water is returned to its source (Ellefson and others, 1993; U.S. Geological Survey, 1990).

The third largest use of water was public water supply, which accounted for 7.8 percent of the total. Cities whose water uses exceeded 1,880 m^3/d are shown in fig. 15. Generally, these communities are on the shores of Lakes Michigan and Winnebago and use surface water for all or part of their water supply (Ellefson and others, 1993). Public supply was also the largest single use of ground water. The locations of 253 public-supply wells within the study unit are shown in fig. 16.

The fourth largest use of water was for industry, such as paper and oil companies, and accounted for 4.9 percent of the total. The largest single industrial use of surface water was by pulpmills and papermills. Many of these companies are downstream of Lake Winnebago, an area noted for having the highest concentration of pulpmills and papermills in the world (Wisconsin Department of Natural Resources, 1992). Industrial use accounted for only about 7 percent of the ground water used in the study unit. In all, 336 wells were used for industrial purposes; most of these wells were in the southern half of the study unit, especially concentrated around Green Bay, Appleton, and Milwaukee (fig. 16).

The remaining water uses (commercial, domestic, livestock, irrigation, animal specialties, and mining) accounted for less than 3 percent of the total water used in the study unit. These are, however, significant

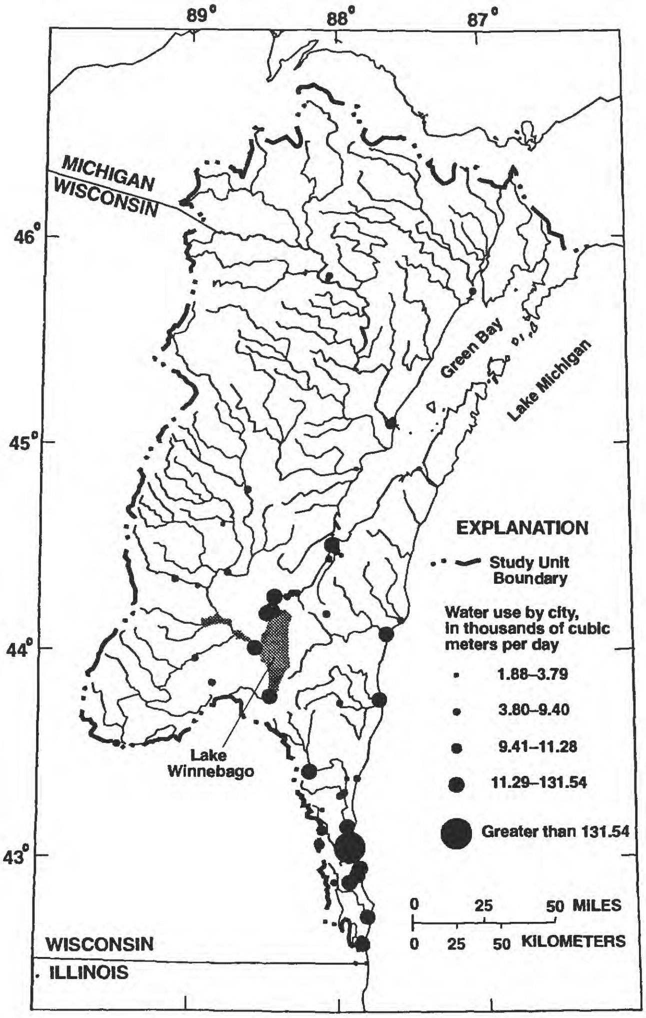


Figure 15. Water use for cities within the Western Lake Michigan Drainages study unit where use is greater than 1,880 cubic meters per day (from Bedell, 1982; Ellefson and others, 1993).

for ground-water use in the study unit. The 188 commercial wells and 595 irrigation wells identified in the study unit were concentrated in the southern half (fig. 16). Irrigation wells were especially concentrated along the west boundary of the study unit.

Water-Quality Problems

Historically, water-quality problems within the WMIC study unit have been caused by a combination of point-source contamination (primarily wastewater discharges and papermill wastes) and nonpoint-source contamination (primarily agricultural and urban runoff). Water-quality issues for specific basins in the study unit are shown in table 3. This table is not an exhaustive list; however, it does contain the primary issues identified to date. The present primary source of water-quality degradation in surface water and ground water is nonpoint-source contaminants, primarily from agriculture. Sediments and nutrients are the largest and most widespread nonpoint source pollutants in surface water. Excess sediment and nutrients adversely affect approximately 40 percent of the streams and threaten another 20 percent of the streams in Wisconsin (Wisconsin Department of Natural Resources, 1992). Polychlorinated biphenyls (PCB's) were the most commonly found contaminant in fish tissues, and their presence in sufficiently high concentrations has often resulted in the issuing of fish-consumption advisories. Nitrate and atrazine were the most common ground-water contaminants. The most common nonagricultural contaminating substances were volatile organic compounds (VOC's); 52 different substances have been detected in Wisconsin waters (Wisconsin Department of Natural Resources, 1992).

Subdivision of the Study Unit Into Relatively Homogeneous Units and Areas of Similar Land Use

One of the goals of the NAWQA program is to better understand how various environmental factors affect water quality. Omernick and others (1988) tried to demonstrate how phosphorus concentrations in lakes were related to differences in various environmental factors. To do this, they subdivided Wisconsin, Michigan, and Minnesota into various ecoregions (based on a conglomeration of various environmental factors—land use, land-surface form, potential vegetation, and soils), then they compared water quality among ecoregions. Their results demonstrated differences among some ecoregions; however, the effects of the individual factors could not be distinguished, since each of their defined areas have various combinations of each of the factors. Most rivers in the WMIC study unit flow through areas having different environmental characteristics, such as that found in specific ecoregions; therefore, it is difficult to determine how the differences in water quality that exist throughout the study unit are related to differences in the specific environmental factors. However, upper reaches of many of the rivers in the WMIC study unit have drainage basins

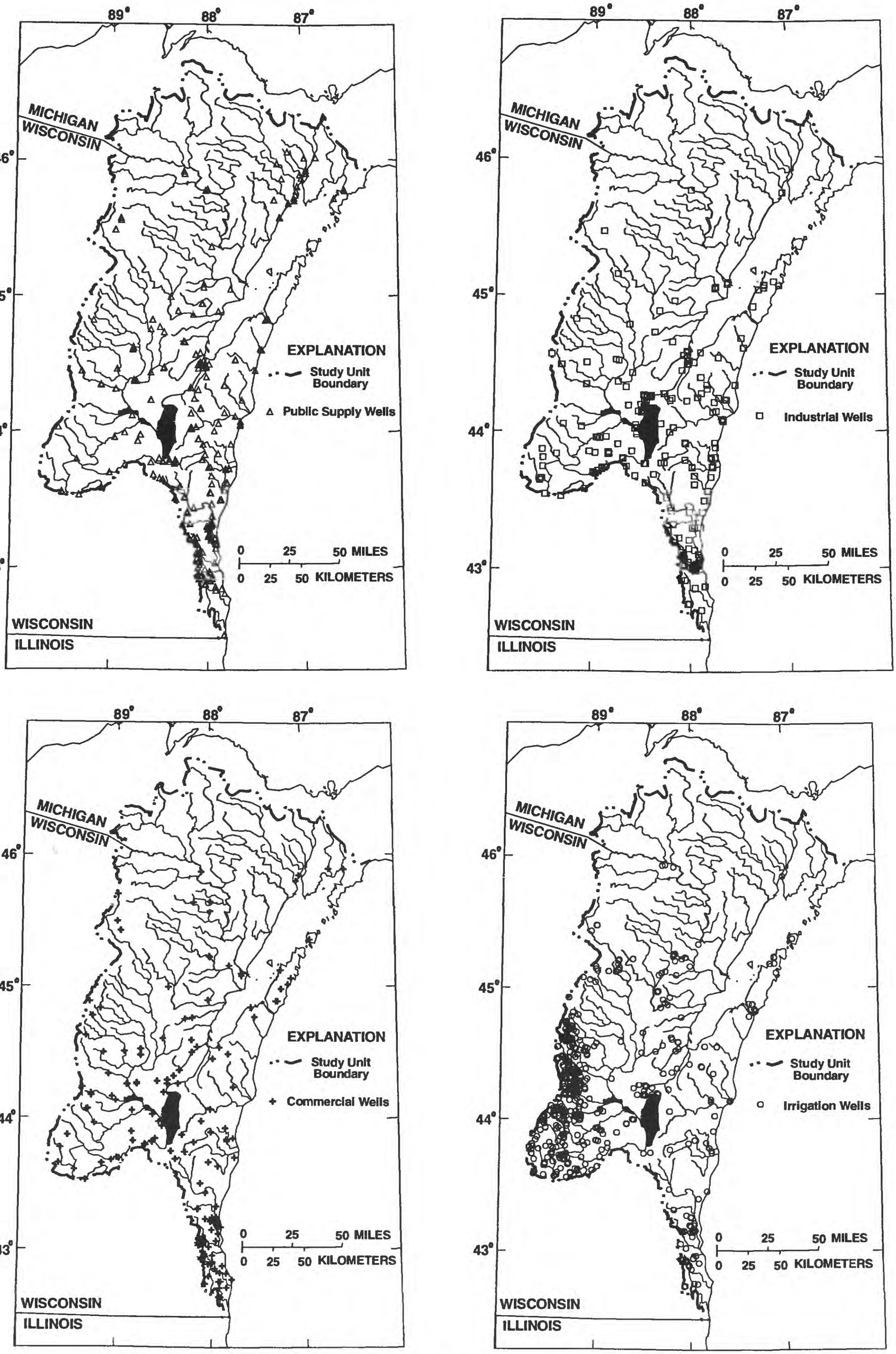


Figure 16. Locations of public supply wells, industrial wells, commercial wells, and irrigation wells in the Western Lake Michigan Drainages study unit.

Table 3. Specific water-quality issues of concern for selected basins in the Western Lake Michigan Drainages study unit
[As identified in the Wisconsin and Michigan 305b Reports to Congress (Wisconsin Department of Natural Resources, 1992; Michigan Department of Natural Resources, 1994)]

Water-quality issue	Basin			
	Ford-Escanaba	Menominee-Oconto-Peshtigo	Fox-Wolf	Lake Michigan
Ammonia toxicity			X	
Animal wastes		X	X	X
Fish toxicity	X		X	
Heavy metals	X	X	X	X
Low dissolved oxygen			X	
Mercury			X	
Nuisance algal blooms			X	
Nutrients		X	X	X
Oil and grease		X		
pH		X		X
Pesticides		X		X
Polychlorinated biphenyls	X		X	X
Polycyclic aromatic hydrocarbon		X		X
Radium	X	X	X	X
Siltation or turbidity		X	X	X
Volatile organic compounds	X	X	X	X

small enough to be dominated by specific combinations of environmental factors. To try to better understand how these environmental factors affect water quality, we subdivided the WMIC study unit into areas dominated by combinations of three environmental factors: land use, texture of surficial deposits, and bedrock type. These areas with specific combinations are referred to as "Relatively Homogeneous Units" (RHU's). In addition, areas dominated by one specific land use were grouped together for comparison because land use was expected to be one of the primary factors that affects water quality. Specific reaches of all of the rivers in the study unit were classified as either indicator reaches (reaches with basins in either one RHU or one land-use type) or integrator reaches (reaches with basins in more than one RHU or one land-use type). The differences in water quality among indicator reaches were compared with their respective environmental characteristics to obtain a better understanding of how each of these natural and anthropogenic factor affects water quality.

Areas of similar bedrock geology (igneous/metamorphic, sandstone, carbonate, or shale), texture of surficial deposit (sand and gravel, sand, loam, peat, or clay), and land use/land cover (urban, agriculture, forest, or wetland) were obtained by use of a GIS to combine the separate coverages. The initial result of this combination was many small, discontiguous areas of similar bedrock, texture of surficial deposit, and land use. Most streams intersected several of these discontiguous areas. In order to categorize stream reaches on the basis of bedrock type, surficial deposit texture, and land use, we had to generalize and simplify these features. The definition of bedrock types was generalized only along contacts between different lithologies. A few geologically complex areas were labeled as mixed (fig. 17). The textures of surficial deposits were combined to create larger contiguous areas of similar types (fig. 17). For example, areas of sand and gravel interfingered with areas of sand were combined into one classification called sand/sand and gravel. Similarly, areas of loam and sand and gravel, and areas of clay and sand, were combined into areas called loam/sand and gravel and clay/sand, respectively. Areas that could not be generalized into a specific category were labeled as mixed.

Land use/land cover was the most difficult to generalize. A few large, contiguous areas were of a single land-use type (fig. 14); therefore, areas dominated by a single land-use/land-cover type were generalized-into that type (fig. 17). For example, an area that was

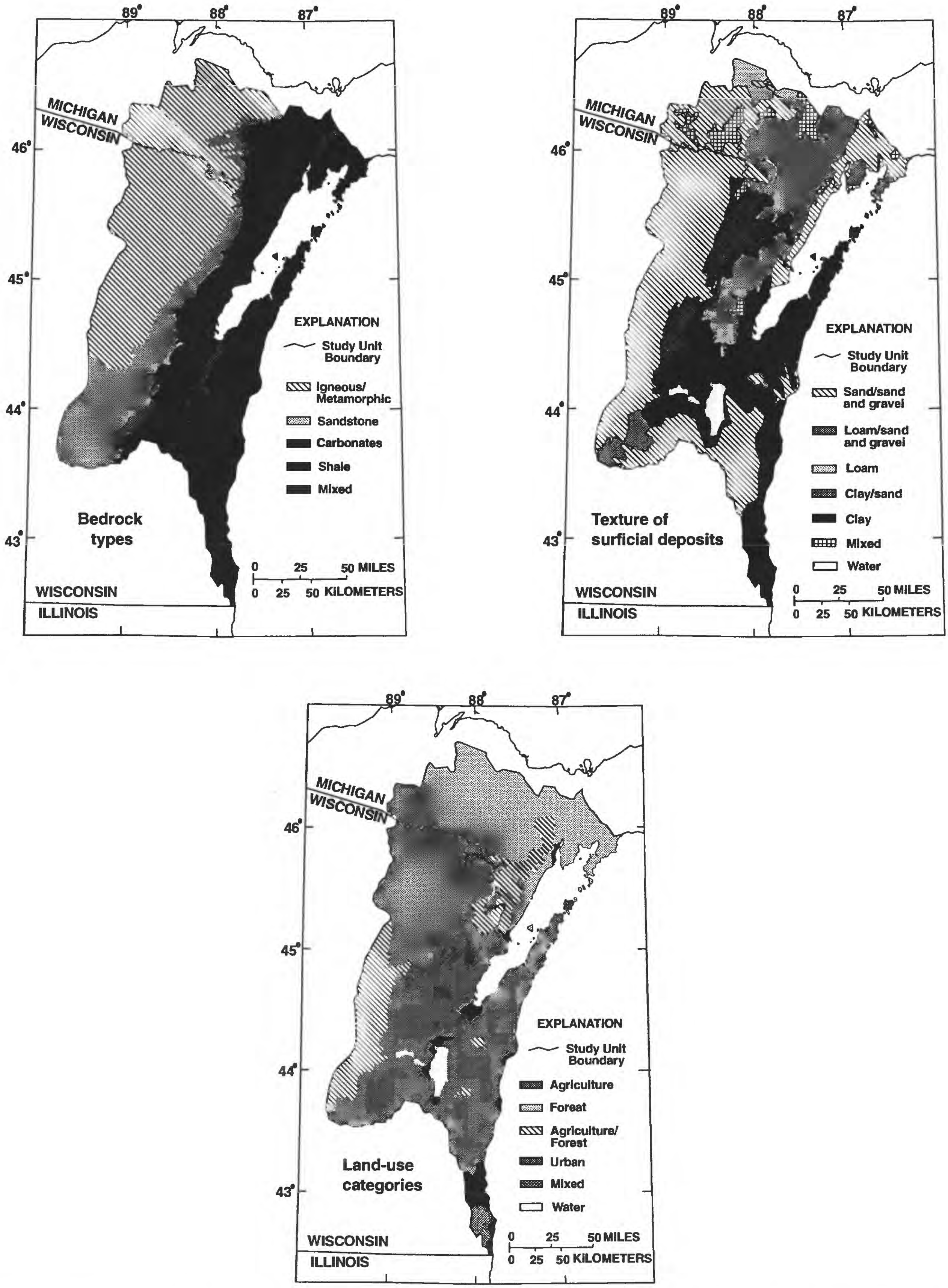


Figure 17. Generalized bedrock types, texture of surficial deposits, and land-use categories in the Western Lake Michigan Drainages study unit.

predominately agriculture but included small areas of forest and wetland was classified as agriculture. Areas not dominated by a single category were labeled as combinations. For example, areas of nearly equal parts of agriculture and forest were labeled as agriculture/forest. Areas that were labeled as forest were further divided into wet or dry forests on the basis of whether more or less than 20 percent of the area contained forested wetland.

These generalized features were digitized into coverages and again overlain by use of a GIS. The result was larger, more contiguous areas of relatively homogeneous bedrock, texture of surficial deposit, and land use (RHU's) (fig. 18). For easy reference, a colored copy of figure 18 is included at the end of this report. In all, 28 RHU's were defined for the study unit; a description of each is given in table 4. Several small discontiguous areas that remained were labeled as mixed areas and were excluded from further analyses.

Land use was expected to be one of the primary factors that affected water quality; therefore, specific land-use areas were determined by combining the RHU's of similar land use. Four general land-use classifications were used: agriculture (Ag), agriculture/forest (AF), forest (F), and urban (U) (table 4). RHU's Ag27 and Ag28 (fig. 18) are areas of agriculture mixed with wetlands and were classified as agricultural areas, even though the percentage of agricultural land was slightly lower than in other agricultural RHU's. AF5 is predominantly an area of forested wetland and agriculture, but was classified as an agricultural area for surface-water summaries because the only river in AF5 originates in and flows back into Ag3, an agricultural area. RHU's AF20, AF26, AF12, and AF5 (for ground-water summaries) were classified as agriculture/forest. RHU's F7, F8, and F21 are areas of forested wetland and forest and were classified as forested areas. Water-quality data and nutrient application rates (described next) also were combined for these four general land-use classifications.

Sources of Nutrients

Concentrations of nutrients in surface water and ground water may be expected to be related directly to the amount of nutrients input to a stream's drainage area or the area near a ground-water well. Sources of nutrients include that added by agricultural practices, nitrogen fixation by plants, atmospheric deposition, and point sources of nutrients. The amount added to each RHU and general land-use category from each of these sources is described in this section.

Agricultural Nutrient Applications

Application of nutrients to croplands, urban lawns, and golf courses, in the form of fertilizers, is commonplace within the WMIC study unit. In agricultural operations, commercial fertilizers and manure are applied to fields. Application rates for nutrients in fertilizers and manure within the WMIC study unit were derived from county application rates estimated by Alexander and Smith (1990) and R.B. Alexander (U.S. Geological Survey, written commun., 1993). These fertilizer-application rates by county were based on allocations of statewide fertilizer sales in 1985 and the proportion of cropland in each county; therefore, estimated fertilizer applications are expected to be biased high in areas dominated by dairy operations, where manure is used as a primary nutrient source, and biased low in cash-cropping areas, where little manure is used. Manure-application rates by county were based on the amount of manure expected to be generated by the number of cows, horses, pigs, and other livestock in each county in 1987; therefore, rates may represent more manure than that being applied to the fields. The following procedure was used to estimate fertilizer and manure application rates for each RHU:

(1) The total amount applied in each county in the study unit was obtained from Alexander and Smith (1990) and R.B. Alexander (U.S. Geological Survey, written commun., 1993). For counties only partly in the study unit, the amount applied was assumed to be equal to the total applied in that county multiplied by the percentage of the area in the study unit.

(2) Application rates per unit agricultural land in each county were computed (application rate multiplied by county area then divided by the area of agricultural land). This computation required the assumption that all the fertilizer and manure was applied on agricultural land. Thus, fertilizers applied on all urban areas and golf courses were not appropriately allocated.

(3) Each RHU was divided into discrete county polygons or sections.

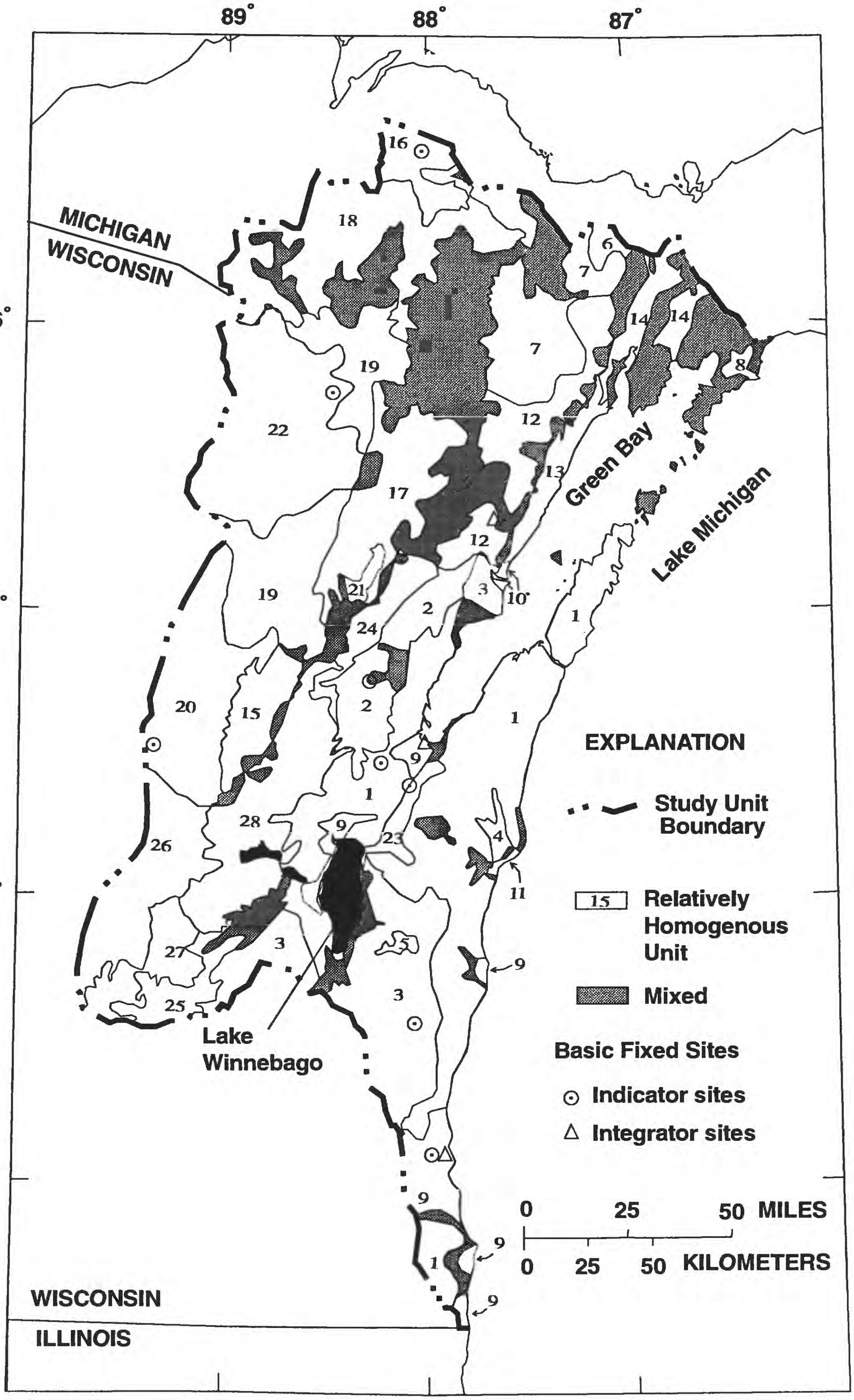


Figure 18. Relatively Homogenous Units in the Western Lake Michigan Drainages study unit. [A description of Relatively Homogenous Units is given in table 4. For easy reference, a color copy of this figure is included at the end of the report.]

Table 4. Description of Relatively Homogeneous Units, general land-use categories, and selected basins within the Western Lake Michigan Drainages study unit

[RHU, Relatively Homogeneous Unit; km^2, square kilometers; no./km^2, number of people per square kilometer; S and G, sand and gravel; Ig/Met, igneous/metamorphic; AF, agriculture/forest; --, not applicable]

RHU, general land-use category, or basin	Land-use type	Surficial deposit	Bedrock type	Area (km^2)	Population density (no./km^2)	Percentage of land use in RHU, general land-use category, or basin					
						Agriculture	Forest	Forested wetland	Nonforested wetland	Urban	Water
RHU											
Agriculture											
Ag1	Agriculture	Clay	Carbonate	7,531	40.6	80.2	9.1	4.8	0.8	3.1	1.2
Ag2	Agriculture	Loam	Carbonate	1,356	19.0	79.3	10.4	8.7	.4	.9	.1
Ag3	Agriculture	Sand	Carbonate	3,548	44.5	79.6	10.7	3.7	1.8	2.9	1.0
Ag4	Agriculture	S and G	Carbonate	142	46.3	77.9	13.8	3.3	0	3.6	.3
Ag15	Agriculture	Loam/S and G	Ig/Met	835	18.3	66.6	18.5	12.4	.7	1.2	.5
Ag23	Agriculture	Clay	Shale	304	36.3	84.2	6.6	1.8	3.8	2.6	.2
Ag24	Agriculture	Loam	Sandstone	650	13.6	67.3	15.9	13.8	.6	.6	1.4
Ag25	Agriculture	Sand	Sandstone	667	12.1	72.2	12.9	1.5	6.5	1.6	5.0
Ag27	Agriculture	Clay and sand	Sandstone	956	12.9	52.4	15.3	8.9	17.7	1.2	4.4
Ag28	Agriculture	Clay	Sandstone	2,480	23.8	57.7	8.2	18.2	9.7	1.6	4.3
Agriculture/forest											
AF5	AF	Sand	Carbonate	81	10.6	30.7	6.2	51.5	8.7	.8	1.9
AF12	AF	Loam	Carbonate	1,642	6.6	31.3	34.0	30.4	.2	.5	.4
AF20	AF	Sand/S and G	Ig/Met	2,519	13.6	44.4	41.9	11.0	.8	.9	.8
AF26	AF	Sand/S and G	Sandstone	1,854	11.9	52.3	40.0	3.3	1.6	.8	1.8
Forest											
F6	Dry forest	Loam	Carbonate	155	<6	2.7	85.4	11.7	0	.1	.1
F7	Wet forest	Loam	Carbonate	1,832	1.8	3.8	47.2	47.4	.3	0	.1
F8	Wet forest	Clay	Carbonate	103	3.1	.7	42.3	54.2	.3	0	2.4
F13	Wet forest	Sand	Carbonate	543	12.1	4.8	63.4	26.7	1.7	1.0	1.9
F14	Wet forest	Sand/S and G	Carbonate	719	7.8	5.2	67.9	22.7	1.0	.9	1.9
F16	Dry forest	Loam	Ig/Met	995	5.8	.4	84.3	5.7	.3	.5	6.4
F17	Dry forest	Loam/S and G	Ig/Met	1,900	3.4	5.6	77.5	13.9	.4	.5	1.9

Table 4. Description of Relatively Homogeneous Units, general land-use categories, and selected basins within the Western Lake Michigan Drainages study unit—Continued

RHU, general land-use category, or basin	Land-use type	Surficial deposit	Bedrock type	Area (km^2)	Population density (no./km^2)	Percentage of land use in RHU, general land-use category, or basin					
						Agriculture	Forest	Forested wetland	Nonforested wetland	Urban	Water
F18	Dry forest	Sand	Ig/Met	3,098	2.4	2.7	81.0	12.3	.8	.1	2.4
F19	Dry forest	Sand/S and G	Ig/Met	3,160	4.6	5.8	81.6	9.1	.3	.3	2.3
F21	Wet forest	Clay	Ig/Met	140	3.5	8.9	23.8	58.7	8.0	.5	.1
F22	Wet forest	Sand/S and G	Ig/Met	3,701	3.0	4.4	65.1	26.6	1.0	.3	2.6
Urban											
U9	Urban	Clay	Carbonate	1,227	1,250.4	19.4	1.5	.2	.6	68.9	8.1
U10	Urban	Sand	Carbonate	40	470.7	10.9	16.1	4.8	0	50.1	17.0
U11	Urban	S and G	Carbonate	35	871.8	6.8	.1	2.2	0	62.7	28.1
General land-use category											
Agriculture	Agriculture	Mixed	Mixed	18,469	33.0	74.3	.5	7.4	3.3	2.4	1.8
AF	AF	Mixed	Mixed	6,096	11.2	43.1	38.7	14.4	1.0	.8	1.0
Forest	Forest	Mixed	Mixed	16,346	3.8	4.2	71.7	20.2	.7	.3	2.3
Urban	Urban	Mixed	Mixed	1,302	1,216.3	18.8	1.9	.4	.6	68.2	8.9
Selected basins											
Escanaba	Forest	Mixed	Mixed	2,256	8.9	4.0	69.9	21.0	1.0	.9	1.6
Ford	Forest	Mixed	Mixed	1,183	3.4	6.8	53.3	39.6	0	.1	.1
Fox	Mixed	Mixed	Mixed	15,630	31.2	50.5	27.9	9.3	4.0	2.2	5.8
Manitowoc	Agriculture	Carbonate	Mixed	1,325	27.9	82.6	6.0	6.6	2.5	1.5	.6
Menominee	Forest	Mixed	Mixed	10,103	5.6	6.0	74.2	15.5	.6	.6	2.6
Milwaukee	Mixed	Carbonate	Mixed	1,782	168.8	74.9	7.9	3.8	.7	11.1	1.2
Popple	Forest	Sand/S and G	Ig/Met	431	0	2.2	61.5	34.1	1.5	.1	.6
White Creek	Agriculture	Carbonate	Sand	8	0	100	0	0	0	0	0

(4) The average application rate for each RHU was determined by weighting the county rate for each polygon by its proportion of the RHU.

(5) All the application rates were converted to kilograms of nitrogen or phosphorus per total hectare of each RHU per year (these data are listed in tables 5 and 6).

(6) Average application rates were also computed for each of the four general land-use categories by weighting each RHU rate by its proportion of the total area of all RHU's with similar land use.

Total annual application rates of phosphorus in fertilizers ranged from 6.96 kg/ha in agricultural areas (highest in Ag25, at 8.16 kg/ha and lowest in Ag27, at 4.67 kg/ha) to less than 0.3 kg/ha in forested areas (table 5; fig. 19). In all forested RHU's, less than 1.0 kg/ha of total phosphorus was applied as fertilizers. The overall rate in agriculture/forest areas (AF5, AF12, AF20, and AF26) was 3.66 kg/ha and in areas classified as urban was 2.01 kg/ha (highest in U9, at 2.09 kg/ha and lowest in U11, at 0.59 kg/ha). Because the areas are not completely homogeneous, almost all of the nonagricultural areas include some land in agricultural use, hence the listed contributions by manure and fertilizers.

The distribution of phosphorus application in the form of manure among land-use types was similar to that for fertilizers; however, manure accounted for approximately one-half (5.73 kg/ha) of the total phosphorus applied in agricultural areas and only about one-third (1.02 kg/ha) in areas classified as urban (table 5; fig. 19). Again, less manure was allocated to the agricultural areas with a high percentage of wetlands (Ag27 and Ag28). All of the RHU's contain at least some agricultural land and associated livestock; therefore, nutrients from fertilizer and manure were allocated to all RHU's.

Application rates of nitrogen from fertilizers and manure were similar to application patterns for phosphorus, except that nitrogen was applied at significantly higher rates (table 6; fig. 20). Total annual nitrogen-application rates in fertilizers ranged from 29.32 kg/ha in agricultural areas (highest in Ag25, at 34.44 kg/ha and lowest in Ag27, at 19.66 kg/ha) to 1.01 kg/ha in forested areas (less than 4.0 kg/ha in all forested RHU's). Application rates in agriculture/forest areas and urban areas were 15.34 and 8.46 kg/ha, respectively.

The differences in nitrogen-application rates from manure among land-use categories and RHU's were similar to that estimated from fertilizers. Manure and fertilizers each accounted for approximately one-third (29 kg/ha) of the total nitrogen applied in agricultural areas and about one-eighth to one-fifth (5 and 8 kg/ha, respectively) of that added in urban areas (table 6; fig. 20). Nitrogen from additional fixation and from atmospheric deposition are discussed in the following sections.

Most agricultural areas with dairy operations within the WMIC study unit are devoted to corn and alfalfa production on a 6- or 7-year rotation, consisting of 2 years of corn followed by either 4 or 5 years of alfalfa. In the first year of the rotation, oats are sometimes substituted for alfalfa. Typical fertilizer- and manure-application rates and dates of application are given in table 7 for 6- and 7-year rotations (K. Erb, U.S. Soil Conservation Service, oral commun., 1993). These rates are typical for dairy operations, which predominate in the WMIC study unit.

In agricultural areas without dairy operations, more fertilizers and little or no manure are applied. A typical 4-year rotation in this type of area may consist of 2 years of corn, followed by 1 year of soybeans, followed by 1 year of sweet corn and winter wheat. This type of operation is typical of the western and southern parts of the study unit. Typical application rates and dates for such areas, such as near Fond du Lac, Wis. (fig. 2), are summarized in table 7 (M. Rankin, University of Wisconsin County Agent, oral commun., 1993). In the absence of dairy operations, much more nitrogen is applied because alfalfa, which fixes nitrogen in the soils, is not grown; however, rates of phosphorus application are similar in all agricultural areas regardless of whether dairy operations area present.

The differences in fertilizer application rates between dairy farms and cash-crop farms (table 7) was not found for the various RHU's (tables 5 and 6), even though differences in general farming practices is present among RHU's. Little variability in the application rates among RHU's was caused by very similar fertilizer-application rates per unit agricultural land throughout the study unit (because of how the statewide totals were allocated to each county), and all of the RHU's having relatively similar percentages of agricultural land. Therefore, as mentioned earlier, the estimated fertilizer applications are probably biased high in areas dominated by dairy operations, where alfalfa is grown and manure is used as a primary nutri-

Table 5. Annual nonpoint-source input rates of phosphorus to Relatively Homogeneous Units, general land-use categories, and selected basins within the Western Lake Michigan Drainages study unit

[RHU, Relatively Homogeneous Unit; kg/ha, kilograms per hectare; km^2, square kilometers; AF, agriculture/forest; fertilizer and manure application rates are annual rates for 1985 (Alexander and Smith, 1990) and 1987 (R.B. Alexander, U.S. Geological Survey, written commun., 1993), respectively]

RHU, general land-use category, or basin	Land-use type	Area (km2)	Phosphorus application rate (kg/ha)		Total atmospheric phosphorus (kg/ha)
			Fertilizer	Manure	
RHU					
Agriculture					
Ag1	Agriculture	7,531	7.21	6.36	0.20
Ag2	Agriculture	1,356	8.04	6.02	.20
Ag3	Agriculture	3,548	7.36	6.19	.20
Ag4	Agriculture	142	6.72	6.93	.20
Ag15	Agriculture	835	6.15	4.99	.20
Ag23	Agriculture	304	6.01	7.27	.20
Ag24	Agriculture	650	6.53	4.49	.20
Ag25	Agriculture	667	8.16	6.44	.20
Ag27	Agriculture	956	4.67	3.32	.20
Ag28	Agriculture	2,480	6.10	4.07	.20
Agriculture/forest					
AF5	AF	81	2.83	2.28	.20
AF12	AF	1,642	2.16	1.16	.20
AF20	AF	2,519	4.18	3.01	.20
AF26	AF	1,854	4.32	2.13	.20
Forest					
F6	Dry forest	155	.04	.02	.05
F7	Wet forest	1,832	.19	.10	.05
F8	Wet forest	103	.01	.00	.05
F13	Wet forest	543	.33	.16	.05
F14	Wet forest	719	.21	.12	.05
F16	Dry forest	995	.04	.04	.05
F17	Dry forest	1,900	.45	.32	.05
F18	Dry forest	3,098	.06	.06	.05
F19	Dry forest	3,160	.41	.28	.05
F21	Wet forest	140	.93	.55	.05
F22	Wet forest	3,701	.20	.21	.05
Urban					
U9	Urban	1,227	2.09	1.05	.38
U10	Urban	40	.85	.46	.38
U11	Urban	35	.59	.61	.38
General land-use category					
Agriculture	Agriculture	18,469	6.96	5.73	.20
AF	AF	6,096	3.66	2.24	.20
Forest	Forest	16,346	.24	.18	.05
Urban	Urban	1,302	2.01	1.02	.38
Selected basins					
Escanaba	Forest	2,256	.57	.33	.05
Ford	Forest	1,183	.35	.19	.05
Fox	Mixed	15,630	5.01	3.59	.20
Manitowoc	Agriculture	1,325	6.73	7.22	.20
Menominee	Forest	10,103	.33	.21	.05
Milwaukee	Mixed	1,782	6.43	5.14	.20
Popple	Forest	431	.08	.09	.05
White Creek	Agriculture	8	11.09	8.83	.20

Table 6. Annual nonpoint-source input rates of nitrogen from fertilizers, manure, and additional fixation not accounted for in the manure rates to Relatively Homogeneous Units, general land-use categories, and selected basins within the Western Lake Michigan Drainages study unit. Input rates of nitrogen from atmospheric deposition are given in table 8

[RHU, Relatively Homogeneous Unit; kg/ha, kilograms per hectare; km^2, square kilometers; AF, agriculture/forest; fertilizer and manure application rates are for 1985 (Alexander 1990) and 1987 (R.B. Alexander, U.S. Geological Survey, written commun., 1993), respectively]

RHU, general land-use category, or basin	Land-use type	Area (km^2)	Nitrogen application rate (kg/ha)		Additional fixation (kg/ha)
			Fertilizer	Manure	
RHU					
Agriculture					
Ag1	Agriculture	7,531	30.37	33.96	28.02
Ag2	Agriculture	1,356	33.80	32.21	28.16
Ag3	Agriculture	3,548	31.05	31.00	28.08
Ag4	Agriculture	142	28.34	37.55	27.41
Ag15	Agriculture	835	25.93	27.62	25.22
Ag23	Agriculture	304	25.33	40.07	29.39
Ag24	Agriculture	650	27.52	24.48	25.27
Ag25	Agriculture	667	34.44	24.64	25.57
Ag27	Agriculture	956	19.66	12.77	23.25
Ag28	Agriculture	2,480	25.71	20.23	23.62
Agriculture/forest					
AF5	AF	81	11.95	11.66	17.65
AF12	AF	1,642	8.81	6.08	16.82
AF20	AF	2,519	17.60	16.71	20.12
AF26	AF	1,854	18.21	9.52	21.92
Forest					
F6	Dry forest	155	.17	.11	10.61
F7	Wet forest	1,832	.76	.50	10.77
F8	Wet forest	103	.02	.01	9.95
F13	Wet forest	543	1.33	.86	10.94
F14	Wet forest	719	.86	.52	10.93
F16	Dry forest	995	.17	.18	9.14
F17	Dry forest	1,900	1.92	1.69	11.08
F18	Dry forest	3,098	.24	.24	10.38
F19	Dry forest	3,160	1.72	1.54	11.04
F21	Wet forest	140	3.91	2.96	12.77
F22	Wet forest	3,701	.84	1.02	10.82
Urban					
U9	Urban	1,227	8.79	5.19	6.68
U10	Urban	40	3.47	2.49	5.67
U11	Urban	35	2.46	3.27	2.46
General land-use category					
Agriculture	Agriculture	18,469	29.32	29.49	26.95
AF	AF	6,096	15.34	11.59	19.74
Forest	Forest	16,346	1.01	.92	10.73
Urban	Urban	1,302	8.46	5.06	6.54
Selected basins					
Escanaba	Forest	2,256	2.32	1.45	11.18
Ford	Forest	1,183	1.42	.90	12.81
Fox	Mixed	15,630	21.11	17.71	21.71
Manitowoc	Agriculture	1,325	28.35	39.52	27.05
Menominee	Forest	10,103	1.35	1.08	12.74
Milwaukee	Mixed	1,782	27.11	25.94	22.41
Popple	Forest	431	.33	.43	10.59
White Creek	Agriculture	8	46.76	36.16	33.00

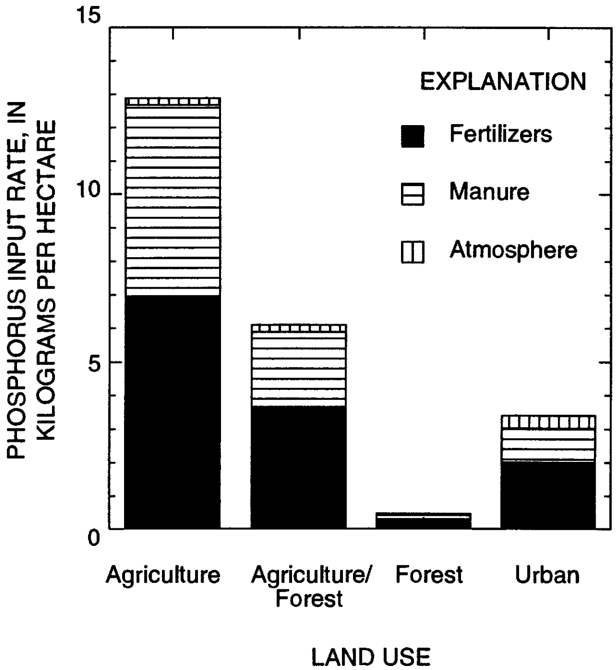


Figure 19. Annual input rates of phosphorus from fertilizers, manure, and atmosphere deposition for general land-use categories in the Western Lake Michigan Drainages study unit. Rates from fertilizers were estimated for 1985 (Alexander and Smith, 1990), manure for 1987 (R.B. Alexander, U.S. Geological Survey, written commun., 1993), and from atmospheric deposition for 1981–90.

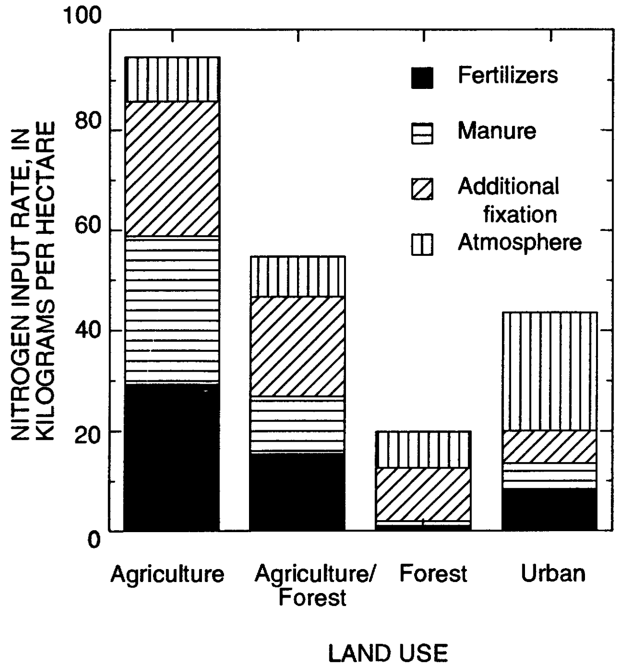


Figure 20. Annual input rates of nitrogen from fertilizers, manure, additional fixation, and atmospheric deposition for general land-use categories in the Western Lake Michigan Drainages study unit. Rates from fertilizers were estimated for 1985 (Alexander and Smith, 1990), from manure for 1987 (R.B. Alexander, U.S. Geological Survey, written commun., 1993), from additional fixation from literature values, and from atmospheric deposition for 1981–90.

ent source, and biased low in cash-cropping areas, where little manure is used.

Nitrogen Fixation

In estimating the total input of nitrogen, symbiotic nitrogen fixation from legumes (mainly alfalfa) and nonsymbiotic fixation from bacteria must be considered. The annual rate of nonsymbiotic fixation of nitrogen in various ecosystems was estimated by Burns and Hardy (1975), and by Jaworski and others (1992) as follows: cropland, 5 kg/ha; forests, 10 kg/ha; and wetlands, 20 kg/ha. Most of the agricultural land in the WMIC study unit with dairy operations is in a rotation of corn and alfalfa. Much of the input of nitrogen that is fixed by alfalfa is already represented in the amount of nitrogen added by manure, because alfalfa is primarily grown as a food crop. However, alfalfa is also grown to increase the nitrogen content of the soils before the planting of corn. This additional nitrogen input due to fixation can be approximated by the nitrogen credit used by farmers in the 2 years following the growth of alfalfa. An average nitrogen credit in the first year after several years of alfalfa is 161 kg/ha (Keeny, 1979; Bundy and others, 1992; Shaw, 1994). An average nitrogen credit in the second year after alfalfa is 51 kg/ha (Bundy and others, 1992; Shaw, 1994). This results in a total nitrogen credit from symbiotic fixation of 212 kg/ha from several years of growing alfalfa. To determine how much additional nitrogen is added per year by alfalfa, one must average the 212 kg/ha over the years of alfalfa growth. If it is assumed that all of the agricultural land within the study unit has a 7-year rotation of corn for 4 years and alfalfa for 3 years, then the additional annual nitrogen input by fixation in agricultural areas would be 33 kg/ha (212 kg/ha added over 3 years plus 20 kg/ha added over 4 years (nonsymbiotic fixation), to obtain an average over the 7-year rotation of 33 kg/ha). To obtain an estimate of the additional nitrogen input by fixation for each of the RHU's, selected basins, and general land-use categories (table 6), these estimates for each land-use category were

Table 7. Typical crop patterns, nitrogen and phosphorus annual application rates, and dates of application of fertilizers and manure on farms in the Western Lake Michigan Drainages study unit

[kg/ha, kilograms per hectare; --, no fertilizer applied or not applicable. Rates are based on application onto agricultural acreage and are not averaged over the entire area.]

Year of crop rotation	Crop type[1]	Application type	Dates of application	Rate of application	
				Nitrogen (kg/ha)	Phosphorus (kg/ha)
Dairy farms[2]					
1	C	Manure	[2]Oct. 1–Nov. 3	101.0	35.0
1	C	Fertilizer	Apr. 30–May 20	20.0	22.0
2	C	Manure	Oct. 1–Nov. 3[3]	168.0	58.0
2	C	Fertilizer	Apr. 30–May 20	20.0	22.0
3	A/O	Manure	Oct. 1–Nov. 3[3]	101.0	35.0
4	A	None	--	0	0
5	A	Fertilizer	May 25–June 7	0	22.0
6	A	Fertilizer	May 25–June 7	0	22.0
(7)	A	Fertilizer	May 25–June 7	0	22.0
Average 6-year	CC(A/O)AAA	Manure	--	61.7	21.3
Average 6-year	CC(A/O)AAA	Fertilizer	--	6.7	14.6
Average 6-year	CC(A/O)AAA	Total	--	68.4	35.9
Average 7-year	CC(A/O)AAAA	Manure	--	52.9	18.3
Average 7-year	CC(A/O)AAAA	Fertilizer	--	5.7	15.7
Average 7-year	CC(A/O)AAAA	Total	--	58.6	34.0
Cash-crop farms[4]					
1	C	Fertilizer	Apr. 30–May 20	145.7	39.2
2	C	Fertilizer	Apr. 30–May 20	145.7	39.2
3	S	Fertilizer	Apr. 30–May 20	22.4	33.6
4	SC	Fertilizer	Apr. 30–May 20	145.7	39.2
4	WW	Fertilizer	Oct.–Nov.	67.3	22.4
Average 4-year	CCS(SC/WW)	Fertilizer	--	131.7	43.4
1	C	Fertilizer	Apr. 30–May 20	145.7	39.2
2	C	Fertilizer	Apr. 30–May 20	145.7	39.2
3	Soybean	Fertilizer	Apr. 30–May 20	22.4	33.6
Average 3-year	CCS	Fertilizer	--	104.6	37.3

[1]Crop type for average 6- and 7-year rotations and typical cash-crop rotation: C, corn; A/O, alfalfa/oats; A, alfalfa; WW, winter wheat; SC, sweet corn; S. soybean.

[2]K. Erb, U.S. Soil Conservation Service, oral commun., 1993.

[3]Manure is applied the fall prior to the year listed for a specific crop.

[4]M. Rankin, University of Wisconsin County Extension Agent, oral commun., 1993.

weighted by the percentage of the land use in each of these areas (table 4).

The additional annual nitrogen input associated with fixation ranges from 23 to 28 kg/ha in agricultural RHU's, to 17 to 22 kg/ha in agricultural/forested RHU's, to 9 to 13 kg/ha in forested RHU's, to 2 to 7 kg/ha in urban RHU's (table 6). In agricultural areas, the additional nitrogen fixation accounts for almost one-third of the total nitrogen input, compared to about 50 percent in agricultural/forested and forested areas and about 15 percent in urban areas (fig. 20). The total nitrogen fixation associated with agriculture is much higher than these estimates, but these values just represent that amount not accounted for in the manure contribution. Urban areas receive additional nitrogen inputs by way of fixation because these are not completely homogeneous areas and they contain some agricultural and forested land.

Atmospheric Nutrient Contributions

Average annual atmospheric-deposition rates of nitrogen were estimated from data collected from sites near the WMIC study unit by the National Atmospheric Deposition Program (NADP) during 1981–90: Trout Lake and Spooner, Wis., Douglas Lake and Wellston, Mich., Argonne, Ill., and Indiana Dunes National Lakeshore, Ind. These data provided direct measurements of the wet deposition of nitrates and ammonia. To obtain average annual deposition rates for each RHU (table 8), we spatially weighted the data from these locations by summing the products of the inverse of the squared distance from each NADP station to the centroid of each RHU and the respective deposition at each NADP site (D.R. Helsel, U.S. Geological Survey, written commun., 1992). Dryfall of nitrate, and adjustments for urban effects on wetfall and dryfall of nitrate were estimated by use of methods described by Sisterson (1990). Urban effects were considered only in urban RHU's (U9, U10, and U11) and were estimated from the percentage of urban area within the RHU (table 4). No corrections were needed for land-surface elevation. Average deposition rates for areas of similar general land use were made by areally weighting deposition rates from individual RHU's. All deposition rates were converted to kilograms of nitrogen per hectare per year. Estimates of dryfall of ammonia were not included in these analyses.

The annual average total atmospheric-deposition rate of nitrogen was relatively uniform across the study unit (table 8; fig. 21) except in urban areas, where wetfall and dryfall of nitrates—especially dryfall—were estimated to be higher than in non-urban areas. Annual deposition in urban areas was computed to be approximately 24 kg/ha of nitrogen deposited, whereas deposition in other areas was approximately 7 to 9 kg/ha. In non-urban areas, nitrogen deposition was almost equally divided among wetfall ammonia, wetfall nitrate, and dryfall nitrate. In addition, dryfall ammonia, which was not included here, would be expected to contribute approximately one-half of that estimated for wetfall ammonia. Deposition rates for all RHU's within a general land-use classification were very similar (table 8).

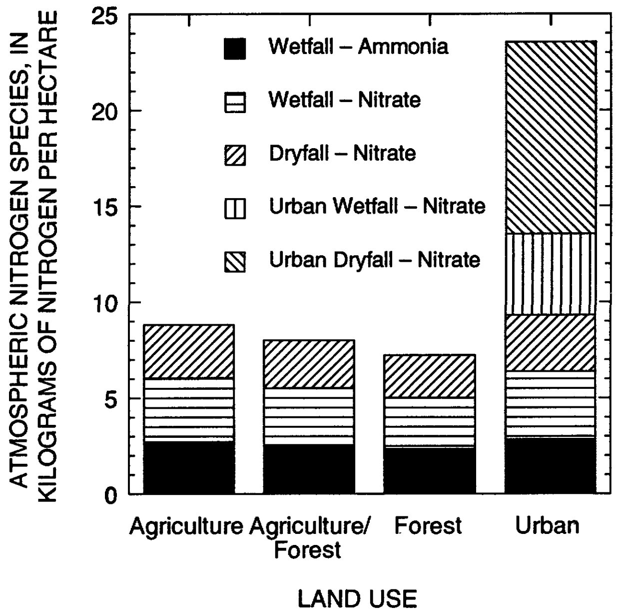


Figure 21. Average annual atmospheric-deposition rates of nitrogen species for general land-use categories in the Western Lake Michigan drainages study unit, 1981–90.

The atmospheric-deposition rate of nitrogen represents only a small fraction (approximately 10 percent) of the total nitrogen input into almost all agricultural areas (fig. 20), but it is a much larger component in the total for forest and urban areas. In urban areas, atmospheric deposition was the predominant source of additional nitrogen.

Phosphorus-deposition rates have been estimated for two areas near the WMIC study unit: Chicago, Ill. (Murphy, 1974) and Spooner, Wis. (Rose, 1993). These two areas are expected to represent the extremes in phosphorus deposition in the study unit. Murphy (1974) estimated total annual deposition of phosphorus in Chicago to be approximately 0.38 kg/ha, whereas Rose (1993) estimated total annual deposition in a remote forested area in northern Wisconsin to be an order of magnitude less, approximately 0.05 kg/ha. In estimating the total input of phosphorus into various basins and RHU's, the total contribution of atmospheric phosphorus was assumed to be 0.05 kg/ha in forested areas, 0.20 kg/ha in agricultural and agricultural/forested areas, and 0.38 kg/ha in urban areas. Therefore, when compared to fertilizer- and manure-application rates, atmospheric deposition of phosphorus represents only a small contribution to almost all areas within the study unit, except for a few forested areas that contain almost no agriculture (F6, F7, F8,

Table 8. Annual atmospheric-deposition rates of nitrogen species to Relatively Homogeneous Units, general land-use categories, and selected basins within the Western Lake Michigan Drainages study unit

[RHU, Relatively Homogeneous Unit; km^2, square kilometers; kg/ha, kilograms per hectare; AF, agriculture/forest; Atmospheric deposition rates are from 1981–90]

RHU, general land-use category, or basin	Land-use type	Area (km^2)	Annual atmospheric deposition of nitrogen species (kg/ha, as N)					
			Ammonia, wetfall	Nitrate, wetfall	Nitrate, dryfall	Nitrate, urban adjusted	Nitrate, total	Nitrogen, total
RHU								
Agriculture								
Ag1	Agriculture	7,531	2.75	3.44	2.85	0	6.29	9.04
Ag2	Agriculture	1,356	2.58	3.13	2.59	0	5.72	8.30
Ag3	Agriculture	3,548	2.81	3.48	2.88	0	6.36	9.17
Ag4	Agriculture	142	2.78	3.55	2.94	0	6.49	9.27
Ag15	Agriculture	835	2.54	2.97	2.46	0	5.42	7.96
Ag23	Agriculture	304	2.72	3.38	2.80	0	6.18	8.91
Ag24	Agriculture	650	2.52	3.02	2.50	0	5.52	8.04
Ag25	Agriculture	667	2.75	3.30	2.74	0	6.04	8.79
Ag27	Agriculture	956	2.73	3.24	2.68	0	5.92	8.65
Ag28	Agriculture	2,480	2.64	3.16	2.62	0	5.78	8.42
Agriculture/forest								
AF5	AF	81	2.81	3.50	2.90	0	6.40	9.21
AF20	AF	2,519	2.48	2.83	2.35	0	5.18	7.66
AF26	AF	1,854	2.66	3.12	2.58	0	5.70	8.36
AF12	AF	1,642	2.49	3.06	2.53	0	5.59	8.09
Forest								
F6	Dry forest	155	2.44	3.00	2.49	0	5.49	7.94
F16	Dry forest	995	2.33	2.69	2.23	0	4.92	7.25
F17	Dry forest	1,900	2.41	2.82	2.33	0	5.15	7.55
F18	Dry forest	3,098	2.32	2.50	2.07	0	4.57	6.80
F19	Dry forest	3,160	2.34	2.66	2.21	0	4.87	7.21
F13	Wet forest	543	2.53	3.16	2.62	0	5.77	8.31

Table 8. Annual atmospheric-deposition rates of nitrogen species to Relatively Homogeneous Units, general land-use categories, and selected basins within the Western Lake Michigan Drainages study unit—Continued

RHU, general land-use category, or basin	Land-use type	Area (km^2)	Annual atmospheric deposition of nitrogen species (kg/ha, as N)					
			Ammonia, wetfall	Nitrate, wetfall	Nitrate, dryfall	Nitrate, urban adjusted	Nitrate, total	Nitrogen, total
F14	Wet forest	719	2.47	3.12	2.58	0	5.70	8.17
F21	Wet forest	140	2.47	2.91	2.41	0	5.32	7.79
F22	Wet forest	3,701	2.20	2.44	2.02	0	4.46	6.66
F7	Wet forest	1,832	2.44	2.96	2.45	0	5.41	7.85
F8	Wet forest	103	2.48	3.22	2.67	0	5.88	8.36
Urban								
U9	Urban	1,227	2.86	3.54	2.94	14.41	20.89	23.75
U10	Urban	40	2.59	3.22	2.67	9.49	15.37	17.96
U11	Urban	35	2.81	3.58	2.97	13.30	19.85	22.65
General land-use category								
Agriculture	Agriculture	18,469	2.72	3.34	2.77	0	6.10	8.82
AF	AF	6,096	2.54	2.99	2.48	0	5.47	8.01
Forest	Forest	16,346	2.34	2.68	2.22	0	4.90	7.22
Urban	Urban	1,302	2.85	3.53	2.93	14.23	20.69	23.54
Selected basins								
Escanaba	Forest	2,256	2.36	2.72	2.25	0	4.97	7.31
Ford	Forest	1,183	2.44	2.94	2.43	0	5.37	7.80
Fox	Mixed	15,630	2.58	3.05	2.53	.24	5.82	8.41
Manitowoc	Agriculture	1,325	2.76	3.45	2.85	0	6.30	9.07
Menominee	Forest	10,103	2.32	2.60	2.16	0	4.76	7.05
Milwaukee	Mixed	1,782	2.81	3.48	2.88	1.22	7.58	10.40
Popple	Forest	431	2.20	2.44	2.02	0	4.46	6.66
White Creek	Agriculture	8	2.75	3.30	2.74	0	6.04	8.79

F16, and F18). In RHU's F6, F8, and F16, atmospheric deposition of phosphorus is small in terms of rates, but considerable in terms of proportion among sources of introduced phosphorus (table 5).

Point Sources of Nutrients

Wisconsin has reached full compliance with Federal standards for release of conventional pollutants, such as suspended sediment and ammonia, from point sources (Wisconsin Department of Natural Resources, 1992). Remaining point sources of nutrient contamination are primarily associated with cheese factories, papermills, and sewage-treatment plants (fig. 22). Most of these point contamination source (PCS) sites are within agricultural and urban areas in the southern half of the study unit.

The locations and estimated annual loads of nitrogen and phosphorus from specific point sources during the 1992 calender year were obtained from the Discharge Monitoring Report Database maintained by the Office of Technical Services within the Wisconsin Department of Natural Resources (WDNR) (G. North, Office of Technical Services, Wisconsin Department of Natural Resources, written commun., 1994). These annual loads were classified into three categories (1) nutrients released directly into surface water; (2) nutrients applied directly to fields; and (3) nutrients not only applied to fields but also to surface water. Only a small proportion of the data was classified as category 3. For purposes of this report, categories 2 and 3 were combined.

The point sources were summed for each RHU, for selected basins (which are discussed in detail later), and for nutrients released directly into Green Bay and Lake Michigan (tables 9 and 10). Within a specific RHU, point sources either released nutrients into a river that is completely contained in the RHU (indicator) or a river that has flowed through several RHU's (integrator). Therefore, the summaries in tables 9 (phosphorus) and 10 (nitrogen) reflect not only the total amount released into the entire RHU, but also the amount released into indicator areas only. In general, nutrient loads from point sources that release into indicator areas of specific RHU's are very small compared to loads from nonpoint sources. However, point-source loads of nutrients at specific locations near major cities (such as at the Fox River near the mouth), or at sites directly releasing into Green Bay or Lake Michigan

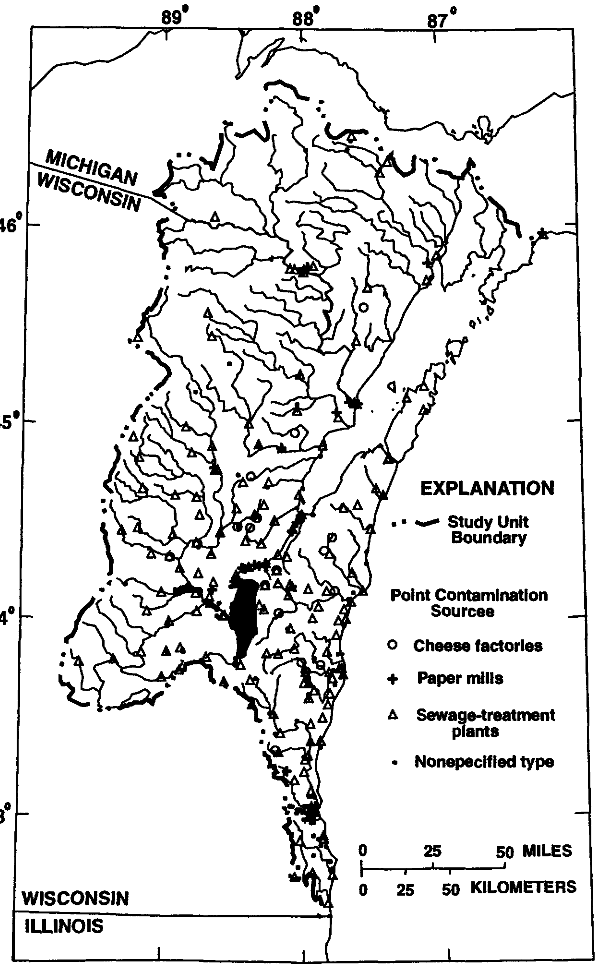


Figure 22. Permit Compliance System (PCS) sites in the Western Lake Michigan Drainages study unit (from Gail Worth, Office of Technical Services, Wisconsin Department of Natural Resources, written commun., 1994).

(especially near Green Bay and Milwaukee) can be very large. Because 100 percent of the nutrient loads from point sources are released directly to surface water, these loads can be very important even if they are very small compared to those from nonpoint sources. The importance of point-source loads relative to nonpoint source loads is discussed in detail later.

DATA USED IN REPORT

Surface-water nutrient, suspended-sediment, and discharge data were compiled from the USGS National Water Information System (NWIS), the U.S. Environmental Protection Agency (USEPA) Storage and Retrieval system (STORET), the Milwaukee Metropolitan Sewerage District (MMSD) data base, the Green Bay Metropolitan Sewerage District (GBMSD) data base, and data files in the Madison, Wis., office of the USGS (not included in NWIS). Ground-water nutrient data were compiled from NWIS, STORET, and the WDNR Groundwater Information Network (GIN).

The nitrogen species considered in this report include dissolved nitrate, dissolved nitrite, dissolved ammonia, particulate ammonia, and organic nitrogen, which were quantified by use of concentrations of dissolved ammonia (STORET and Water Storage and Retrieval system (WATSTORE) code 00608, hereafter referred to collectively as "parameter code"), total ammonia (00610), dissolved nitrite (00613), total ammonia plus organic nitrogen (Kjeldahl nitrogen) (00625), and dissolved nitrite plus nitrate (00631).

The phosphorus species that were considered in this report include particulate phosphorus, dissolved organic phosphorus, and dissolved inorganic phosphorus, and were quantified using concentrations for total phosphorus (00665), dissolved phosphorus (00666), dissolved orthophosphate (inorganic phosphorus) (00671), and total orthophosphate (70507).

All suspended sediment information is based on data contained under parameter code 80154.

Methods of Sample Collection and Laboratory Analysis

Surface-water samples were collected by use of several techniques. The USGS used two primary sampling techniques: cross-sectionally integrated, flow-weighted composite sampling (commonly referred to as "integrated" or "EWI") and automated sampling. Integrated sampling is done by use of depth-integrating, nozzled samplers that fill isokinetically; in other words, fill with no change in stream velocity upon entering the sampler intake (Martin and others, 1992). In automated sampling, a device is used to obtain a sample from a single location in the stream at specified times or flows, generally, the sampler includes a peristaltic pump. Most gaging stations operated by the USGS to estimate chemical or sediment loads were equipped with automated samplers that were calibrated with reference to a small number of samples collected by use of integrated sampling techniques. At USGS stations instrumented for long-term monitoring of selected water-quality characteristics, samples were collected primarily by use of integrated sampling techniques. The principal sampling method for the MMSD, GBMSD, and other studies archiving their data within STORET was surface-grab sampling, in which samples are collected in an open container from a single point at or near the stream surface. Surface-grab and cross-sectionally-integrated sampling methods were compared by Martin and others (1992). For samples collected during high flows, cross-sectionally-integrated samples were shown to yield higher concentrations than those collected by use of surface-grab methods for constituents containing particulate forms; however, concentrations of dissolved species were similar. For samples collected during low flows, concentrations were similar for dissolved and particulate forms.

Methods of sample collection for ground water varied and were not thoroughly documented. Strict procedures, such as those in the USGS ground-water sampling protocols (Hardy and others, 1989) were used at times; however, the most common technique used to obtain a sample from an existing well seems to have been turning on a faucet or spigot for 5 to 20 minutes then collecting a sample from some point in the waterline between the wellhead and any softener or filter.

Data in this report were determined by several different laboratories, all of which used more than one analytical technique over the period of interest. Most data within the NWIS data base were determined by the USGS National Water-Quality Laboratory (NWQL) in Atlanta, Ga., during water years 1971–85 and by the USGS NWQL in Denver, Colo., during water years 1986–90. Analytical techniques used by these laboratories followed standard USGS methods (Fishman and Friedman, 1989). Some data within NWIS were determined by the Wisconsin State Laboratory of Hygiene (WSLOH). The methods of analysis used by the WSLOH follow the USEPA-recommended guidelines outlined in the "Manual of Analytical Methods, Inorganic Chemistry Unit" (Wisconsin State Laboratory of Hygiene, 1993). Analytical methods used by the NWQL's and the WSLOH are summarized in tables 11 and 12.

Data within the STORET database, were submitted by State and Federal agencies, as well as by contractors, universities, and individuals. The USEPA strongly encourages, but does not require, adherence to guidelines for data definition and quality. Thus, it is likely that the STORET data base contains results for water-quality samples that were analyzed by several laboratories, all using different methods. The primary

Table 9. Annual point-source inputs of phosphorus to Relatively Homogeneous Units, selected basins within the Western Lake Michigan Drainages study unit, and adjacent bodies of water

[RHU, Relatively Homogeneous Unit; km^2, square kilometers; kg, kilograms; kg/ha, kilograms per hectare; AF, agriculture/forest; --, not applicable. Inputs were estimated for 1992 and obtained from the Technical Transfer Division, Wisconsin Department of Natural Resources]

RHU, basin, or body of water	Land-use type	Area (km^2)	Point-source inputs to surface water			Point-source inputs to land	
			All streams (kg)	Indicator areas		Indicator areas	
				kg	kg/ha	kg	kg/ha
RHU							
Agriculture							
Ag1	Agriculture	7,531	62,647	4,113	0.01	968	0
Ag2	Agriculture	1,356	3,142	1,680	.01	0	0
Ag3	Agriculture	3,548	8,229	5,785	.02	227	0
Ag4	Agriculture	142	0	0	0	0	0
Ag15	Agriculture	835	60	60	0	0	0
Ag23	Agriculture	304	0	0	0	0	0
Ag24	Agriculture	650	0	0	0	0	0
Ag25	Agriculture	667	0	0	0	0	0
Ag27	Agriculture	956	0	0	0	0	0
Ag28	Agriculture	2,480	9,547	1,267	.01	0	0
Agriculture/forest							
AF5	AF	81	0	0	0	0	0
AF12	AF	1,642	0	0	0	0	0
AF20	AF	2,519	1,035	1,035	0	0	0
AF26	AF	1,854	0	0	0	300	0
Forest							
F6	Dry forest	155	0	0	0	0	0
F7	Wet forest	1,832	0	0	0	0	0
F8	Wet forest	103	0	0	0	0	0
F13	Wet forest	543	0	0	0	0	0
F14	Wet forest	719	0	0	0	0	0
F16	Dry forest	995	0	0	0	0	0

Table 9. Annual point-source inputs of phosphorus to Relatively Homogeneous Units, selected basins within the Western Lake Michigan Drainages study unit, and adjacent bodies of water—Continued

RHU, basin, or body of water	Land-use type	Area (km^2)	Point-source inputs to surface water			Point-source inputs to land	
			All streams (kg)	Indicator areas		Indicator areas	
				kg	kg/ha	kg	kg/ha
F17	Dry forest	1,900	12,960	5	0	0	0
F18	Dry forest	3,098	0	0	0	0	0
F19	Dry forest	3,160	73	73	0	0	0
F21	Wet forest	140	0	0	0	0	0
F22	Wet forest	3,701	0	0	0	0	0
Urban							
U9	Urban	1,227	62,058	23	0	0	0
U10	Urban	40	1,217	0	0	0	0
U11	Urban	35	0	0	0	0	0
Selected basins							
Escanaba	Forest	2,256	0	0	0	0	0
Ford	Forest	1,183	0	0	0	0	0
Fox	Mixed	15,630	121,668	121,668	.08	7,179	0.01
Manitowoc	Agriculture	1,325	1,027	1,027	.01	0	0
Menominee	Forest	10,103	12,955	12,955	.01	0	0
Milwaukee	Mixed	1,782	7,445	7,445	.04	227	0
Popple	Forest	431	0	0	0	0	0
White Creek	Agriculture	8	0	0	0	0	0
Green Bay[1]	--	--	22,108	22,108	0	0	0
Lake Michigan[1]	--	--	187,541	187,541	.04	0	0

[1]Input rates based on application over Western Lake Michigan Drainage area.

Table 10. Annual point-source inputs of nitrogen to Relatively Homogeneous Units, selected basins within the Western Lake Michigan Drainages study unit, and adjacent bodies of water

[RHU, Relatively Homogeneous Unit; km^2, square kilometers; kg, kilograms; kg/ha, kilograms per hectare; AF, agriculture/forest; --, not applicable. Inputs were estimated for 1992 and obtained from the Technical Transfer Division, Wisconsin Department of Natural Resources]

RHU, basin, or body of water	Land-use type	Area (km^2)	Point-source inputs to surface water			Point-source inputs to land	
			All streams (kg)	Indicator areas		Indicator areas	
				kg	kg/ha	kg	kg/ha
RHU							
Agriculture							
Ag1	Agriculture	7,531	335,917	3,193	0	84,961	0.11
Ag2	Agriculture	1,356	306	108	0	28,354	.21
Ag3	Agriculture	3,548	13,010	4,466	0.01	32,000	.09
Ag4	Agriculture	142	774	0	0	881	.06
Ag15	Agriculture	835	126	126	0	0	0
Ag23	Agriculture	304	0	0	0	0	0
Ag24	Agriculture	650	355	0	0	2,542	.04
Ag25	Agriculture	667	0	0	0	1,035	.02
Ag27	Agriculture	956	0	0	0	0	0
Ag28	Agriculture	2,480	6,564	732	0	25,064	.10
Agriculture/forest							
AF5	AF	81	0	0	0	0	0
AF12	AF	1,642	0	0	0	0	0
AF20	AF	2,519	301	301	0	12,823	.05
AF26	AF	1,854	15	15	0	3,212	.02
Forest							
F6	Dry forest	155	0	0	0	0	0
F7	Wet forest	1,832	0	0	0	0	0
F8	Wet forest	103	0	0	0	0	0
F13	Wet forest	543	0	0	0	0	0
F14	Wet forest	719	0	0	0	0	0
F16	Dry forest	995	0	0	0	0	0

Table 10. Annual point-source inputs of nitrogen to Relatively Homogeneous Units, selected basins within the Western Lake Michigan Drainages study unit, and adjacent bodies of water—Continued

RHU, basin, or body of water	Land-use type	Area (km^2)	Point-source inputs to surface water			Point-source inputs to land	
			All streams (kg)	Indicator areas		Indicator areas	
				kg	kg/ha	kg	kg/ha
F17	Dry forest	1,900	30,674	0	0	0	0
F18	Dry forest	3,098	0	0	0	0	0
F19	Dry forest	3,160	0	0	0	3,867	.01
F21	Wet forest	140	0	0	0	0	0
F22	Wet forest	3,701	0	0	0	9,922	.03
Urban					0		
U9	Urban	1,227	417,567	6	0	0	0
U10	Urban	40	0	0	0	10	0
U11	Urban	35	0	0	0	0	0
Selected basins							
Escanaba	Forest	2,256	0	0	0	0	0
Ford	Forest	1,183	0	0	0	0	0
Fox	Mixed	15,630	558,561	558,561	.36	147,777	.10
Manitowoc	Agriculture	1,325	3,671	3,671	.03	10,759	.08
Menominee	Forest	10,103	30,674	30,674	.03	5,267	.01
Milwaukee	Mixed	1,782	3,670	3,670	.02	5,165	.03
Popple	Forest	431	0	0	0	0	0
White Creek	Agriculture	8	0	0	0	0	0
Green Bay[1]	--	--	451,036	451,036	.09	0	0
Lake Michigan[1]	--	--	1,470,429	1,470,429	.29	0	0

[1]Input rates based on applications over Western Lake Michigan Drainage area.

Table 11. Analytical methods used by the U.S. Geological Survey National Water-Quality Laboratory
[STORET, U.S. Environmental Protection Agency Storage and Retrieval system]

Constituent	STORET number[1]	Method number[2]	Description of method
Ammonia, dissolved	00608	I-1520-85	Colorimetric, distillation, nesslerization
Ammonia, dissolved	00608	I-2521-85	Colorimetric, salicylate-hypochlorite, automated-discrete
Ammonia, dissolved	00608	I-2522-85	Colorimetric, salicylate-hypochlorite, automated-segmented flow
Ammonia, dissolved	00608	I-2523-85	Colorimetric, indophenol, automated-segmented flow
Ammonia, dissolved	00608	I-1524-85	Electrometric, ion-selective electrode
Ammonia, total	00610	I-3520-85	Colorimetric, distillation, nesslerization
Ammonia, total	00610	I-4521-85	Colorimetric, salicylate-hypochlorite, automated-discrete
Ammonia, total	00610	I-4522-85	Colorimetric, salicylate-hypochlorite, automated-segmented flow
Ammonia, total	00610	I-4523-85	Colorimetric, indophenol, automated-segmented flow
Ammonia, total	00610	I-3524-85	Electrometric, ion-selective electrode
Kjeldahl nitrogen, total	00625	I-4552-85	Colorimetric, block digestor-salicylate-hypochlorite, automated-segmented flow
Kjeldahl nitrogen, total	00625	I-4558-85	Colorimetric, block digestor-salicylate-hypochlorite, automated-discrete
Nitrite, dissolved	00613	I-1540-85	Colorimetric, diazotization
Nitrite, dissolved	00613	I-2540-85	Colorimetric, diazotization, automated-segmented flow
Nitrite, dissolved	00613	I-2539-85	Colorimetric, diazotization, automated-discrete
Nitrite, dissolved	00613	I-2057-85	Ion-exchange chromatograph, automated
Nitrite plus nitrate, dissolved	00631	I-2545-85	Colorimetric, cadmium reduction-diazotization, automated-segmented flow
Nitrite plus nitrate, dissolved	00631	I-2543-85	Colorimetric, hydrazine reduction-diazotization, automated-discrete
Orthophosphate, dissolved	00671	I-1601-85	Colorimetric, phosphomolybdate
Orthophosphate, dissolved	00671	I-2601-85	Colorimetric, phosphomolybdate, automated-segmented flow
Orthophosphate, dissolved	00671	I-2598-85	Colorimetric, phosphomolybdate, automated-discrete
Orthophosphate, dissolved	00671	I-2057-85	Ion-exchange chromatographic, automated
Orthophosphate, total	70507	I-4601-85	Colorimetric, phosphomolybdate, automated-segmented flow
Orthophosphate, total	70507	I-4598-85	Colorimetric, phosphomolybdate, automated-discrete
Phosphorus, total	00665	I-2600-85	Colorimetric, phosphomolybdate, automated-segmented flow
Phosphorus, total	00665	I-4599-85	Colorimetric, phosphomolybdate, automated-discrete
Phosphorus, dissolved	00666	I-1600-85	Colorimetric, phosphomolybdate
Phosphorus, dissolved	00666	I-2600-85	Colorimetric, phosphomolybdate, automated-segmented flow
Phosphorus, dissolved	00666	I-2599-85	Colorimetric, phosphomolybdate, automated-discrete

[1]U.S. Environmental Protection Agency's STORET parameter code number.

[2]Method number from Fishman and Friedman, 1989.

Table 12. Analytical methods used by Wisconsin State Laboratory of Hygiene (WSLOH), and Green Bay and Milwaukee Metropolitan Sewerage Districts

[STORET, U.S. Environmental Protection Agency Storage and Retrieval system; USEPA, U.S. Environmental Protection Agency; --, no corresponding EPA method number]

Constituent	STORET number[1]	Method number WSLOH/USEPA[2]	Description of method
Wisconsin State Laboratory of Hygiene			
Ammonia, dissolved	00608	220.3/350.1	Automated colorimetric phenate
Ammonia, total	00610	220.3/350.1	Automated colorimetric phenate
Kjeldahl nitrogen, total	00625	230.1/--	Described in Bowman and Delphino (1982)
Nitrite, total	00613	220.5/353.2	Automated colorimetric
Nitrite plus nitrate, dissolved	00631	353.2/353.2	Automated colorimetric cadmium reduction
Orthophosphate, dissolved	00671	310.1/365.1	Automated colorimetric ascorbic acid
Phosphorus, total	00665	230.1/--	Described in Bowman and Delphino (1982)
Green Bay Metropolitan Sewerage District			
Ammonia, dissolved	00608	--/350.1	Automated colorimetric phenate
Kjeldahl nitrogen, total	00625	--/351.2	Semiautomated colorimetric block digester
Nitrite, dissolved	00613	--/353.2	Automated, cadmium reduction
Nitrite plus nitrate, dissolved	00631	--/353.2	Automated, cadmium reduction
Orthophosphate, dissolved	00671	--/365.1	Colorimetric, ascorbic acid reduction
Phosphorus, total	00665	--/365.4	Colorimetric, ascorbic acid reduction
Milwaukee Metropolitan Sewerage District			
Ammonia, total	00608	--/350.1	Automated colorimetric phenate
Kjeldahl nitrogen, total	00625	--/351.3	Colorimetric, block digester, auto anal. II
Phosphorus, total	00665	--/365.1	Colorimetric, ascorbic acid reduction
Phosphorus, dissolved	00671	--/365.1	Colorimetric, ascorbic acid reduction

[1]U.S. Environmental Protection Agency's STORET parameter code number.

[2]Method numbers from Wisconsin State Laboratory of Hygiene (1993) and U.S. Environmental Protection Agency (1983).

data contained within STORET and GIN were collected by the WDNR. These data were primarily determined by the WSLOH.

Samples collected by the MMSD and GBMSD were analyzed by their respective laboratories using standard USEPA methods listed in table 12.

Quality-Assurance Programs

The NWQL follows quality-assurance practices described by Fishman and Friedman, 1989. Precision and accuracy of analyses are monitored in the laboratory by analyzing at least 15 percent of all samples for each constituent as split samples, laboratory blanks, reagent-water spikes, instrument-calibration mixtures, and surrogate-compound additions. These are in addition to project-submitted Quality-Assurance/Quality-Control (QA/QC) samples such as field-equipment blanks, field-matrix spikes, laboratory-matrix spikes, trip blanks, and replicate samples. The NWQL is required to participate in a quality-control program that requires frequent analysis of standard-reference and blind samples of known composition. In addition, completed analytical reports are reviewed by quality-control staff aided by more than 100 computerized checks including ionic balance, error-curve comparison, and a check on the constituents known to interfere with current analytical methods.

The WSLOH, which is affiliated with the University of Wisconsin–Madison, follows quality-assurance practices that are outlined in the "Manual of Analytical Methods, Inorganic Chemistry Unit" (Wisconsin State Laboratory of Hygiene, 1993). Precision and accuracy of methods are routinely verified. Ten percent of all samples are analyzed in duplicate, and replicates are intermixed with routine samples to verify precision under normal operating conditions. Accuracy is monitored by analysis of standards (spiked samples) and control samples. Approximately 5 percent of all samples are analyzed as spiked samples. The laboratory also participates in a variety of quality-assurance programs such as the USEPA Performance Evaluation Studies and the USGS Standard Reference Water Sample Program.

The MMSD and GBMSD are certified with the WDNR for analysis of all nutrient constituents listed in table 12. Certification requires that the individual districts analyze reference samples that are distributed by the WSLOH for each constituent on a routine basis and submit the results to the WDNR. MMSD and GBMSD analyze reference samples two and four times per year, respectively. In addition, precision and accuracy of analyses are monitored by analyzing at least 10 percent of all samples for each constituent as duplicates and 5 to 10 percent as spikes. Laboratory blanks are analyzed daily. In addition, GBMSD and MMSD participate in the USGS Standard Reference Water Sample Program (Richard Sachs, Green Bay Metropolitan Sewerage District, written commun., 1993; Christopher Magruder, Milwaukee Metropolitan Sewerage District, oral commun., 1993).

Analytical and Sampling Biases and Their Implications for Data Analyses

During water years 1971–90, several changes were made in analytical and sample-collection techniques; however, none of these changes warrant omitting data from the data set or application of bias corrections. Sometime after 1973, an error was introduced into the analytical method for surface-water total phosphorus by the USGS NWQL (D.A. Rickert, U.S. Geological Survey, written commun., 1992). This error resulted in the use of insufficient amounts of persulfate and sulfuric acid in the digestion step that, in turn, resulted in measured total phosphorus concentrations that were likely to be too low. The bias toward low concentrations was most extreme in samples having high concentrations of total phosphorus, suspended sediment, and total organic carbon. This same bias was also observed in dissolved phosphorus in surface water, but this bias probably does not significantly affect ground-water data because of lower phosphorus and particulate concentrations in ground water. This error was not corrected for until May 1, 1990. The analytical procedure was later completely changed on October 1, 1991. The few simultaneous total phosphorus determinations that were done by use of all three techniques indicate that historical data cannot be corrected because of a nonsystematic relation between the three analyses. Therefore, bias adjustments are not able to be applied for data collected before October 1, 1991.

Total ammonia and total orthophosphate determined by the USGS NWQL are all of questionable quality because the digestion step was not included in the analysis (D.A. Rickert, U.S. Geological Survey, written commun., 1992). All these constituents were analyzed by use of colorimetric techniques; therefore, reported concentrations of these constituents in samples containing high concentrations of suspended sediment may be biased high because of interference by suspended particles.

These biases may not be important in examinations of large spatial differences in water quality; however, the changes and biases in analytical techniques may be important in examinations of data from a specific location where changes through time may be subtle. For example, small negative biases early in the record can cause an apparent upward trend in concentrations of specific constituents whose concentrations actually have not changed. Likewise, changes in analytical techniques can introduce enough variability to mask actual changes in water quality.

The number of samples collected during a given year dramatically changed during water years 1971–90. At most of the intensively sampled sites examined in this report (described later), frequency of sampling was reduced from twice per month, to once per month, to once every 3 months. The reduced frequency of sampling may reduce the apparent variability at specific locations and make trend identification more difficult, especially for trends during the late 1980's.

Screening of Data

As previously mentioned, the water-quality data used in this report were limited to those collected from October 1, 1970, through September 30, 1990 (water years 1971–90). Data collected by MMSD and GBMSD began in 1975 and 1986, respectively, and continued through September 30, 1990. Data from an additional short-term study by the USGS on the East River and Bower Creek near Green Bay in 1985 and 1986, but not contained in NWIS, were included in this analysis. Only wells that were used for water withdrawals were included. Data obtained from monitoring or observation wells at solid-waste and wastewater sites and wells of unknown use were excluded from this analysis.

The spatial distribution of surface-water sampling sites was fairly uniform across the study unit, except for certain urban areas that were intensively sampled by the MMSD and the GBMSD. Therefore, to obtain average urban concentrations, a subset of the data collected by the MMSD and GBMSD was included in this report: six sites near Milwaukee (three sites on the Milwaukee River; one on the Menomonee River; one on the Kinniccinnic River; and one on Oak Creek), and three sites near Green Bay (two on the Fox River; and one on the East River). Data from all other sites were excluded from this report.

At a few sites near the mouths of major rivers sampled by the MMSD and GBMSD, thermal stratification often results in differences in the concentrations of the constituents with depth. Therefore, these organizations commonly collected samples at several discrete depths. For this report, these samples were averaged to obtain a mean concentration before any statistical analyses were done.

A surface-water site was considered to be representative of a single RHU only if the entire reach above the site was contained in that RHU. A surface-water site was considered to be representative of a single general land-use category only if the entire reach above the site was contained in the specified general land-use category (fig. 17). Therefore, the number of samples used for a general land-use category is generally larger than the sum of those used for RHU's of similar land use. Many streams intersect several of the 28 RHU's and more than one of the four general land-use categories; therefore, these streams were suitable only for overall study-unit statistics. Water wells were identified solely by their geographic locations, not by the recharge area where the water originates.

The number of samples collected at each surface-water site varied widely, from several hundred per year at USGS load-computation sites to one or two at many synoptic sites. Therefore, to obtain representative statistical summaries that were not primarily indicative of only a few intensively sampled sites, the data were subsampled for computation of most statistical summaries. For each site, only one sample per constituent per month per year was used in most analyses. The sample chosen was the one collected closest to the middle of the month. If more than one sample was collected on the 15th of the month, the first sample collected on that day was chosen. These data are referred to as "midmonth" samples.

The spatial distribution of the wells used in this report was fairly uniform throughout the study unit. At most of these sites, only one water-quality sample was collected during the entire 20-year period. Few wells were sampled more than twice, and only one well was sampled as many as seven times. In computing statistical summaries, all but the most recent sample collected at a site was excluded to prevent a single site from having an unbalanced influence on the statistical analyses.

For each of the constituents, except suspended sediment, some data were reported as less than a minimum detection limit (MDL). All data whose concentrations were reported as "less than" were set to half of the MDL prior to being included in all summaries and statistics. For many constituents, more than one MDL was reported; only the highest MDL is reported in this report. A few concentrations reported with a very high MDL were of little quantitative value; therefore, these data were omitted from all summaries and statistics.

QUANTITY, LOCATION, AND TIMING OF SURFACE-WATER SAMPLES

In table 13, the total number of surface-water samples is given, by constituent, for each of the four data sources. Total phosphorus was the most frequently determined constituent in all four data bases, with 21,413 total determinations. Almost all analyses for suspended sediment were samples collected by the USGS; most other agencies analyzed the samples for total solids. Midmonth samples were statistically analyzed to prevent data from a few intensively sampled locations from biasing the results. The total number of midmonth samples for each constituent is given, by

Table 13. Total number of samples for surface-water constituents collected in the Western Lake Michigan Drainages study unit, by data source
[MSD, Metropolitan Sewerage District]

Constituent	Total number	Data source			
		NWIS[1]	STORET[2]	Milwaukee MSD	Green Bay MSD
Nitrite plus nitrate, dissolved	12,458	1,122	11,102	0	234
Nitrite, dissolved	1,031	318	479	0	234
Kjeldahl nitrogen, total	6,551	1,375	3,324	1,620	232
Ammonia, total	5,091	1,434	1,995	1,662	0
Ammonia, dissolved	12,489	1,107	11,253	0	229
Phosphorus, total	21,413	3,875	15,737	1,576	225
Phosphorus, dissolved	2,168	711	0	1,576	0
Orthophosphate, total	1,438	96	1,342	0	0
Orthophosphate, dissolved	13,928	1,054	12,727	0	147
Suspended sediment	11,022	11,003	19	0	0

[1]U.S. Geological Survey National Water Information System.

[2]U.S. Environmental Protection Agency Storage and Retrieval system.

Table 14. Number of midmonth samples for surface-water constituents collected in the Western Lake Michigan Drainages study unit, by data source
[MSD, Metropolitan Sewerage District]

Constituent	Total number	Data source			
		NWIS[1]	STORET[2]	Milwaukee MSD	Green Bay MSD
Nitrite plus nitrate, dissolved	5,705	772	4,861	0	72
Nitrite, dissolved	711	236	403	0	72
Kjeldahl nitrogen, total	4,258	943	2,746	494	75
Ammonia, total	2,780	646	1,628	506	0
Ammonia, dissolved	5,671	657	4,939	0	75
Phosphorus, total	9,441	1,302	7,562	506	71
Phosphorus, dissolved	1,105	618	0	487	0
Orthophosphate, total	1,163	38	1,125	0	0
Orthophosphate, dissolved	6,134	508	5,569	0	57
Suspended sediment	1,980	1,961	19	0	0

[1]U.S. Geological Survey National Water Information System.

[2]U.S. Environmental Protection Agency Storage and Retrieval system.

Table 15. Number of surface-water sampling sites in the Western Lake Michigan Drainages study unit for each constituent determined, by data source
[MSD, Metropolitan Sewerage District]

Constituent	Total number	Data source			
		NWIS[1]	STORET[2]	Milwaukee MSD	Green Bay MSD
Nitrite plus nitrate, dissolved	381	263	115	0	3
Nitrite, dissolved	101	56	42	0	3
Kjeldahl nitrogen, total	289	71	208	7	3
Ammonia, total	241	66	168	7	0
Ammonia, dissolved	366	66	297	0	0
Phosphorus, total	561	79	472	7	3
Phosphorus, dissolved	51	44	0	7	0
Orthophosphate, total	123	5	118	0	0
Orthophosphate, dissolved	373	55	315	0	3
Suspended sediment	80	76	4	0	0

[1]U.S. Geological Survey National Water Information System.

[2]U.S. Environmental Protection Agency Storage and Retrieval system.

data base, in table 14. For most constituents, about one-half of the samples were omitted when the data sets were edited. The exception was suspended sediment, for which about 80 percent of the samples were omitted.

Spatial distributions of sampling sites for most constituents were relatively uniform over the study unit, except for dissolved nitrite sites, which were concentrated around Green Bay, Milwaukee, and some tributaries of the Wolf River, and dissolved phosphorus sites, which were concentrated around Green Bay and the tributaries of the Wolf River. Site locations for total phosphorus and dissolved nitrite plus nitrate, the most cited and interpreted data, are shown in fig. 23, and site locations for suspended sediment are shown in fig. 24. Sampling sites for the remaining constituents are shown in appendix 1. Total phosphorus data are available for the most sampling sites (561) and also have the best spatial distribution. The total number of sampling locations is given in table 15 for each constituent. For most constituents, only a small amount of data was collected in Upper Michigan, except at a few sites on the Escanaba and Ford Rivers. Only a small amount of data was collected in the northeast corner of Wisconsin, except on the Menominee River. Most sampling sites were concentrated in the downstream areas (integrator sites) of most rivers; few sites were in headwater areas (indicator sites). This was especially true for suspended sediment. Suspended-sediment sampling sites also represent the location of most current or historical stream gages. (The spatial coverage for each constituent, is further discussed in later sections of the report.) MMSD and GBMSD collect data at many sites around Green Bay and Milwaukee; only subsets of their sites were used in the analyses.

The temporal distribution of samples at each site depends on the purpose for sampling the site. The distribution of the number of samples analyzed for total phosphorus during each month is shown in fig. 25 for all sites in the study unit and for three selected sites. At most monitoring sites, such as the Popple River, samples were collected relatively uniformly throughout the year. At sites sampled to estimate loads of specific constituents, such as White Creek, most samples were collected during high flows that occur most often during spring. Some sites, such as the Milwaukee River, are sampled for multiple purposes and have served as monitoring stations and as part of many synoptic surveys that are commonly done during the summer. When data from all three types of sites were combined, most samples were found to have been collected during the summer, especially in August; the fewest samples were collected in December and January. A secondary peak in the number of samples corresponds to high, spring-

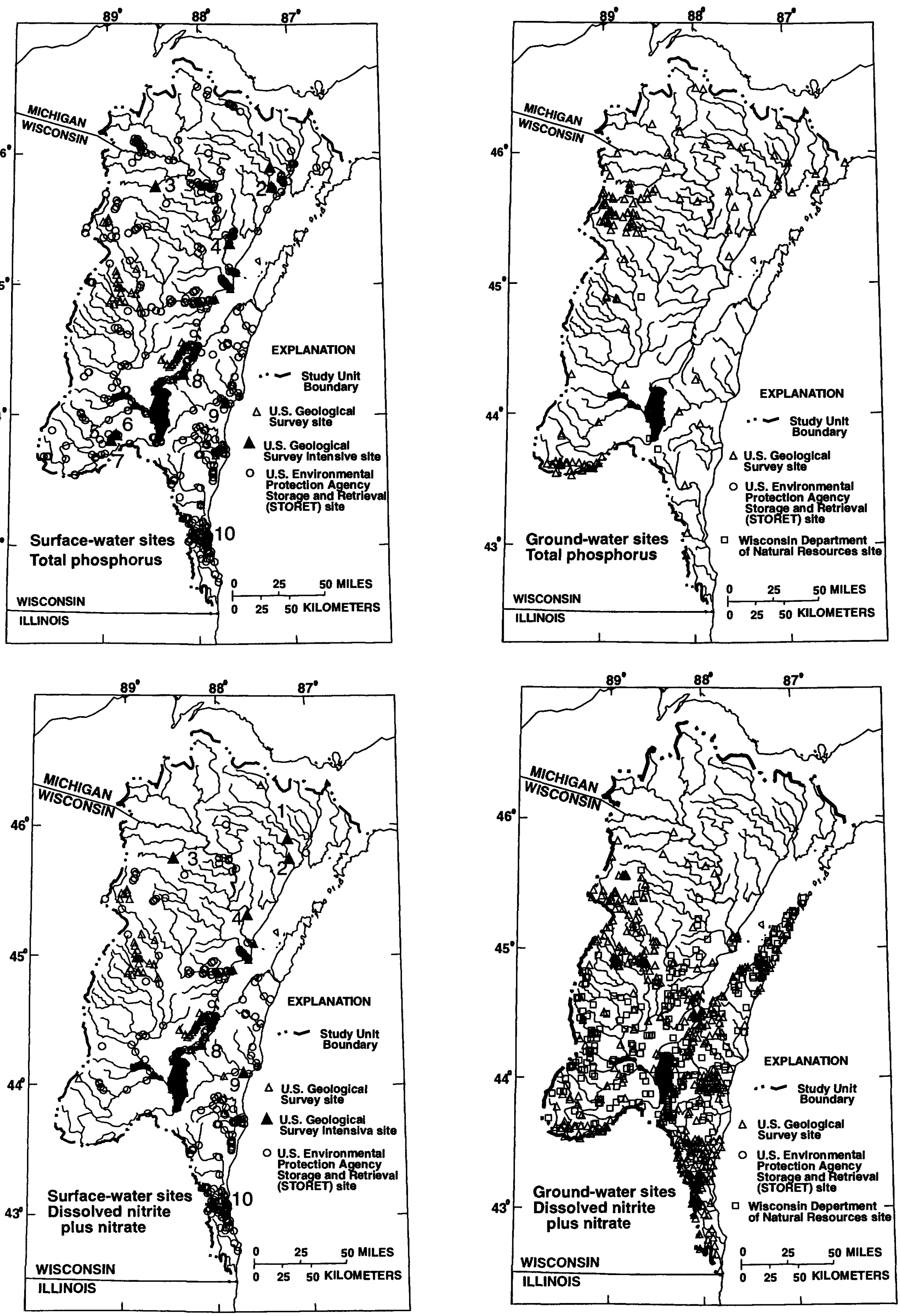


Figure 23. Location of surface- and ground-water sites sampled for total phosphorus and dissolved nitrite plus nitrate in the Western Lake Michigan Drainages study unit, water years 1971–90. [River names of the numbered U.S. Geological Survey intensive sites are given in the text on page 49.]

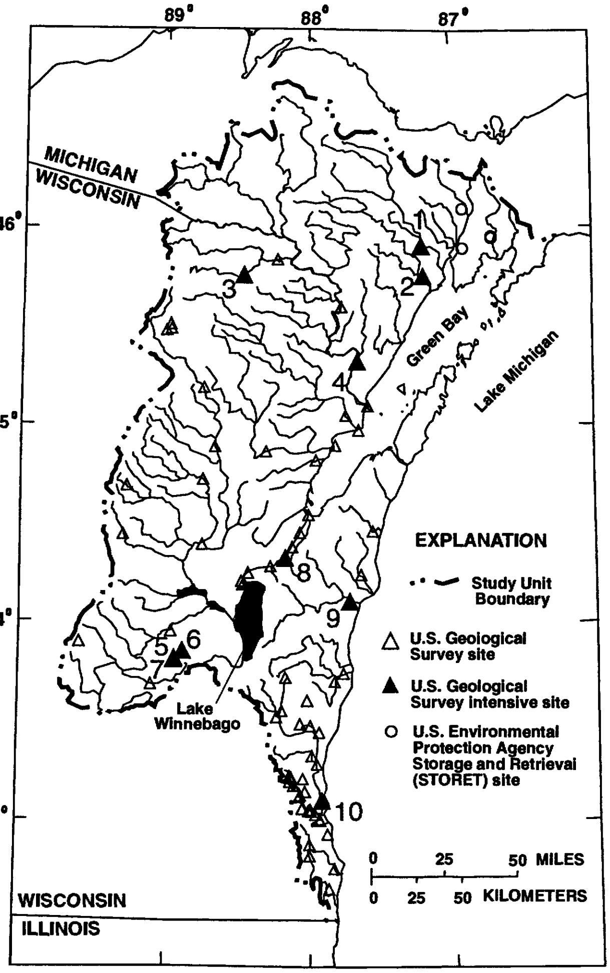


Figure 24. Location of surface-water sites sampled for suspended sediments in the Western Lake Michigan Drainages study unit, water years 1971–90. [Rivers names of the numbered U.S. Geological Survey intensive sites are given in the text listed below.]

time flow which occurs in March throughout much of the study unit. The distribution of samples for all the other constituents was very similar and is summarized in table 16.

Extensive water-quality data were collected at 10 sites within the WMIC study unit during water years 1971–90 (fig. 24) and are referred to throughout this report. These include seven sites that were part of the National Stream-Quality Accounting Network (NASQAN) program: Escanaba (1) and Ford (2) Rivers in Upper Michigan, and the Popple (3), Menominee (4), Fox (8), Manitowoc (9), and Milwaukee (10) Rivers in Wisconsin. The Menominee River (4) site was discontinued in 1986. Three additional sites were intensively sampled as part of a study aimed at estimating nutrient and suspended-sediment loads: White Creek (5), Silver Creek (6), and Green Lake Inlet (7). The monthly distribution of total phosphorus samples for each of these sites is summarized in table 17 and summarized for other remaining constituents, except total orthophosphate, in appendix 2; samples collected at these 10 sites were not analyzed for total orthophosphate.

Water-quality and flow information were simultaneously available at only a few sites. The distributions of samples collected for each of the constituents at the 10 intensively sampled sites are summarized by decile of flow in appendix 3. Samples collected at these 10 sites were not analyzed for total orthophosphate; therefore, total orthophosphate is not included in appendix 3. In general, the distribution of samples by decile of flow for other constituents was similar to that presented in fig. 26 for total phosphorus. Samples at most monitoring and (or) synoptic sampling sites, such as the Popple and Milwaukee Rivers, were collected relatively uniformly throughout the range in flows. Samples collected at sites used for load estimation, such as White Creek, were nonuniformly distributed; most samples were collected during high flows. Commonly, 80 to 90 percent of the samples at this type of site were collected within the highest decile of flow.

QUANTITY, LOCATION, AND TIMING OF GROUND-WATER SAMPLES

The total number of samples and the total number contained in each of the three ground-water data bases are summarized by constituent in table 18. Dissolved nitrite plus nitrate was the most frequently determined constituent listed in the NWIS and GIN data bases, whereas total Kjeldahl nitrogen and total ammonia were the only constituents listed in the STORET data base. All but the most recent sample collected at each ground-water site were excluded from statistical summaries. Therefore, the total number of samples used in the analyses was the same as the number of wells sampled for each constituent (table 19).

The spatial distribution of 919 selected wells where water-quality data were collected during water years 1971–90 is shown in fig. 27. The distribution of wells is fairly uniform except in the northern one-third of the study unit. No single constituent was sampled for throughout the entire study unit. Sampling locations for dissolved nitrate plus nitrate were the most extensive, even though few samples were collected in the north-

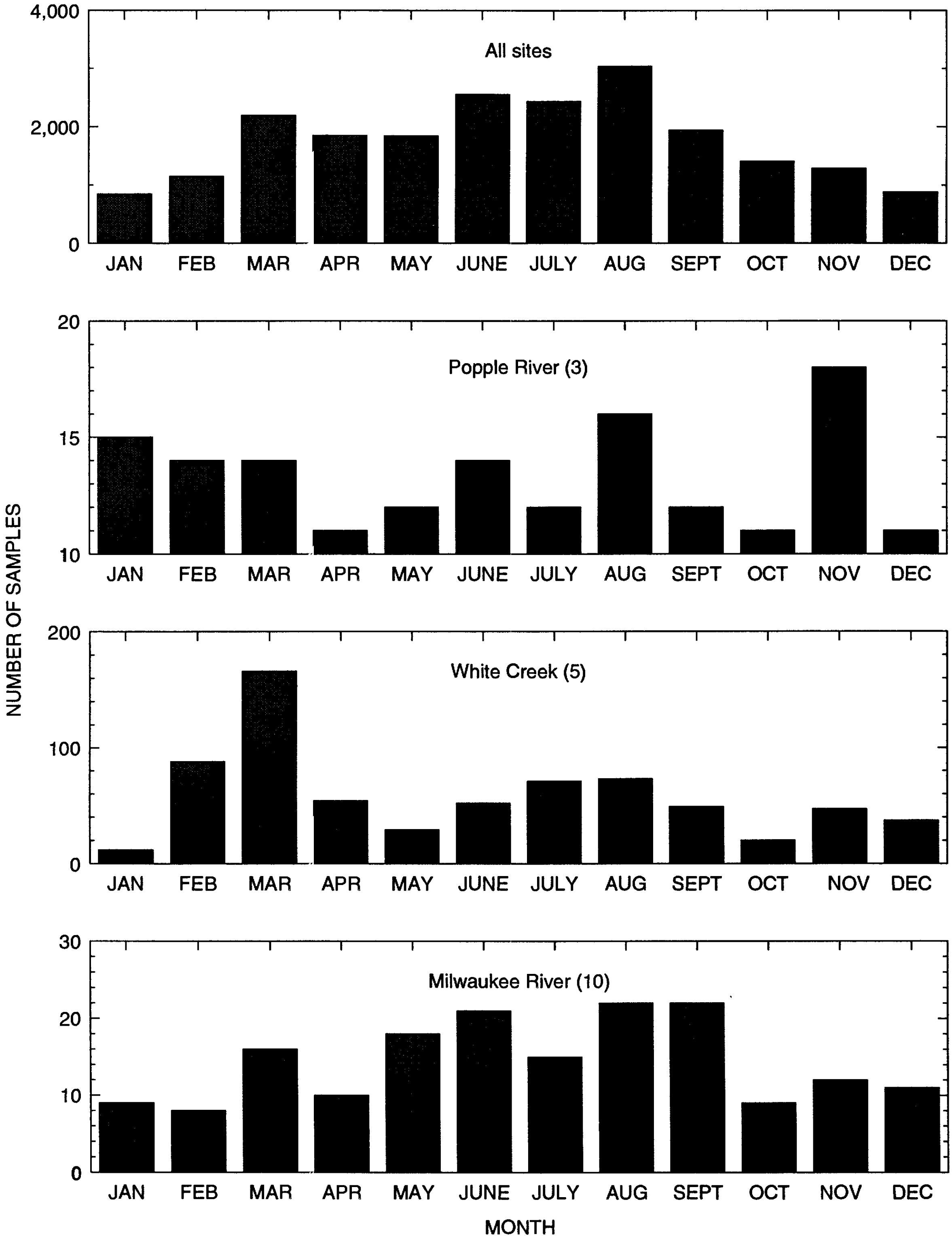


Figure 25. Number of samples analyzed for total phosphorus, by month, during water years 1971–90, for all sites and three selected sites in the Western Lake Michigan Drainages study unit. [River locations (identification numbers are in parentheses) are shown in figure 24.]

Table 16. Number of surface-water samples collected in the Western Lake Michigan Drainages study unit, by month, for each constituent, water years 1971–90

Constituent	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
Nitrate plus nitrite, dissolved	542	720	1,331	1,066	961	1,593	1,458	1,725	991	793	731	547
Nitrite, dissolved	44	36	105	64	111	115	136	169	84	67	63	37
Kjeldahl nitrogen, total	330	292	458	498	621	681	814	852	643	530	513	319
Ammonia, total	221	281	474	444	496	510	465	764	424	379	374	259
Ammonia, dissolved	573	732	1,329	1,059	936	1,574	1,462	1,719	986	802	736	581
Phosphorus, total	842	1,144	2,191	1,851	1,842	2,557	2,434	3,042	1,945	1,402	1,285	878
Phosphorus, dissolved	81	61	171	173	258	232	233	254	205	186	203	111
Orthophosphate, total	79	80	98	113	110	147	107	335	113	107	99	50
Orthophosphate, dissolved	607	807	1,458	1,248	1,197	1,729	1,595	1,947	1,152	860	724	604
Suspended sediment	469	594	1,422	1,100	969	1,103	1,076	1,179	1,038	781	788	503

Table 17. Number of surface-water samples, by month, for total phosphorus for the Western Lake Michigan Drainages study unit and selected basins, water years 1971–90
[site locations are shown in figure 24]

Site (site number)	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
All sites	842	1,144	2,191	1,851	1,842	2,557	2,434	3,042	1,945	1,402	1,285	878
Escanaba River (1)	11	7	15	11	11	12	11	12	12	9	10	9
Ford River (2)	15	8	8	11	10	7	16	7	8	11	9	6
Fox River (8)	7	7	16	7	11	15	9	13	9	9	12	10
Green Lake Inlet (7)	6	5	35	16	15	34	20	23	16	8	7	1
Manitowoc River (9)	3	1	11	4	9	21	13	20	12	3	6	4
Menominee River (4)	8	5	5	6	9	5	7	5	7	2	7	5
Milwaukee River (10)	9	8	16	10	18	21	15	22	22	9	12	11
Popple River (3)	15	14	14	11	12	14	12	16	13	11	18	11
Silver Creek (6)	4	15	125	57	66	54	56	60	69	20	22	3
White Creek (5)	12	88	166	54	29	52	71	73	49	20	47	37

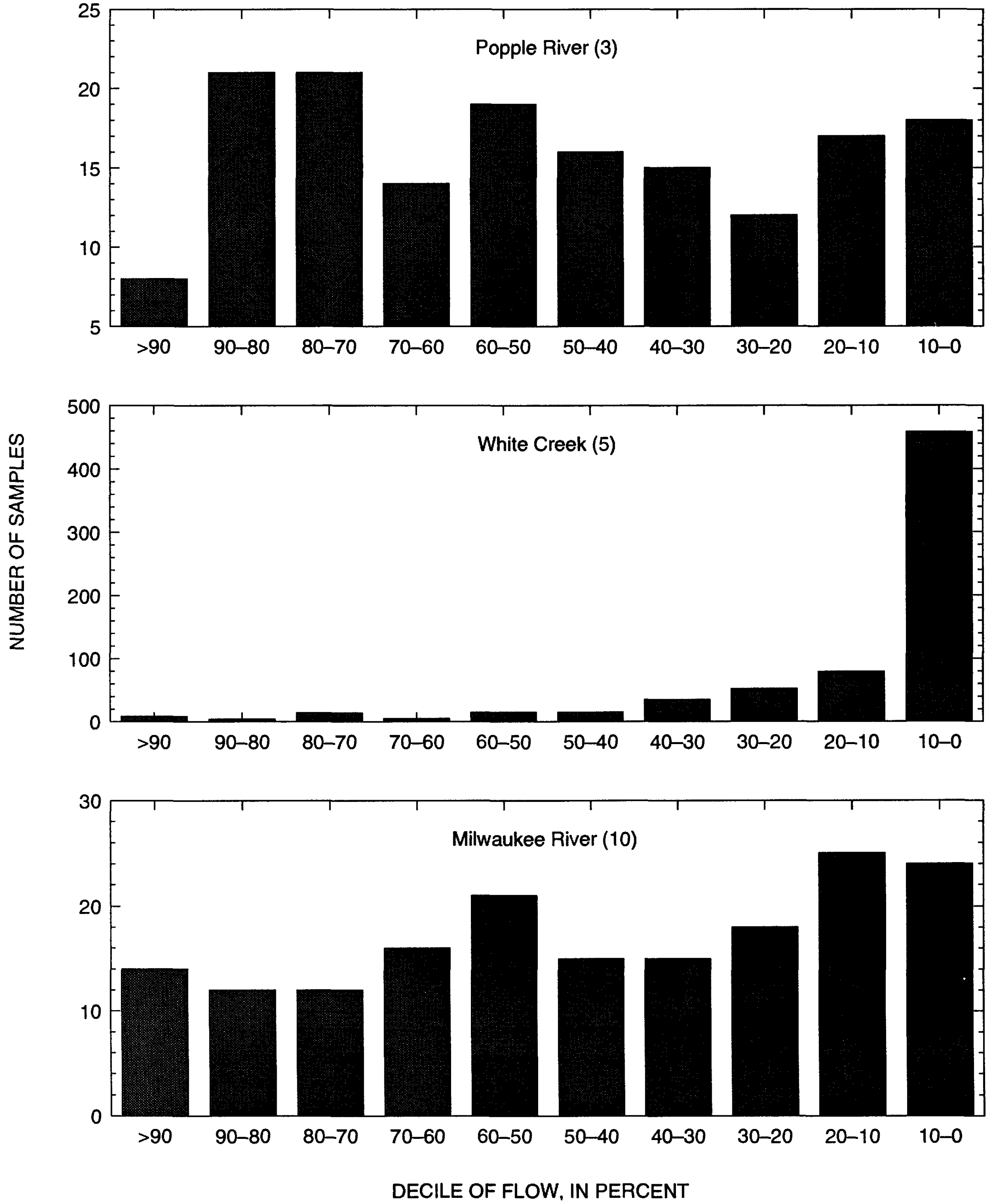


Figure 26. Number of samples analyzed for total phosphorus, by decile of flow, during water years 1971–90, for three sites in the Western Lake Michigan Drainages study unit. [River locations (identification numbers are in parentheses) are shown in figure 24.]

Table 18. Total number of samples for ground-water constituents collected in the Western Lake Michigan Drainages study unit, by data source

Constituent	Total number	Data source		
		NWIS[1]	GIN[2]	STORET[3]
Nitrite plus nitrate, dissolved	949	458	491	0
Nitrite, dissolved	350	350	0	0
Kjeldahl nitrogen, total	93	55	10	28
Ammonia, total	62	41	0	21
Ammonia, dissolved	200	175	25	0
Phosphorus, total	138	133	5	0
Phosphorus, dissolved	118	118	0	0
Orthophosphate, total	34	34	0	0
Orthophosphate, dissolved	15	15	0	0

[1]U.S. Geological Survey National Water Information System.
[2]Wisconsin Department of Natural Resource Groundwater Information Network.
[3]U.S. Environmental Protection Agency Storage and Retrieval system.

ern one-third of the study unit (fig. 23). For the rest of the constituents, distribution patterns consisted of small concentrations of wells in several locations, as illustrated for total phosphorus in fig. 23. The spatial distributions of the other constituents are shown in appendix 1.

Only a few sites were sampled more than once or twice. Therefore, temporal distribution of samples and seasonal changes in water quality are not discussed.

The distributions of samples by aquifer, well type, and well depth are summarized in table 19. In general, most samples for each constituent were evenly distributed within the sandstone, Silurian dolomite, and sand and gravel aquifers, but fewer samples were collected in the basement complex aquifer. Domestic wells were the most frequently sampled for all constituents, followed by public-supply wells.

Wells for which depth information were available were divided into five well-depth categories, listed in table 19. In general, the wells were fairly evenly distributed over the well-depth categories, but slightly more wells were in the greater than 70 m (200 ft) and 15.3–30.5 m (51–100 ft) depth categories.

NUTRIENT CONCENTRATIONS

Nitrogen and phosphorus are essential for algal and macrophyte growth in aquatic environments; in sufficiently high concentrations, however, these nutrients can adversely affect water quality by causing excess biological growth or, in some extreme cases, by

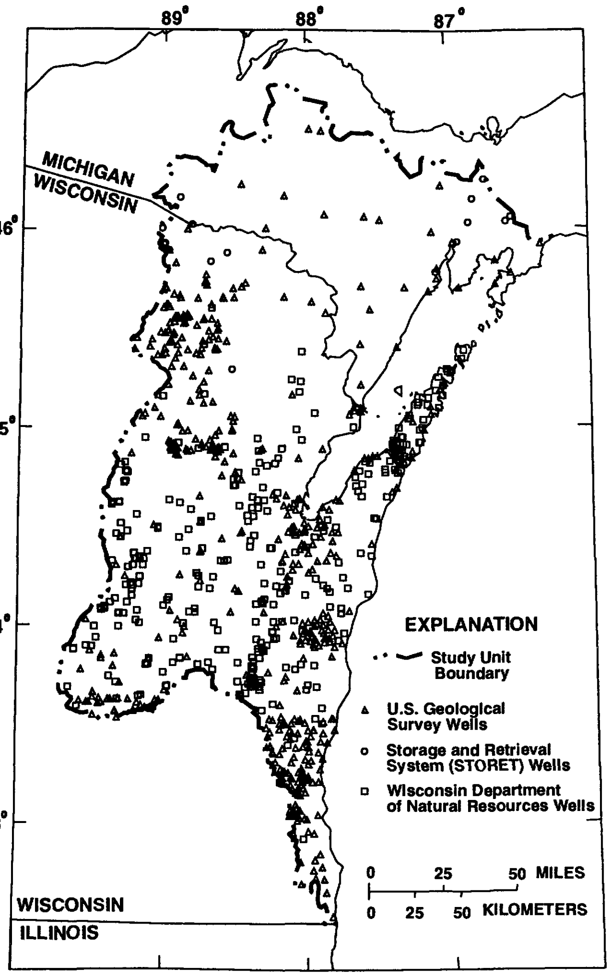


Figure 27. Location of wells in the Western Lake Michigan Drainages study unit for which nutrient data are available for water years 1971–90.

Table 19. Total number of wells in the Western Lake Michigan Drainages study unit sampled for nutrients, by data source, aquifer, well type, and well-depth category

Constituent	Total number	Data source			Aquifer				Well type									Well-depth category				
		NWIS[1]	GIN[2]	STORET[3]	Basement complex	Sandstone	Silurian dolomite	Sand and gravel	Commercial	Domestic	Irrigation	Industrial	Public-supply	Recreation	Stock	Institution	Other	0–15.2 m	15.3–30.5 m	30.6–45.7 m	45.8–61 m	>61 m
Nitrite plus nitrate, dissolved	789	404	385	0	27	104	188	159	13	636	8	13	72	5	13	9	3	74	124	96	75	197
Nitrite, dissolved	337	337	0	0	21	85	117	113	9	239	4	10	46	4	12	7	3	23	66	62	47	139
Kjeldahl nitrogen, total	80	47	8	25	6	18	7	20	0	44	0	0	2	1	3	1	0	33	20	7	4	16
Ammonia, total	53	34	0	19	2	17	4	11	0	22	0	0	1	1	1	2	0	17	15	4	3	14
Ammonia, dissolved	184	164	20	0	12	74	26	61	5	113	3	7	29	3	7	4	3	23	39	33	21	68
Phosphorus, total	128	125	3	0	21	40	9	56	0	82	0	1	6	1	8	1	0	21	37	28	9	33
Phosphorus, dissolved	108	108	0	0	9	36	18	45	4	66	1	6	20	2	1	0	2	15	28	16	9	40
Orthophosphate, total	27	27	0	0	2	17	4	4	0	0	0	0	0	1	0	0	26	3	5	2	3	14
Orthophosphate, dissolved	9	9	0	0	0	1	1	7	0	5	1	0	1	1	1	0	0	2	3	2	0	2

[1]U.S. Geological Survey National Water Information System.

[2]Wisconsin Department of Natural Resource Groundwater Information Network.

[3]U.S. Environmental Protection Agency Storage and Retrieval system.

being toxic to aquatic and terrestrial life (Rinella and others, 1992). Not all forms of nitrogen and phosphorus are directly usable by the biota; only nitrite, nitrate, ammonia, and orthophosphate are available for biotic uptake.

Surface- and ground-water nutrient data are summarized by general land use and RHU in appendix 4. The MDL used for each constituent is also given in this appendix. Because nutrient concentrations in ground water are affected by several factors, including general land use, summary statistics are also provided by data source, well type, aquifer, well depth, and RHU.

Nitrogen

Nitrogen is introduced into aquatic environments from agricultural fertilizers and manures, organic wastes in sewage and industrial effluent, atmospheric deposition, decomposition of organic material, biotic fixation, and ambient soils and rocks. Nitrogen is generally introduced as nitrate, ammonia, organic nitrogen, or molecular nitrogen, which can be rapidly transformed from one form to another by way of short-lived intermediate forms. The primary intermediate form of concern in this report is nitrite. The various forms of nitrogen are actively cycled in aquatic environments in what is commonly referred to as "the nitrogen cycle" (Stumm and Morgan, 1981; Wetzel, 1983). Nitrogen fixation is required to convert molecular nitrogen into ammonia, which can then be assimilated into various forms of organic nitrogen or be nitrified into dissolved nitrate. Nitrogen fixation is mediated in aquatic environments only by cyanobacteria (blue-green algae) and other specific bacteria. Ammonia is produced by the decomposition of organic nitrogen, such as amino acids and proteins. During nitrification, ammonia is oxidized into nitrate with nitrite as an intermediate transient. Nitrification occurs fairly rapidly in aerobic environments. Nitrates may be converted to molecular nitrogen in anaerobic environments through denitrification (again with nitrite as an intermediate form) or may be reduced to ammonia in an assimilatory pathway leading to the synthesis of amino acids.

Several forms of dissolved nitrogen are essential for algal and macrophyte growth and can be toxic to aquatic and terrestrial life. High concentrations of nitrite and nitrate can be harmful if consumed by warm-blooded animals. Nitrite reacts with hemoglobin to cause impairment of oxygen transport. Nitrate can be converted to nitrite within the gastrointestinal tract and therefore is potentially harmful. The maximum contaminant level (MCL) is 1 mg/L for nitrite, as quantified as measured nitrogen (as N), and 10 mg/L for dissolved nitrite plus nitrate (as N) (U.S. Environmental Protection Agency, 1986). Un-ionized ammonia also can be toxic to aquatic organisms. The proportion of ammonia in the un-ionized form depends on the concentration of ammonia, water temperature, and pH.

Total nitrogen was partitioned into its various forms in the following manner: median dissolved-nitrate concentration was estimated by subtracting the median nitrite concentration from the median dissolved nitrate plus nitrate concentration; particulate ammonia was estimated by subtracting the median dissolved ammonia concentration from the median total ammonia concentration; and organic nitrogen was estimated by subtracting the median total ammonia concentration from median total ammonia plus organic nitrogen concentration.

Land use and its associated rates of nitrogen input likely control the total nitrogen concentrations in the surface water of the WMIC study unit. Total nitrogen concentrations, as well as median concentrations for each form of nitrogen, and nitrogen inputs are shown for each general land-use category in fig. 28. Total nitrogen concentrations in surface water mirror the sum of the known inputs for the various general land-use categories, an indication that land use is the primary factor affecting total nitrogen concentrations in the surface water of the WMIC study unit. Median concentrations of total nitrogen were highest in agricultural areas (2 mg/L) and lowest in forested areas (0.5 mg/L).

Dissolved nitrate and organic nitrogen were the two principal forms of nitrogen in surface water for all general land-use categories except urban, where ammonia also was a large fraction. In agricultural areas, total nitrogen was somewhat evenly divided between dissolved nitrate (42 percent) and organic nitrogen (52 percent). In agricultural/forested areas, dissolved nitrate was the dominant form (67 percent) and organic nitrogen was the secondary form (28 percent). In forested areas, almost all nitrogen was in organic forms (82 percent), 13 percent of the total present as dissolved nitrate. In urban areas, nitrogen was somewhat evenly divided among ammonia (43 percent), dissolved nitrate (33 percent), and organic forms (21 percent).

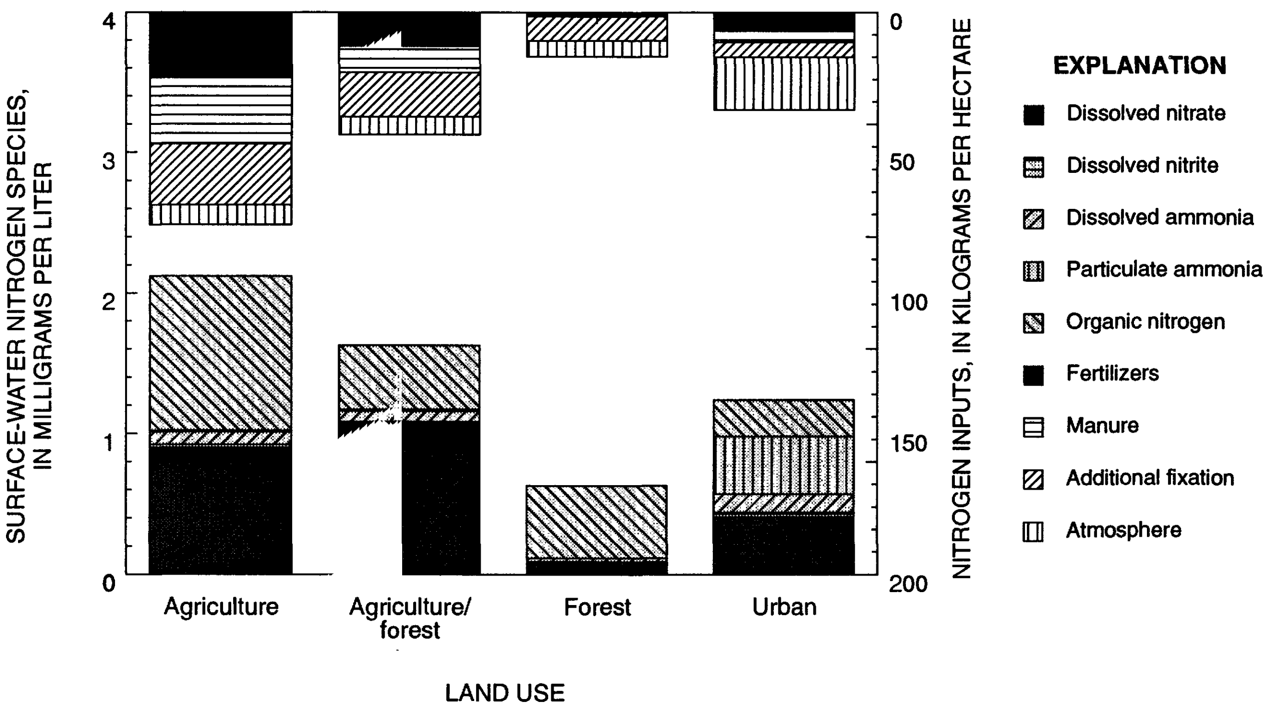


Figure 28. Median concentrations of nitrogen species in surface water (bottom) and nitrogen inputs (top) (fertilizers, manure, additional fixation not accounted for in manure, and atmospheric deposition) for general land-use categories in the Western Lake Michigan Drainages study unit.

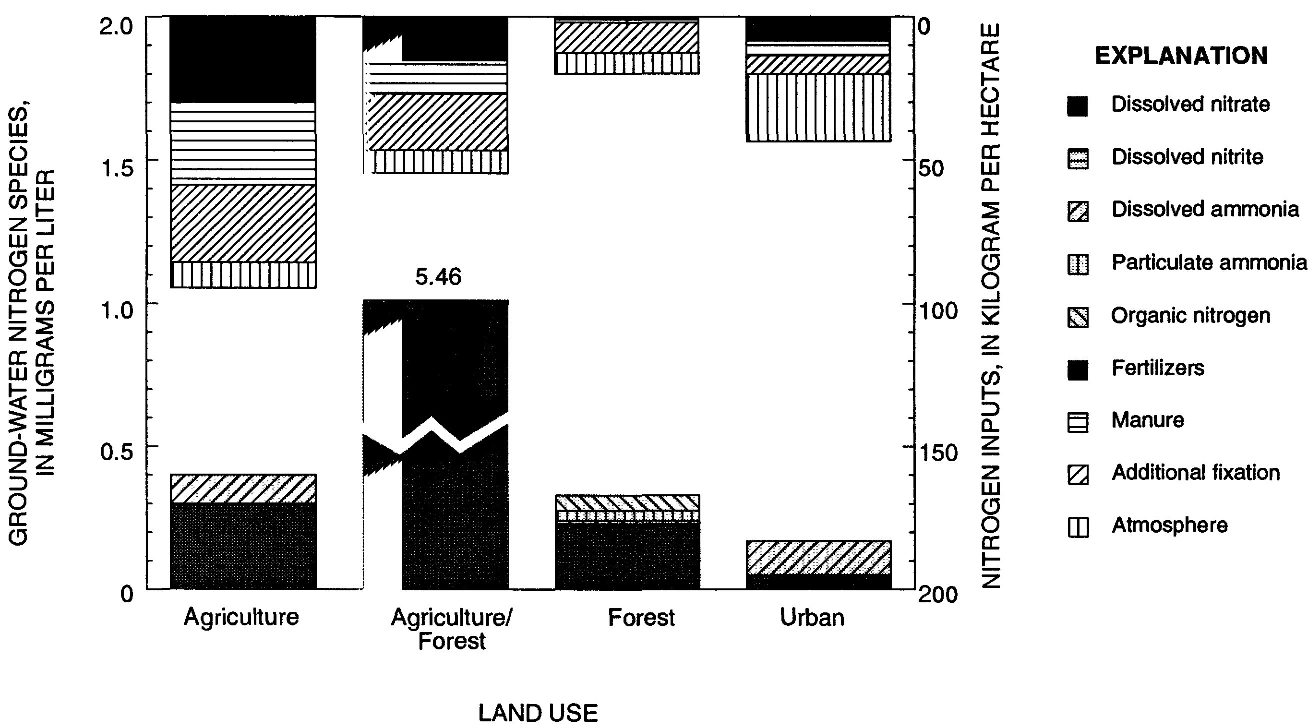


Figure 29. Median concentrations of nitrogen species in ground water (bottom) and nitrogen inputs (top) (fertilizers, manure, additional fixation not accounted for in manure, and atmospheric deposition) for general land-use categories in the Western Lake Michigan Drainages study unit. [Median concentration of dissolved nitrate for Agriculture/forest was 5.45 mg/L, which results in a total nitrogen concentration of 5.46 mg/L for that category.]

Total ammonia was partitioned into dissolved and particulate forms. Particulate forms of ammonia (presumably mostly ammonium adsorbed on clays) were important only in urban areas. Ammonia data were available for only one urban site, most of which were measured as total ammonia concentrations. This site was immediately adjacent to a sewage-treatment facility. Therefore, whether the high ammonia concentrations were truly representative of urban areas or whether the ammonia was actually dissolved or in particulate forms is uncertain.

Nitrite concentrations were very low in all areas, and they represent only a very small fraction of the total nitrogen in the systems.

Nitrogen concentrations in ground water can only be partially explained by land use and nitrogen-application rates. Total nitrogen concentrations and inputs of nitrogen are shown for each general land-use category in figure 29. The nitrogen-input rates were highest and lowest in agricultural and forest areas, respectively. In contrast, the highest median concentrations in ground water were found in agricultural/forested areas (5.5 mg/L) and the lowest in urban areas (0.2 mg/L). Factors that help explain the differences in nitrogen concentrations in ground water are discussed in this report.

The dominant form of nitrogen found in ground water for all general land-use categories, except urban, was dissolved nitrate. Dissolved nitrate accounted for 74 percent of the nitrogen found in agricultural areas, the remainder being primarily dissolved ammonia. In agricultural/forested areas, dissolved nitrate accounted for 99 percent of the total nitrogen concentration. In forested areas, nitrogen was present as dissolved nitrate (71 percent), organic nitrogen (17 percent), and particulate ammonia (11 percent). Urban areas were dominated by dissolved ammonia (71 percent) and dissolved nitrate (26 percent). Dissolved nitrite was a very minor fraction of the total nitrogen found in ground water throughout the study unit.

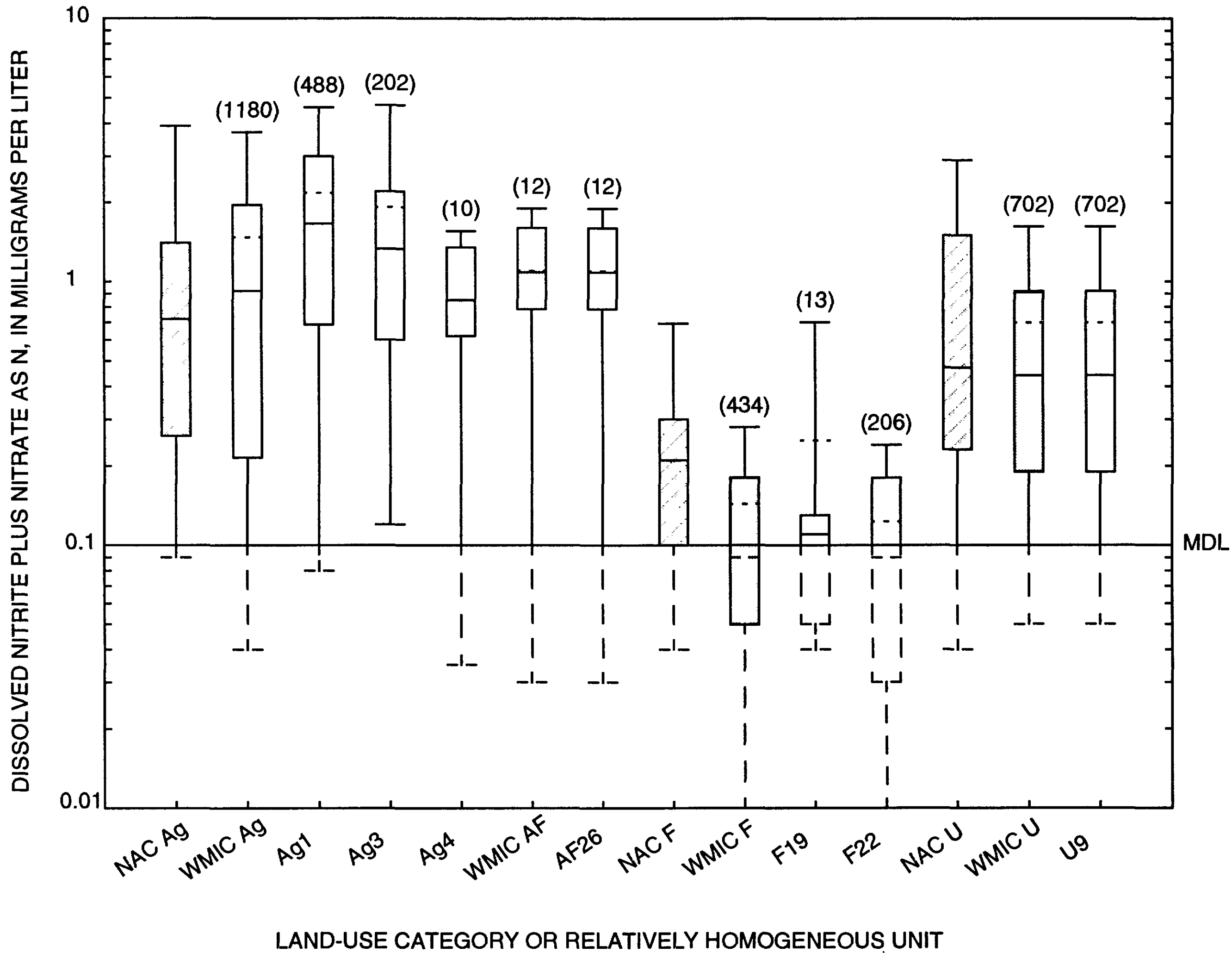
Dissolved Nitrite Plus Nitrate

Many samples were analyzed for dissolved nitrate (as N) or dissolved nitrate (as NO_3) instead of dissolved nitrite plus nitrate (as N). Because nitrite was usually present in very low concentrations and because these concentrations were found to be much lower than dissolved nitrite plus nitrate concentrations in surface water and ground water (as will be shown), these data were converted to concentrations as N and were considered along with the dissolved nitrate plus nitrate data. Many ground-water samples, especially those recorded in the GIN data base, were analyzed for total nitrite plus nitrate. Because particulate concentrations are very low in ground water, these concentrations also were considered along with the dissolved nitrate plus nitrate data.

Surface Water

Water samples analyzed for dissolved nitrite plus nitrate were collected throughout the study unit, but the highest density of sampling sites was around Milwaukee and Green Bay (fig. 23). Only a few samples were collected in the southwestern and northwestern parts of the study unit and in northern Wisconsin. Most samples were collected at downstream, integrator sites. The overall median concentration of dissolved nitrite plus nitrate (as N) was 0.50 mg/L, and the mean concentration was 0.93 mg/L. These concentrations primarily represent the concentrations of dissolved nitrate, because dissolved nitrite (discussed later in the report) represents only about 5 percent of these values. All median concentrations and statistics for each constituent described in the following sections were obtained using midmonth samples, except for the overall mean and median concentrations for each constituent, which were calculated from all the data. These data are summarized in appendix 4.

Dissolved nitrate plus nitrate concentrations were highest in agricultural and agricultural/forested areas and lowest in forested areas; median concentrations were 0.92, 1.09, and 0.09 mg/L, respectively (fig. 30; appendix 4.1). The median concentration in urban areas was 0.44 mg/L. In forested areas, the median concentration was below the 0.10-mg/L MDL. To determine whether any apparent differences shown by these boxplots (and in comparisons of other groupings of data in this report) were statistically significant at the 95-percent probability level ($\rho < 0.05$), analyses of variance were used on the ranks of the data, in conjunction with the Tukey multiple-comparison procedure, by use of the computer program SAS (SAS Institute, Inc., 1990). The differences among general land-use categories were all statistically significant (agriculture> urban> forest) except for agricultural/forested areas, which were not statistically different from agricultural and urban areas. The relative magnitudes of the concentrations coincide well with the total nitrogen



EXPLANATION

(404) Number of samples
90th percentile
Mean
75th percentile
Median
25th percentile
10th percentile

NAC–National average concentration (cross hatched)
(from Alexander and Smith, 1990)

WMIC–Western Lake Michigan Drainages study unit (shaded)

Ag–Agricultural area (where followed by number, denotes a particular Relatively Homogenous Unit (RHU))

AF–Agricultural/forested area (where followed by number, denotes a particular RHU)

F–Forested area (where followed by number, denotes a particular RHU)

U–Urban area (where followed by number, denotes a particular RHU)

MDL–Highest Minimum Detection Limit
(Values below MDL are dashed)

Figure 30. Boxplots of dissolved nitrite plus nitrate concentrations in surface water, for National land-use categories, and land-use categories and Relatively Homogeneous Units in the Western Lake Michigan Drainages study unit, water years 1971–90.

applied for these land-use categories (fig. 28). For this constituent, the agricultural/forested areas resemble the agricultural areas more than the forested areas; however, only 12 samples were collected in agricultural/forested areas. Concentrations exceeding the 10-mg/L MCL for dissolved nitrite plus nitrate were found only in agricultural areas.

Concentrations in agricultural and urban general land-use categories were similar to the "national average" surface-water concentrations (NAC's) for these types of land use (fig. 30; appendix 4.1) (Smith and others, 1993); however, concentrations in forested areas within the WMIC (0.09 mg/L, median concentration) were lower than the national concentrations (median of 0.21 mg/L).

Concentrations of dissolved nitrite plus nitrate in samples collected by the USGS were fairly similar to those collected by other agencies for all general land-use categories except agricultural/forested areas, for which only six samples were collected by both groups (appendix 4.1). The median concentration for samples collected by the USGS in agricultural/forested areas was 1.60 mg/L, whereas the median concentration in samples collected by other agencies was 0.78 mg/L. In agricultural areas, the median concentration of samples collected by USGS was slightly lower than that for samples collected by other agencies (0.64 and 0.95 mg/L, respectively). The median concentrations in samples collected by the USGS and by other agencies were similar for forested areas.

Distinct seasonality was found in dissolved nitrate plus nitrate concentrations. Median summer concentrations (lowest in July, 0.21 mg/L) were lower than median winter and early spring concentrations (highest in February, 1.09 mg/L) (concentrations from May through September were significantly lower than those from December through March). This seasonality was found for each land-use category. Median concentrations were lowest in July for each land-use category. This seasonality may have been caused by organisms, use of nitrates as a nitrogen source during summer, resulting in lower nitrate concentrations and higher organic nitrogen concentrations. The highest concentrations in individual samples in agricultural areas were, however, found during summer.

Because of the small number of samples in indicator areas, concentrations can be discussed only for a few RHU's (fig. 30). Concentrations are discussed only for RHU's where at least 10 midmonth samples were collected. No statistical differences were detected among RHU's of similar general land use. Most samples in agricultural areas were collected in Ag1 and Ag3; only 10 samples were collected in Ag4. All RHU abbreviations are listed in table 4. Ag1 and Ag3 were the only areas where concentrations exceeded the MCL. These three areas differ only in texture of surficial deposit: Ag1 (clayey deposits), Ag3 (sandy deposits), and Ag4 (sand and gravel deposits). Nitrogen applications in all 3 RHU's were similar. Therefore, the similarity in concentrations indicates that these differences in the texture of surficial deposits had little effect on dissolved nitrate plus nitrate concentrations in surface water. Most samples in forested areas were collected in F19 and F22. These two areas differ only with respect to forest type: F19 is dry forest and F22 is wet forest. Therefore, because concentrations were not significantly different, the difference in forest types (wet as opposed to dry) appears to have had little effect on dissolved nitrate plus nitrate concentrations in surface water. The concentrations in agricultural RHU's (Ag1, Ag3, and Ag4) were significantly higher than that in the urban RHU (U9), which in turn was significantly higher than those in the forested RHU's (F19 and F22).

Ground Water

Wells sampled for dissolved nitrite plus nitrate cover the southern two-thirds of the study unit; however, the northern part of the study unit is not well represented by sampled wells (fig. 23). The median concentration of dissolved nitrite plus nitrate was 0.40 mg/L, and the mean concentration was 3.08 mg/L (appendix 4.11). All summary statistics were computed from only the most recent sample collected at each well.

Dissolved nitrate plus nitrate data were obtained from two data bases, NWIS and GIN. The median nitrite plus nitrate concentration in the GIN data base (2.90 mg/L) was about two orders of magnitude higher than that from the NWIS data base (0.05 mg/L) (fig. 31). Because many of the samples in the GIN data base were analyzed for total concentrations and most of the samples in the NWIS data base were analyzed for dissolved, it was thought that including the total concentrations in the GIN data base may result in higher overall concentrations and account for the difference. Within the GIN data base, the median total nitrite plus nitrate concentration was lower than the median dissolved concentration (2.8 and 9.8 mg/L, respectively); therefore, omitting the samples analyzed for total

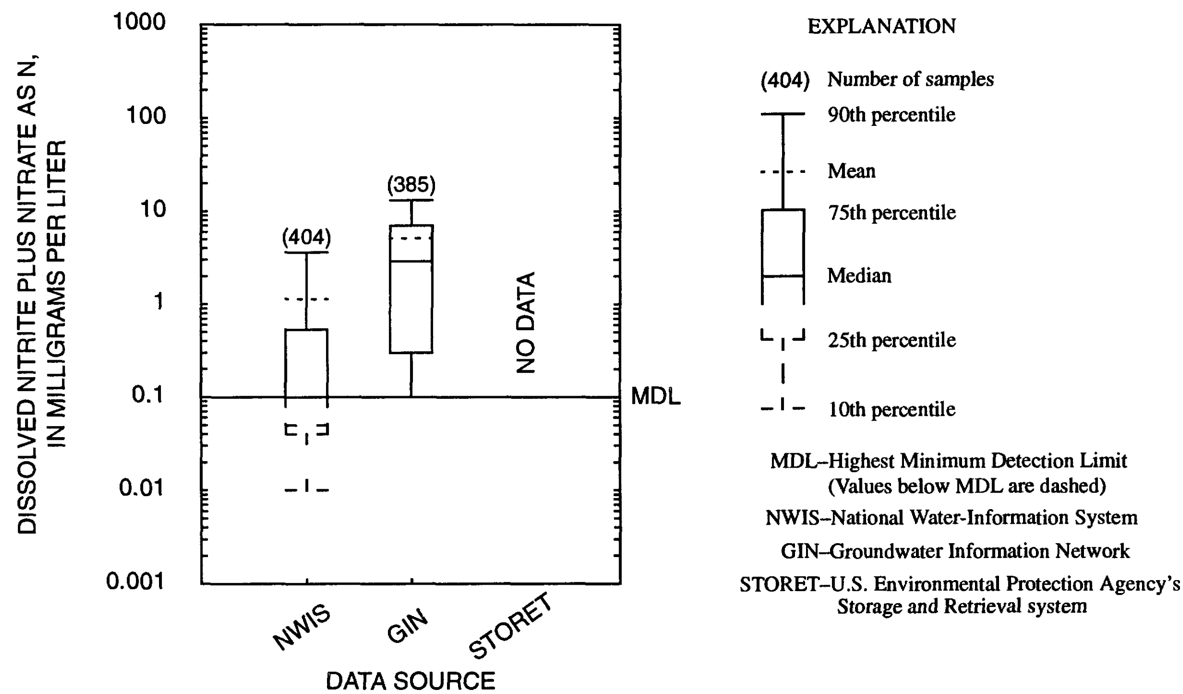
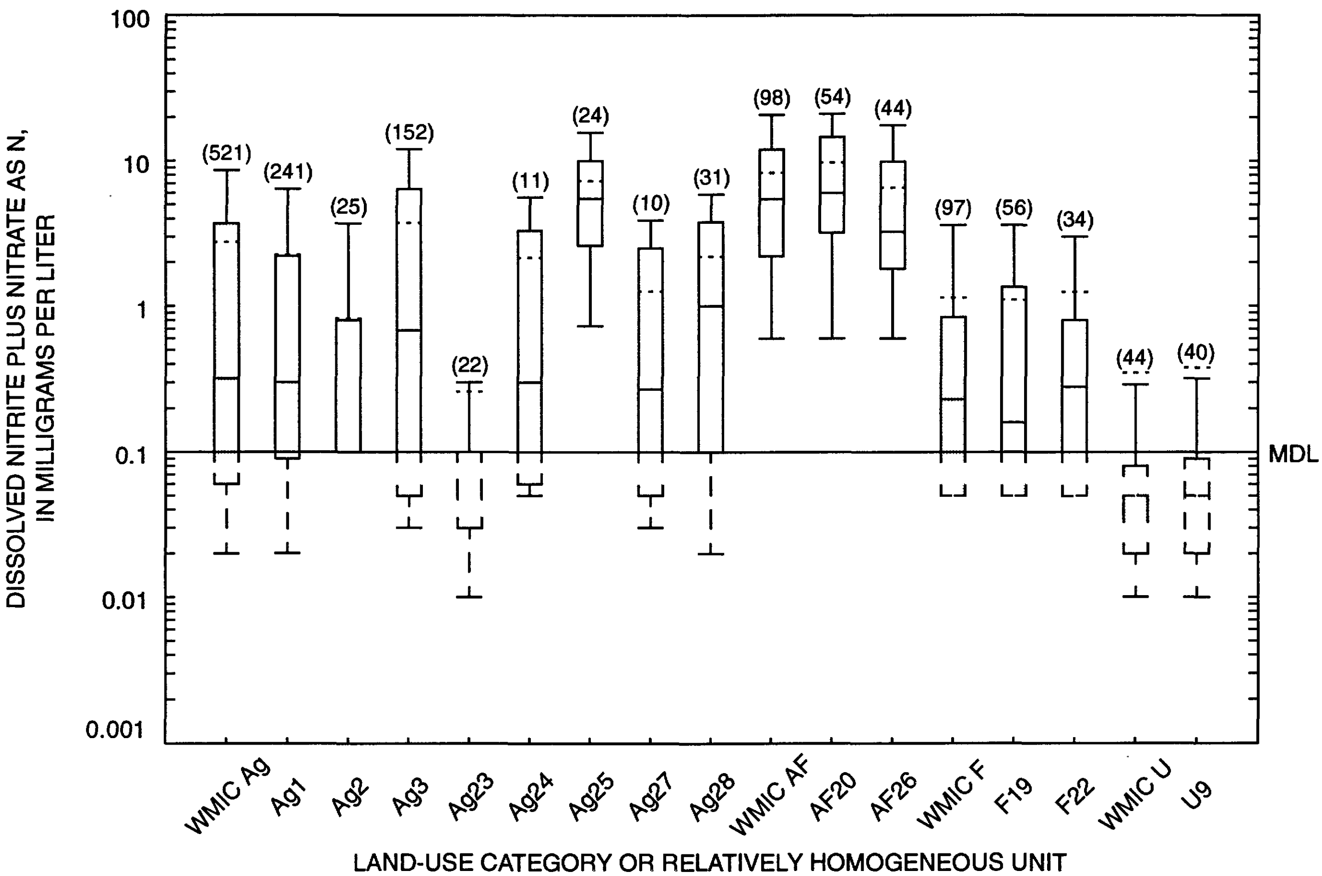


Figure 31. Boxplots of dissolved nitrite plus nitrate concentrations in ground water, by data source, for wells sampled in the Western Lake Michigan Drainages study unit, water years 1971–90.

nitrite plus nitrate would only increase the difference between the data bases. Dissolved and total nitrite plus nitrate concentrations in ground water should be similar because particulates, in general, are negligible in ground water. The most probable cause of the difference between the two data bases is that most of the data included in the GIN data base were from wells in areas of known or suspected water-quality problems, whereas NWIS data were primarily from wells that represent background water quality. Collective use of these data bases better represents ambient groundwater quality than use of data from any one data base separately.

Land use was found to be the single most influential factor influencing the distribution of nitrate plus nitrate concentrations in surface water; however, this was not the case for ground water. Highest concentrations of nitrite plus nitrate were found in the agriculture/forest areas, where the median concentration was 5.45 mg/L (fig. 32). This concentration was an order of magnitude higher than the median concentrations in agricultural and forested areas (0.32 and 0.23 mg/L, respectively) and two orders of magnitude higher than the median concentration in urban areas (0.05 mg/L). The areas with the largest nitrogen inputs (fig. 29) did not correspond to the areas with the highest nitrogen concentrations in ground water. The agriculture/forest area had the second largest nitrogen inputs, but it had the highest median concentrations in ground water. These differences can perhaps be explained by consideration of well type, texture of surficial deposits, aquifer type, bedrock type, and well depth.

The highest concentrations of nitrite plus nitrate were generally found in water from stock, domestic, and public-supply wells, whereas the lowest were found in water from commercial and industrial wells (fig. 33). Water from wells used for stock had the highest median concentration (2.3 mg/L). The lowest median concentration was found in water from industrial wells (0.03 mg/L). Some well types are associated with specific land uses. Stock and irrigation wells are associated with agriculture, whereas commercial and industrial wells are associated with urban land use. This association is reflected in median concentrations of nitrite plus nitrate, which are higher in water from wells associated with agriculture than in water from wells associated with urban land use. It is difficult to determine an association for domestic and public-supply wells because they are in all land-use areas.



EXPLANATION

(404) Number of samples

90th percentile

Mean

75th percentile

Median

25th percentile

10th percentile

WMIC–Western Lake Michigan Drainages study unit (shaded)

Ag–Agricultural area (where followed by number, denotes a particular Relatively Homogenous Unit (RHU))

AF–Agricultural/forested area (where followed by number, denotes a particular RHU)

F–Forested area (where followed by number, denotes a particular RHU)

U–Urban area (where followed by number, denotes a particular RHU)

MDL–Highest Minimum Detection Limit (Values below MDL are dashed)

Figure 32. Boxplots of dissolved nitrite plus nitrate concentrations in ground water, for general land-use categories and Relatively Homogenous Units, for wells sampled in the Western Lake Michigan Drainages study unit, water years 1971–90.

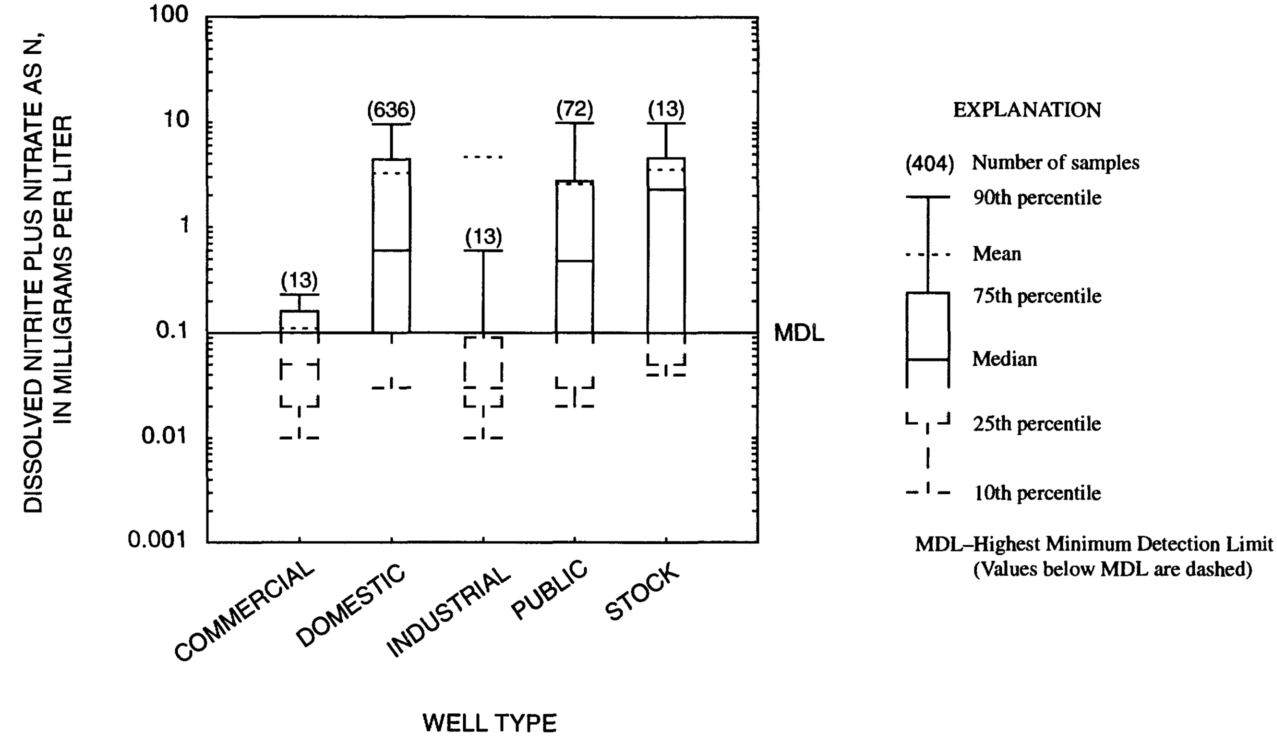


Figure 33. Boxplots of nitrite plus nitrate concentrations in ground water, by well type, for wells sampled in the Western Lake Michigan Drainages study unit, water years 1971–90.

The texture of surficial deposits affects the rate at which water is transmitted from land surface to ground water; therefore, texture affects the amount and rate of the downward movement of nutrients (and therefore was also used as a criterion in defining RHU's). The data used in this report were mostly from wells finished in areas overlain by either sand/sand and gravel or clay. Ground water from areas overlain by the most permeable deposit type (sand/sand and gravel) had significantly higher concentrations of nitrite plus nitrate (median of 1.6 mg/L) than ground water from areas overlain by the least permeable (clay) (median of 0.20 mg/L) (fig. 34).

The agricultural/forested areas are completely underlain by very permeable sand/sand and gravel deposits, and ground water from these areas had the highest nitrite plus nitrate concentrations. The urban land-use category is almost completely underlain by clays of low permeability. Clayey surficial deposits in these urban areas are consistent with the presence of the lowest concentrations of nitrite plus nitrate found. Most of the agricultural areas are underlain by clay; thus, even though the agricultural area had the highest nitrogen inputs, the underlying clays may have precluded correspondingly high concentrations of nitrite plus nitrate in ground water.

The aquifer from which ground-water samples were withdrawn for determination of nitrite plus nitrate was known for about 61 percent (478 out of 789) of the wells. Of these wells, about 94 percent were finished in either the Silurian dolomite, the sand and gravel, or the sandstone aquifer. These three aquifers account for about 99 percent of the ground water used in the WMIC study unit. Median concentrations of nitrite plus nitrate ranged from 0.24 mg/L for the Silurian dolomite aquifer to 0.05 mg/L for the sandstone aquifer (fig. 35); however, these concentrations were not significantly different.

Bedrock type identifies the shallowest bedrock lithology in the vicinity of the well; it does not necessarily indicate the type of lithology in which the well is finished, nor is it equivalent to "aquifer." In general, different bedrock types transmit water at different rates; however, the ability to transmit water may vary significantly even within a particular bedrock type. Bedrock type was also used as a criterion in defining

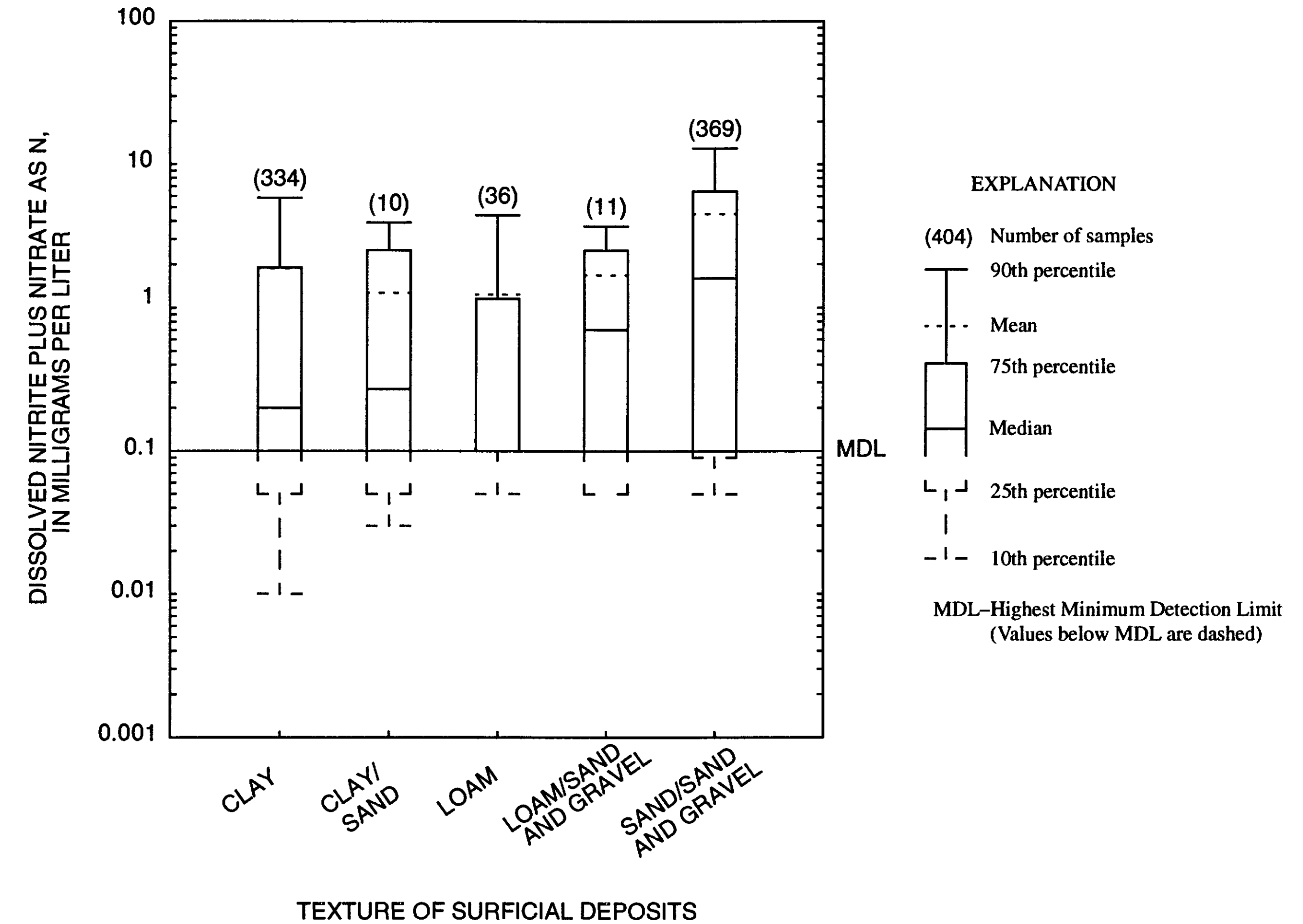


Figure 34. Boxplots of dissolved nitrite plus nitrate concentrations in ground water, by texture of surficial deposits, for wells sampled in the Western Lake Michigan Drainages study unit, water years 1971–90.

RHU's and was interpreted similarly to the texture of surficial deposits. The highest concentrations of nitrite plus nitrate were found in areas underlain by sandstone and igneous/metamorphic rocks (median concentrations of 2.75 and 0.71 mg/L, respectively) (fig. 36). Significantly lower concentrations of nitrite plus nitrate were found in areas underlain by carbonates and shale (median concentrations of 0.20 and 0.10 mg/L, respectively). In general, areas underlain by sandstone and igneous/metamorphic rocks are associated with areas also underlain by sand/sand and gravel, whereas areas underlain by carbonates and shales are associated with areas also underlain by clay.

Nitrate plus nitrate concentrations generally decreased with increasing well depth. This trend was investigated by dividing the data into five well-depth categories: 0–15 m (0–50 ft), 15–31 m (51–100 ft), 31–46 m (101–150 ft), 46–61 m (151–200 ft), and >61 m (>200 ft) (fig. 37). Median concentrations ranged from 3.1 mg/L in the shallowest wells (0–15 m) to 0.07 mg/L in the deepest wells (>61 m).

Based on the median well depth, the shallowest wells were in the agricultural/forested areas, and the next shallowest were in areas of forest and agriculture (fig. 38). The deepest wells were in urban areas. The well depth was not recorded for all wells; therefore, the number of wells in fig. 38 is less than the total number of wells for the respective land-use categories in Appendix 4.11. As discussed in the previous paragraph, water from the shallowest wells generally had the highest nitrate plus nitrate concentrations and water from the deepest wells generally had the lowest concentrations. It may seem from this pattern that variations in nitrate plus nitrate concentrations can be explained by a well-depth relation independent of land use. However, a comparison of concentrations by land

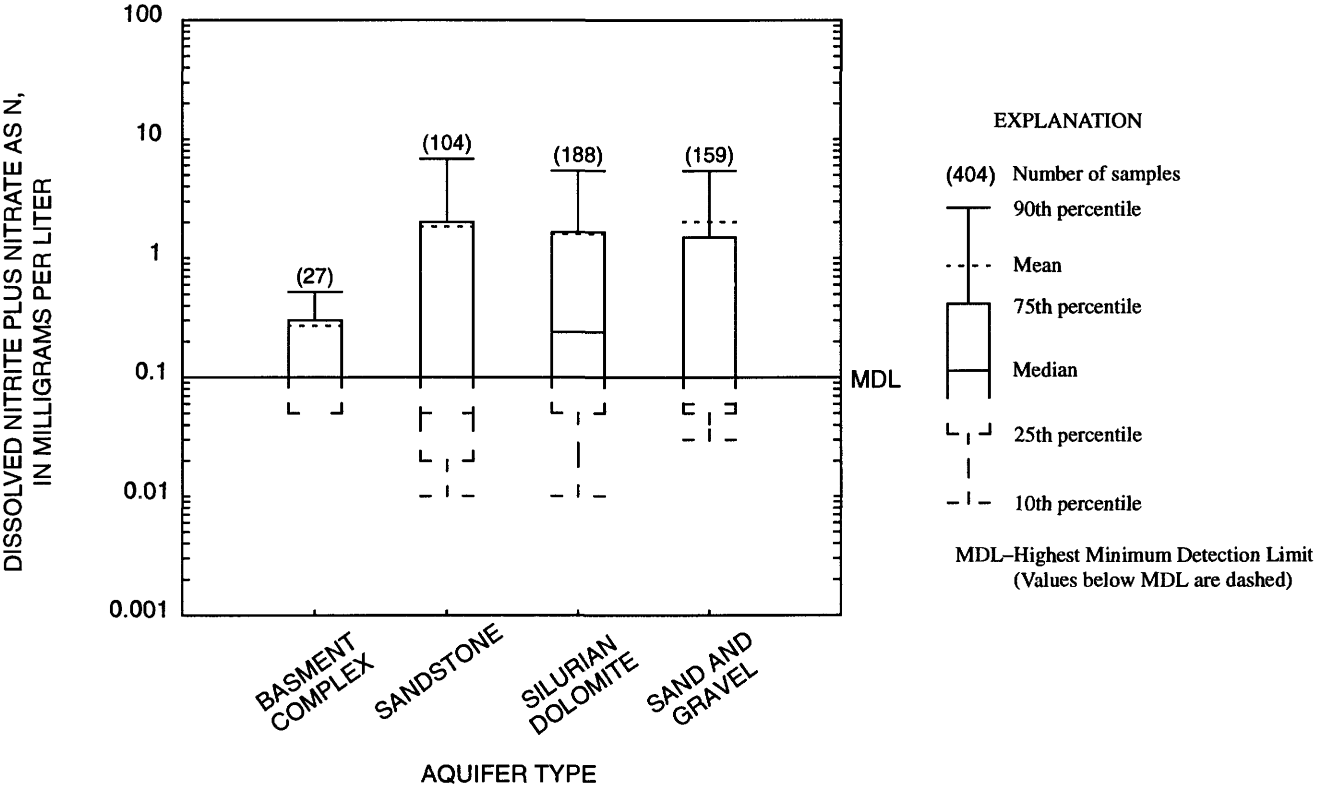


Figure 35. Boxplots of dissolved nitrite plus nitrate concentrations in ground water, by aquifer, for wells sampled in the Western Lake Michigan Drainages study unit, water years 1971–90.

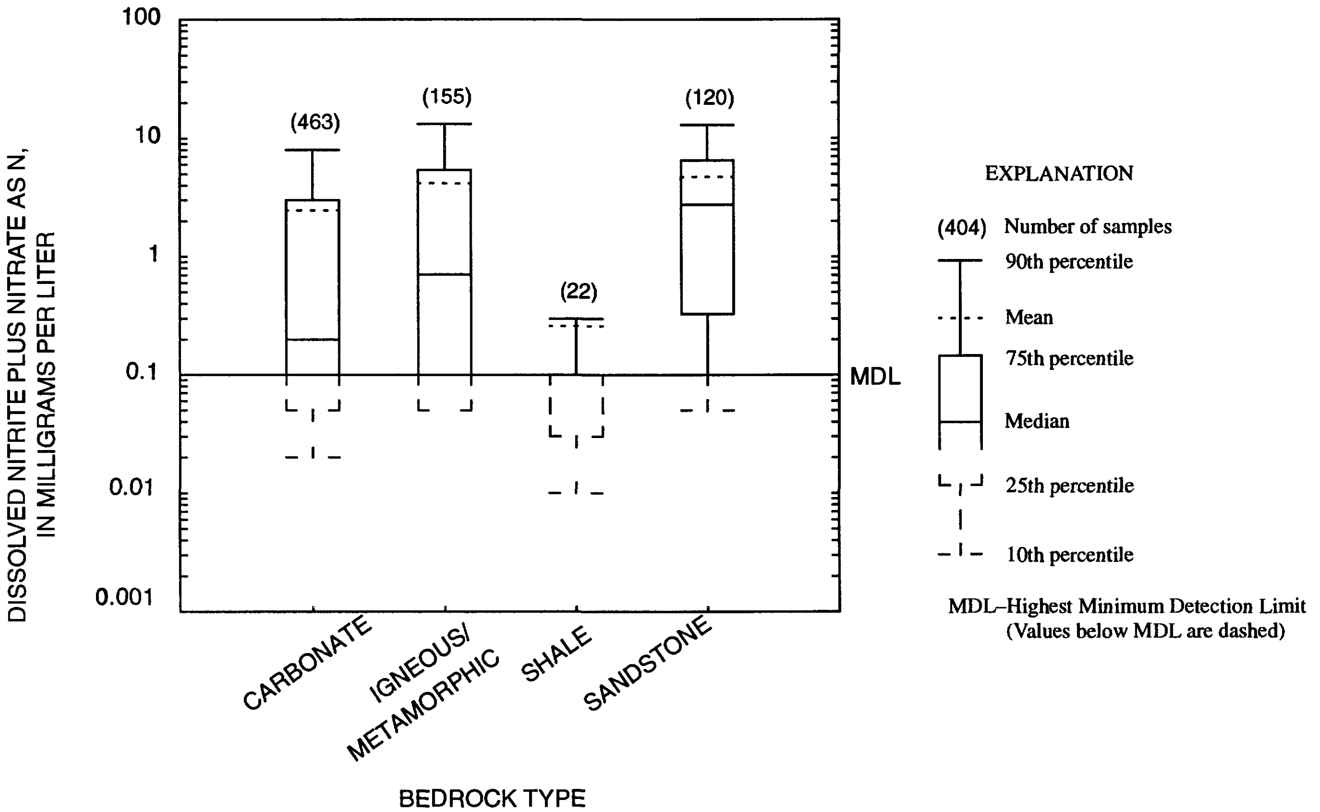


Figure 36. Boxplots of dissolved nitrite plus nitrate concentrations in ground water, by bedrock type, for wells sampled in the Western Lake Michigan Drainages study unit, water years 1971–90.

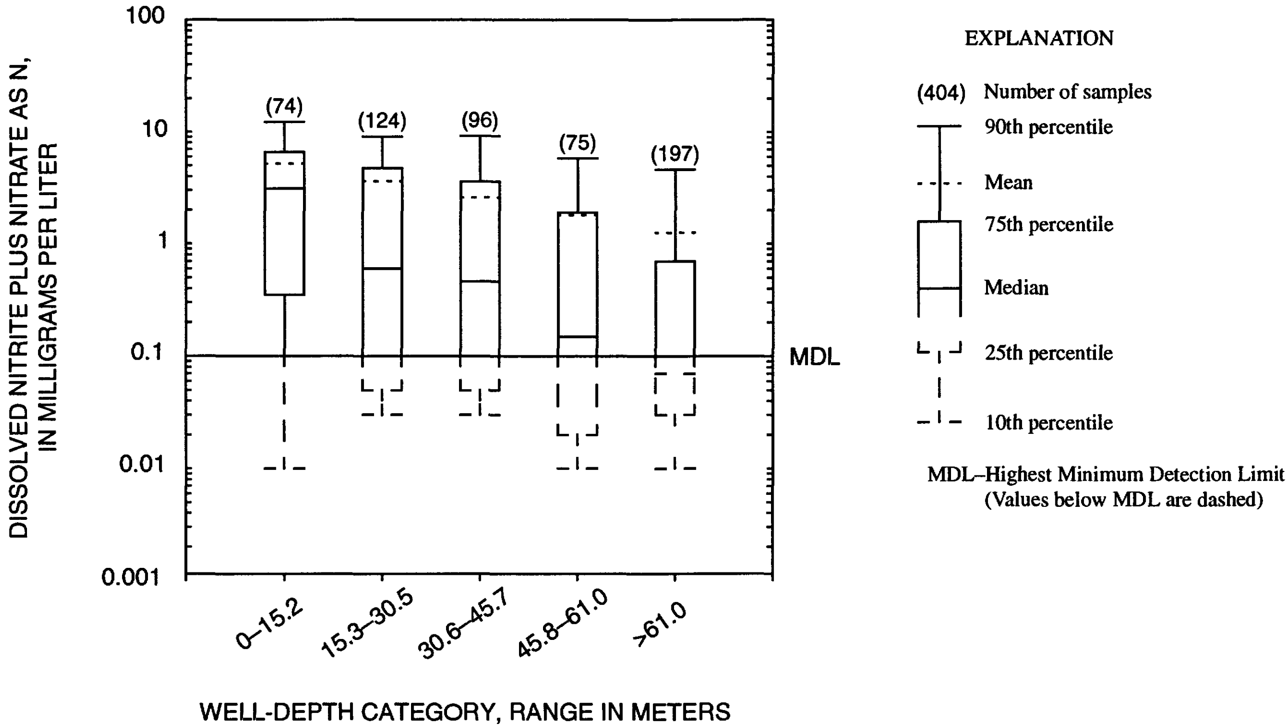


Figure 37. Boxplots of dissolved nitrite plus nitrate concentrations in ground water, by well-depth category, for wells sampled in the Western Lake Michigan Drainages study unit, water years 1971–90.

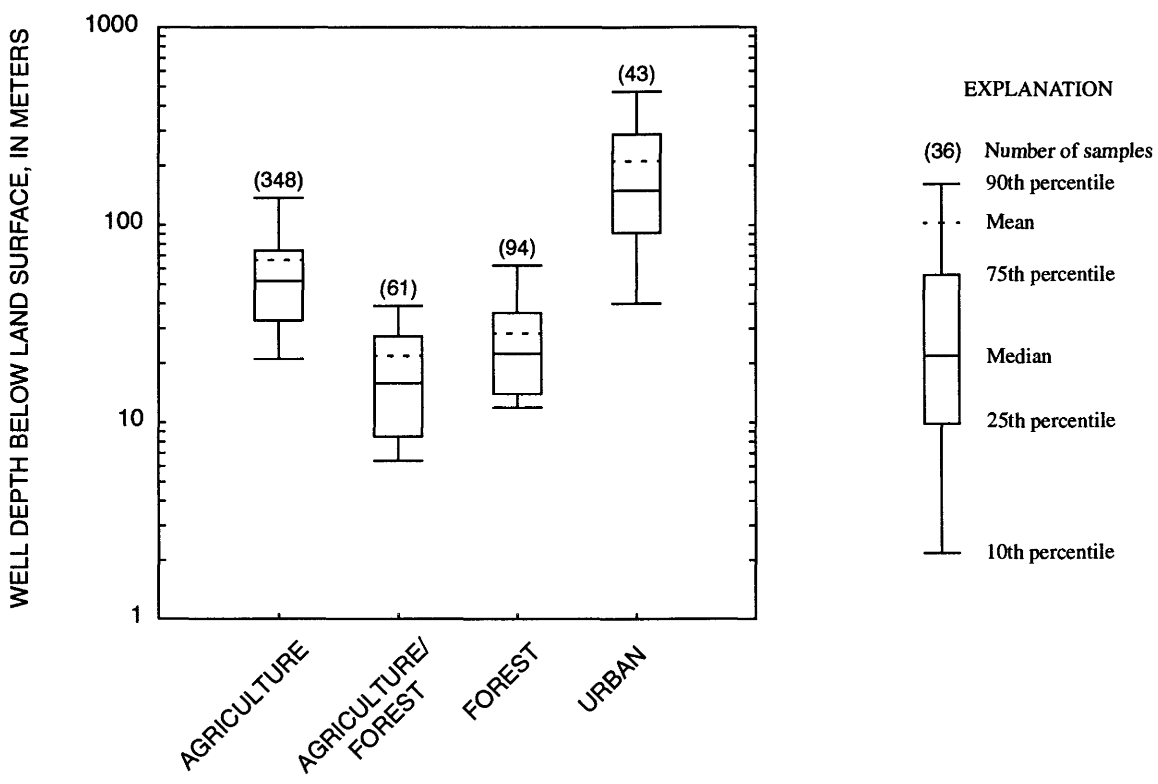


Figure 38. Boxplots of well depths, by general land-use category, for wells sampled in the Western Lake Michigan Drainages study unit, water years 1971–90.

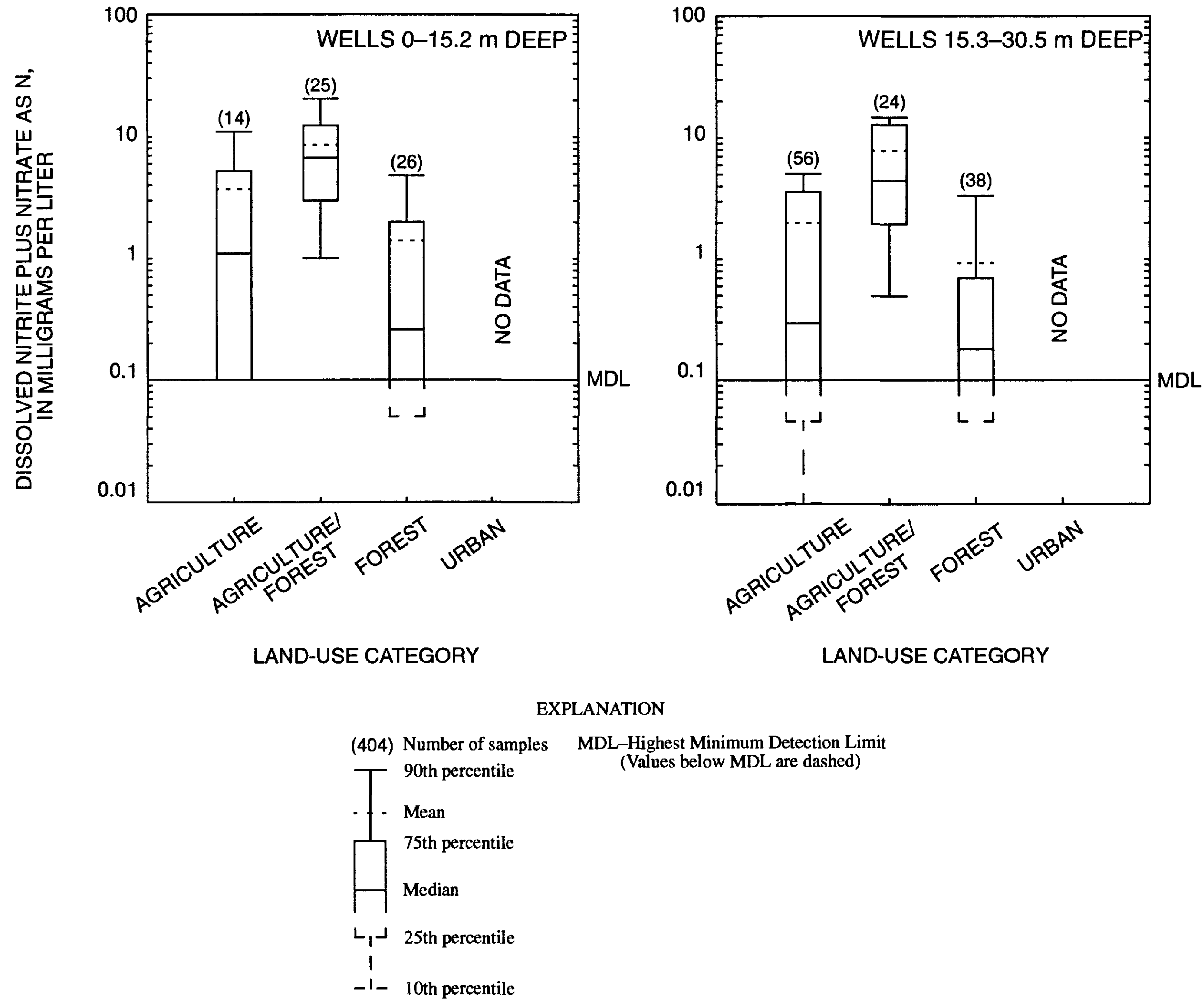


Figure 39. Boxplots of dissolved nitrite plus nitrate concentrations in ground water, by general land-use category, for wells 0–15.2 m deep and 15.3–30.5 m deep in the Western Lake Michigan Drainages study unit, water years 1971–90.

use for two well-depth categories (0–15 and 15–31 m) demonstrates that median concentrations were still highest in the agricultural/forested areas, followed by agricultural areas, and forested areas (fig. 39). Thus, well depth alone is insufficient to explain the differences in nitrite plus nitrate concentrations found in ground water.

For several RHU's, the number of nitrate plus nitrate samples was sufficient to permit examination of the effects of land use, texture of surficial deposit, and bedrock type (fig. 32). The agricultural/forested RHU's (AF20 and AF26) had the highest concentrations, whereas the forested and urban RHU's (F19, F22, and U9) had the lowest concentrations. These differences are similar to those described earlier for general land-use categories. In the agricultural RHU's, however, concentrations varied considerably. Water from 1 RHU (Ag25) had concentrations as high as water from the agricultural/forested areas, but water from most others had very low concentrations. Ag25, as well as AF20 and AF26, is underlain by sand or sand/sand and gravel (permeable) surficial deposits and had high nitrite plus nitrate concentrations, whereas RHU's underlain by clay (relatively impermeable) (Ag1, Ag23, Ag27, and

Ag28) generally had the lowest concentrations. Water from the urban RHU (U9), which is underlain by clay, also had the lowest nitrate plus nitrate. This pattern is consistent with that seen for the effect of surficial-deposit texture on nitrate plus nitrate concentrations.

All the factors just described collectively result in the observed distribution of nitrate plus nitrate concentrations. The three factors that appear to be most influential are land use, texture of surficial deposits, and well depth. The land use determines how much nitrogen is applied in an area. The texture of surficial deposits determines how much of the nitrogen penetrates downward and how quickly it moves. The well depth, with these other two factors, then determines the concentrations found in the ground water. Well depth was strongly related to nitrate plus nitrate concentrations, but it alone does not elucidate transport pathways; it only indicates attenuated or diluted nitrate plus nitrate concentrations with depth below land surface, perhaps reflecting increased denitrification in the deepest wells. In areas where agriculture was a significant part of the land use and surficial deposits were permeable, high concentrations of nitrite plus nitrate in ground water were likely. Well type, aquifer, and bedrock type appeared to be only minor factors in explaining the observed differences in concentrations in ground water.

Relations Between Concentrations in Surface Water and Ground Water

Data for only a few RHU's were sufficient to allow comparisons of nitrate plus nitrate concentrations in surface water and ground water (see fig. 30 and 32). In Ag1 (clayey surficial deposits), nitrate plus nitrate concentrations were relatively high in surface water and relatively low in ground water. High surface-water runoff and low ground-water recharge in this area explain this pattern. In AF26, which is underlain by permeable sand/sand and gravel, concentrations were relatively high in surface water and ground water. These textures, which result in high ground-water recharge and corresponding rapid ground-water discharge to streams, would explain the observed pattern. Concentrations in Ag3 did not fit this general pattern. Although available information shows that Ag3 is underlain by sandy surficial deposits, nitrate plus nitrate concentrations were relatively high in surface water and relatively low in ground water. The relative concentrations in surface water and ground water were similar to those in Ag1 but were expected to be similar to those in AF26. Inspection of numerous well-drillers' reports indicates much sand and gravel in the area, but also significant amounts of clay. Additionally, the well-depth distribution in Ag3 was similar to that in Ag1. Most of the wells in Ag3 and Ag1 are more than 46 m deep, whereas most of the wells in AF26 are less than 31 m deep. The effects of this clay on recharge and similar well depths may explain why overall concentrations in surface water and ground water in Ag3 were similar to those in Ag1. However, if only shallow wells (less than 31 m) in Ag3 are examined, the median concentration of dissolved nitrite plus nitrate increases to 4.1 mg/L. Given the subset of data, the relation between concentrations in surface water and ground water in Ag3 is more like that in AF26 than that in Ag1.

Dissolved nitrite plus nitrate was the most extensively determined constituent among the ground-water samples. This wealth of data enabled comparisons among many of the land-use, surficial-deposit, bedrock, well-type, aquifer, well-depth categories, as well as comparisons of surface-water and ground-water relations. Because the data sets for the other constituents were much smaller, a similar detailed analysis could not be done.

Dissolved Nitrite

Surface Water

Most surface-water samples for which dissolved nitrite concentrations were determined were collected at the NASQAN sites described earlier and in the Menomonee River near Milwaukee, Duck Creek near Green Bay, and in some of the tributaries of the Wolf River (appendix 1.1). Very few samples were collected in headwater, indicator areas. The overall median concentration of dissolved nitrite (as N) was 0.02 mg/L (at the 0.02-mg/L MDL) and the mean concentration was 0.05 mg/L.

Dissolved nitrite concentrations were highest in urban areas and lowest in forested areas; median concentrations were 0.03 and 0.01 mg/L, respectively (figs. 28 and 40; appendix 4.2). Median concentrations were below the 0.02-mg/L MDL in forested areas and at the MDL in agricultural areas. No samples were collected in the agricultural/forested areas. The differences among land-use categories were all statistically significant (urban>agriculture>forest). Only two sam-

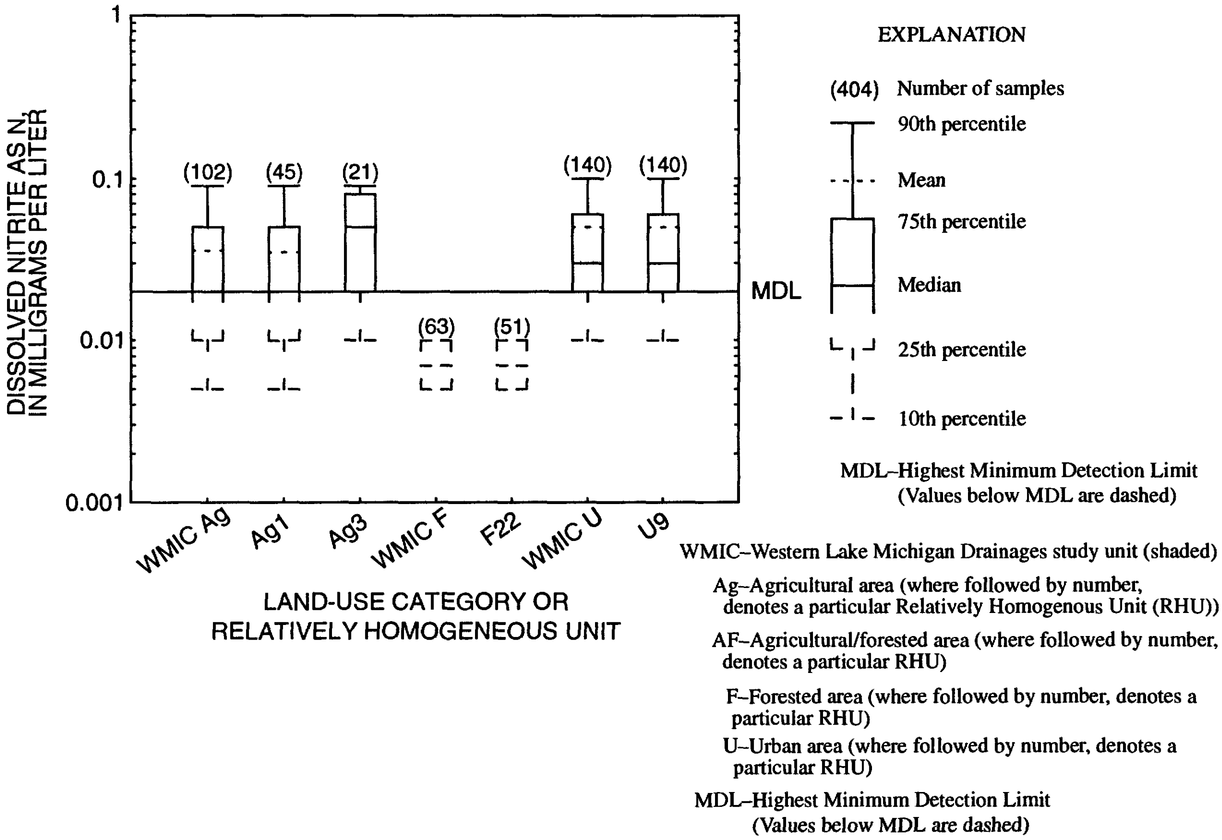


Figure 40. Boxplots of dissolved nitrite concentrations in surface water, by general land-use category and Relatively Homogenous Unit, Western Lake Michigan Drainages study unit, water years 1971–90.

ples exceeded the 1-mg/L MCL for dissolved nitrite; both were from mixed land-use areas (integrator sites).

Concentrations in samples collected by the USGS were fairly similar to those collected by other agencies for all land uses (appendix 4.2). Insufficient data were available to examine seasonal differences in dissolved nitrite concentrations.

Because of the small number of samples in indicator areas, concentrations can be discussed for only 4 RHU's (fig. 40). The available data indicate a statistical difference between Ag1 and Ag3, which indicates that dissolved nitrite concentrations were higher in surface water surrounded by agriculture on sandy deposits than in surface water surrounded by agriculture on clayey deposits.

Ground Water

Wells sampled for dissolved nitrite were predominantly in the east-central and southeastern parts of the WMIC study unit, along the upper reaches of the Wolf River and the headwaters of the Fox River (appendix 1.1). The overall median concentration of dissolved nitrite was 0.005 mg/L, and the mean was 0.009 mg/L. Dissolved nitrite concentrations were available only from the NWIS data base. The median concentration of 0.005 mg/L indicated that at least half the concentrations were reported at less than the 0.01-mg/L MDL because values at half of the detection limit were used in all statistical analyses when less than values were recorded. No significant differences were detected among land-use categories except for forest, which had significantly lower concentrations than urban areas. No significant differences were found in concentrations by well type, aquifer type, or well depth.

More than 88 percent (299 out of 337) of the wells sampled for dissolved nitrite were completed in areas of clay or sand/sand and gravel surficial deposits (appendix 4.12). These deposits were at opposite ends of the range of texture categories, and concentrations in clay areas were significantly higher than those in sand/

sand and gravel areas. This difference is likely due to the greater tendency toward anaerobic conditions in clays and the transient buildup of nitrite during denitrification.

About 60 percent of the wells were in areas underlain by carbonate bedrock (appendix 4.12). Only carbonate and igneous/metamorphic bedrock yielded waters whose nitrite concentrations were significantly different; concentrations in wells in carbonate bedrock were significantly higher than those in igneous/metamorphic bedrock.

At least 10 samples were collected in 7 RHU's. The only significant difference found among all RHU's was that the urban RHU (U9) had significantly higher dissolved nitrite concentrations than both forested RHU's (F19 and F22). This difference may be due to the higher nitrogen inputs in urban areas than in forested areas (fig. 29). Even though the urban area had higher dissolved nitrite concentrations, at least 75 percent of those concentrations were still below the MDL.

Total Ammonia Plus Organic (Kjeldahl) Nitrogen

Surface Water

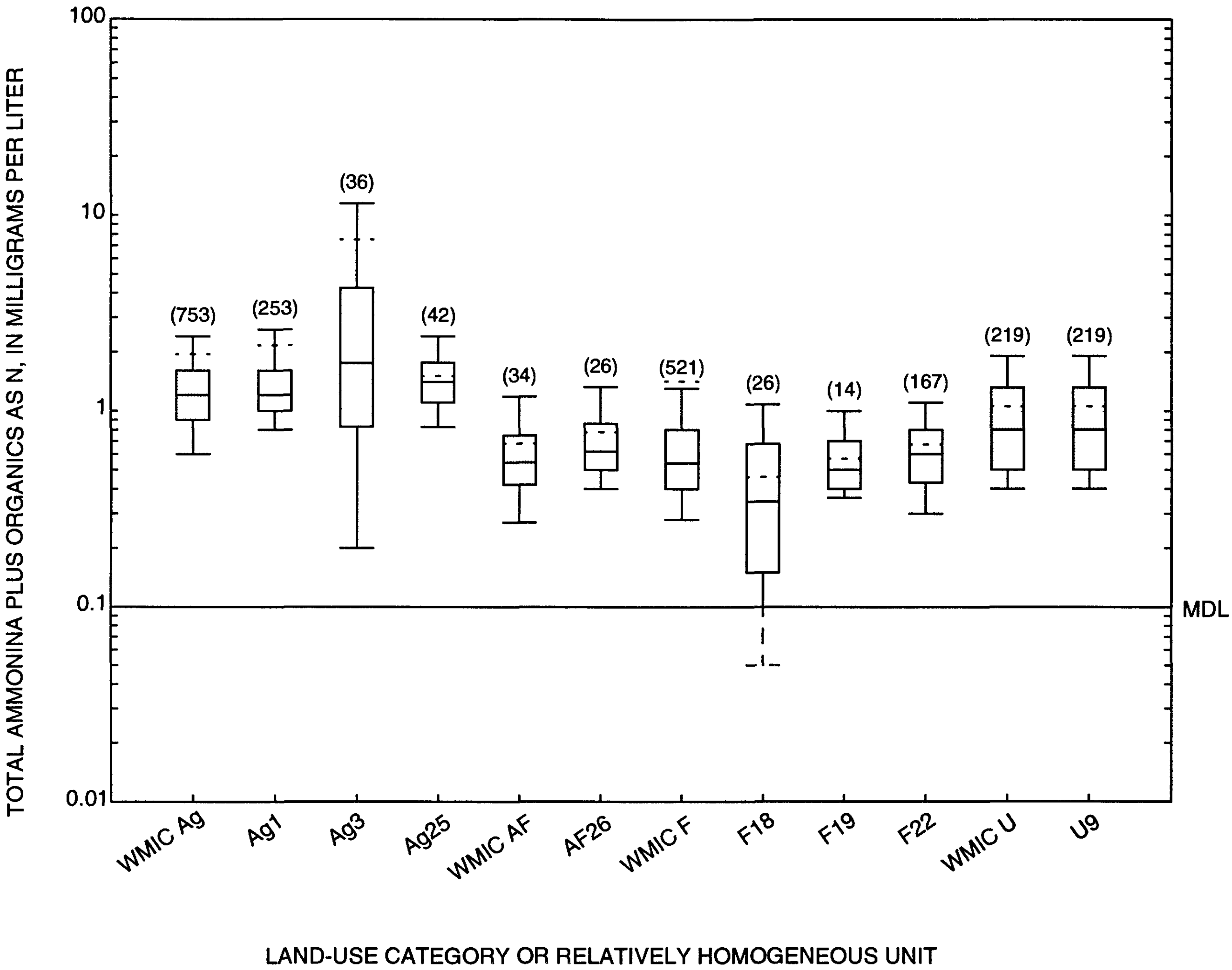
Surface-water samples analyzed for Kjeldahl nitrogen were collected throughout the study unit. The highest sampling densities were in a few tributaries to Green Bay: Lower Fox, Duck Creek, Oconto, Peshtigo, and Menominee Rivers (appendix 1.2). Only a few samples were collected in the southwestern and northwestern parts of the study unit and in northern Wisconsin. Most samples were collected at downstream, integrator sites. The overall median concentration for Kjeldahl nitrogen (as N) was 1.00 mg/L, and the mean concentration was 1.34 mg/L. These concentrations primarily represent organic forms of nitrogen (such as combined nitrogen in proteins and amino acids), because total ammonia (discussed next) represents only a small fraction of the total, except in urban areas. In urban areas, total ammonia represented more than one-half of the total Kjeldahl nitrogen concentration.

Kjeldahl nitrogen concentrations were highest in agricultural areas and lowest in forested and agricultural/forested areas (median concentrations of 1.20, 0.54, and 0.55 mg/L, respectively) (fig. 41; appendix 4.3). The differences among land-use categories were all statistically significant (agriculture>urban>forest), except that agricultural/forested areas were not statistically different from agricultural or forested areas. The concentrations found for each land-use category coincided with the relative magnitude in total nitrogen applied (fig. 28) except in the agricultural/forested areas, where concentrations were less than expected given the amount of nitrogen applied. For this constituent, the agricultural/forested areas resemble the forested areas more than they do the agricultural areas.

Concentrations in samples collected by the USGS were similar to those determined by other agencies in forested areas, at median concentrations of 0.50 and 0.57 mg/L, respectively (appendix 4.3). The median concentration for samples collected by the USGS in agricultural areas was 1.60 mg/L, whereas the median for other agencies was 1.18 mg/L. This difference may be due to the fact that many samples collected by the USGS were biased toward high flows (events), when high concentrations may be present. Few or no samples were collected by the USGS in urban and agricultural/forested areas.

No seasonality was found in Kjeldahl nitrogen concentrations in urban and agricultural areas. However, a statistically significant seasonality was found in forested areas, where higher concentrations occurred during the summer than during the winter and early spring (concentrations from May through September were significantly higher than those from January through March). The highest median concentration was for July (0.71 mg/L), and the lowest median concentration was for February (0.39 mg/L). Because most Kjeldahl nitrogen existed in organic forms in forested areas, the seasonality reflects a seasonality in the organic forms of nitrogen, perhaps the growth of algae in summer.

No statistical differences were detected among RHU's of similar land use. Most samples from agricultural areas were collected in Ag1 (253 samples). In addition, Ag3 and Ag25 were sampled, but not as intensively (36 and 42 samples, respectively). These three areas differ in texture of surficial deposit and bedrock type: Ag1, clayey deposits and carbonate bedrock; Ag3, sandy deposits and carbonate bedrock; and Ag25, sandy deposits and sandstone bedrock. All 3 RHU's had similar nitrogen inputs. Because concentrations were not significantly different, the results indicate that these differences in texture of surficial deposit and bedrock types have little effect on total Kjeldahl nitrogen concentrations in surface water. Most samples from forested areas were collected in RHU F22 (167 samples). In addition, a small number of samples were col-



EXPLANATION

(404) Number of samples

90th percentile

Mean

75th percentile

Median

25th percentile

10th percentile

WMIC–Western Lake Michigan Drainages study unit (shaded)

Ag–Agricultural area (where followed by number, denotes a particular Relatively Homogenous Unit (RHU))

AF–Agricultural/forested area (where followed by number, denotes a particular RHU)

F–Forested area (where followed by number, denotes a particular RHU)

U–Urban area (where followed by number, denotes a particular RHU)

MDL–Highest Minimum Detection Limit (Values below MDL are dashed)

Figure 41. Boxplots of total Kjeldahl nitrogen (ammonia plus organics) concentrations in surface water, by general land-use category and Relatively Homogenous Unit, Western Lake Michigan Drainages study unit, water years 1971–90.

lected in F18 and F19 (26 and 14 samples, respectively). These three areas differ in forest type and surficial deposits: F18 is dry forest with sandy deposits, F19 is dry forest with sand/sand and gravel deposits, and F22 is wet forest with sand/sand and gravel deposits. Therefore, because concentrations were not significantly different, the results indicate that these differences in texture of surficial deposit and forest types also have little effect on total Kjeldahl nitrogen concentrations in surface water. The concentrations in agricultural RHU's (Ag1, Ag3, and Ag25) were significantly higher than those in the urban RHU (U9), which in turn were significantly higher than those in the forested RHU's (F18, F19, and F22).

Ground Water

Most of the 80 wells sampled for Kjeldahl nitrogen were in northern Wisconsin and Upper Michigan (appendix 1.2). The overall median concentration of Kjeldahl nitrogen was 0.10 mg/L, and the mean concentration was 0.31 mg/L. These data were obtained from all three data bases, and median concentrations ranged from 0.05 to 0.30 mg/L (appendix 4.13). Concentrations in the GIN data were significantly higher than those in the STORET data, but not significantly different from those in the NWIS data. Most of the wells sampled for Kjeldahl nitrogen were domestic wells and less than 31 m deep. No significant differences were detected among well types, aquifer type, well depths, or land uses. Urban areas had the highest median concentrations (0.40 mg/L), whereas the lowest concentrations were in agricultural/forested and forested areas (median, 0.10 mg/L) (appendix 4.13).

Concentrations in areas underlain by clay (median concentration of 0.40 mg/L) were significantly higher than those in areas underlain by sand/sand and gravel (median concentration of 0.10 mg/L). The concentration of Kjeldahl nitrogen was significantly higher in areas underlain by carbonates (median concentration of 0.24 mg/L from 26 samples) than in areas underlain by igneous/metamorphic bedrock (median concentration of 0.07 mg/L from 29 samples). Only a few wells were listed for areas underlain by sandstone, and none were listed for shale areas.

In only 2 RHU's were more than 10 samples collected for Kjeldahl nitrogen: F14 and F22. Concentrations within these two areas were not significantly different.

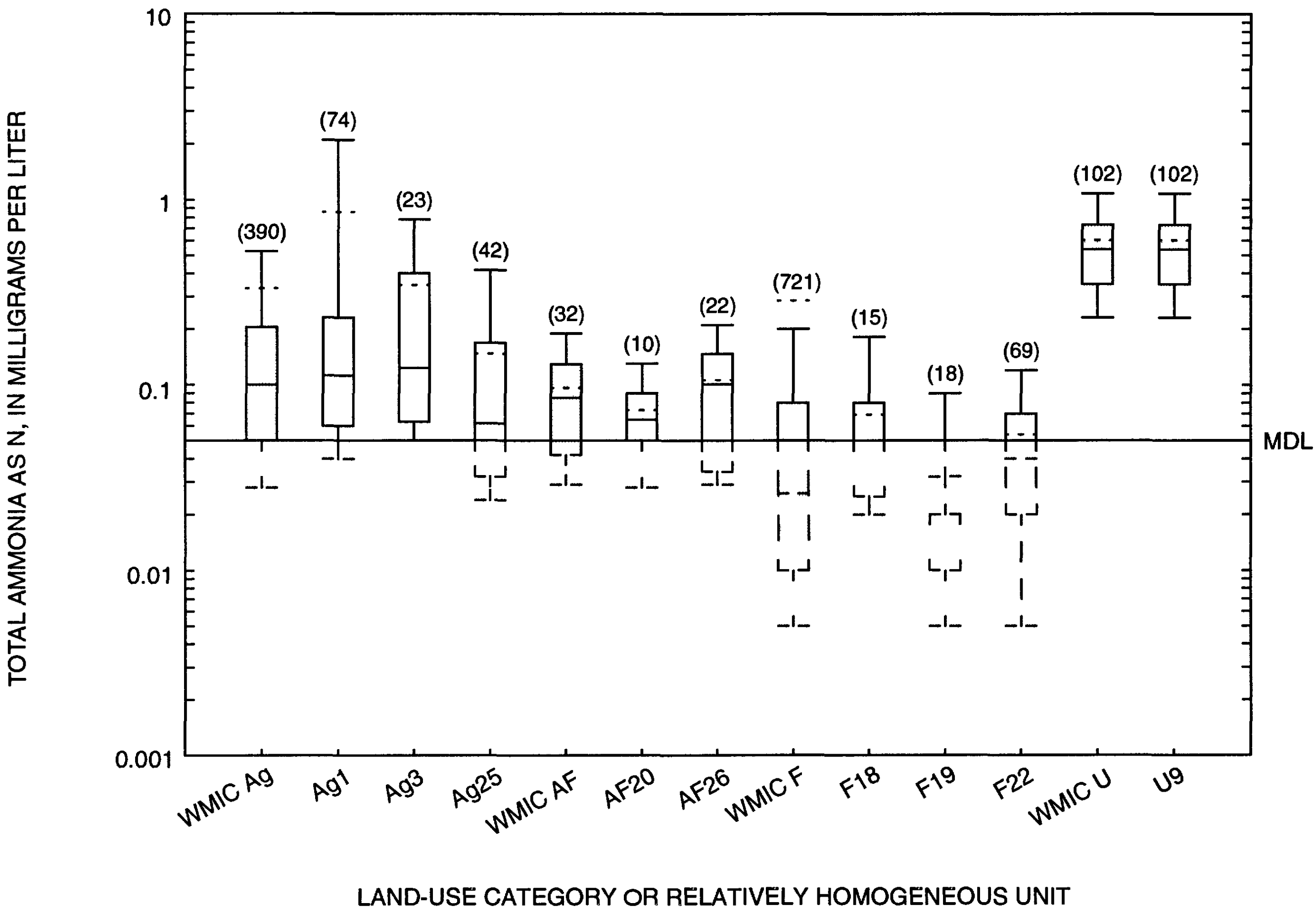
Total Ammonia

Surface Water

Surface-water samples analyzed for total ammonia were collected primarily at the NASQAN sites and in a few additional areas: Duck Creek, tributaries to the Wolf and Upper Fox River, Menominee River and its headwaters, and sites near Escanaba, Mich. (appendix 1.3). Little, if any, information was available for many areas within the study unit. The overall median concentration of total ammonia (as N) was 0.10 mg/L, and the mean concentration was 0.29 mg/L. These concentrations represent primarily dissolved ammonia, since dissolved concentrations (discussed later in the report) were very similar to total concentrations except in urban areas, where total ammonia concentrations were much higher than dissolved ammonia concentrations. However, only a few samples analyzed for dissolved ammonia (filtered) were available for urban areas; most of these samples were collected by the MMSD and were analyzed for total ammonia (unfiltered). Therefore, whether the higher total ammonia concentrations reflected higher dissolved ammonia concentrations in urban areas or perhaps some fraction of particulate ammonia is uncertain.

Total ammonia concentrations were highest in urban areas and lowest in forested areas (median concentrations of 0.54 and 0.03 mg/L, respectively) (fig. 42; appendix 4.4). Median concentrations in forested areas were below the 0.05-mg/L MDL. Median concentrations in agricultural and agricultural/forested areas were 0.10 and 0.09 mg/L, respectively. The differences among land-use categories were statistically significant (urban>agriculture>forest) except for concentrations in agricultural/forested areas, which were not statistically different from those in agricultural areas. For this constituent, the agricultural/forested areas resemble the agricultural areas more than they do the forested areas.

Samples collected by the USGS generally had lower concentrations than those collected by other agencies (appendix 4.4). The median concentration for samples collected by the USGS in agricultural areas was 0.06 mg/L, whereas that for other agencies was 0.12 mg/L. The median concentration for samples collected by the USGS in forested areas was 0.02 mg/L, whereas that for other agencies was 0.03 mg/L (these concentrations were below the 0.05-mg/L MDL). These differences, although not statistically significant,



EXPLANATION

(404) Number of samples

90th percentile

Mean

75th percentile

Median

25th percentile

10th percentile

WMIC–Western Lake Michigan Drainages study unit (shaded)

Ag–Agricultural area (where followed by number, denotes a particular Relatively Homogenous Unit (RHU))

AF–Agricultural/forested area (where followed by number, denotes a particular RHU)

F–Forested area (where followed by number, denotes a particular RHU)

U–Urban area (where followed by number, denotes a particular RHU)

MDL–Highest Minimum Detection Limit
(Values below MDL are dashed)

Figure 42. Boxplots of total ammonia concentrations in surface water, by general land-use category and Relatively Homogenous Unit, Western Lake Michigan Drainages study unit, water years 1971–90.

may have resulted from a difference in sampling approach: most samples collected by the USGS represented background conditions, whereas many samples collected by other agencies were from suspected problem areas. Few or no samples were collected by the USGS in urban and agricultural/forested areas.

Little seasonality was found in total ammonia concentrations in urban and forested areas. However, higher concentrations occurred during winter than during summer in agricultural areas (concentrations from February and March were significantly higher than those from April through September). The highest median concentration occurred in March (0.39 mg/L), and the lowest occurred in May (0.05 mg/L). The fact that most of the total ammonia in agricultural areas is dissolved indicates seasonality in dissolved ammonia concentrations (discussed more fully in the section "Dissolved Ammonia").

Although samples were collected over only a small part of the study unit, sufficient numbers of samples (10 or more midmonth samples) were collected in 3 agricultural RHU's (Ag1, Ag3, and Ag25), 2 agricultural/forested RHU's (AF20 and AF26), and 3 forested RHU's (F18, F19, and F22) to allow for statistical comparisons. No statistical differences were detected among any RHU's of similar land use. The three agricultural areas differed in texture of surficial deposit and bedrock type: Ag1, clayey deposits and carbonate bedrock; Ag3, sandy deposits and carbonate bedrock; and Ag25, sandy deposits and sandstone bedrock. Nitrogen inputs were similar in all 3 RHU's. The three forested areas differed in forest type and texture of surficial deposit: F18, dry forest with sandy deposits; F19, dry forest with sand/sand and gravel deposits; and F22, wet forest with sand/sand and gravel deposits. Because concentrations were not significantly different, these differences in surficial deposits, bedrock types, and forest types seem to have had little effect on total ammonia concentrations in surface water. The concentrations in urban RHU (U9) were significantly higher than those in agricultural RHU's (Ag1, Ag3, and Ag25), which were in turn significantly higher than those in the forested RHU's (F18, F19, and F22). However, concentrations in F18 were not statistically different from those in Ag25.

Ground Water

Many wells sampled for Kjeldahl nitrogen were also sampled for total ammonia. These wells were mainly in the northern one-third of the study unit (appendix 1.3) and obtained from the NWIS and STORET data bases. The overall median concentration of total ammonia was 0.05 mg/L, and the mean concentration was 0.08 mg/L (appendix 4.14). No significant differences in concentration were detected between databases, well types, or well depths. Only concentrations in waters from the sandstone aquifer (median concentration of 0.08 mg/L) and the sand and gravel aquifer (median concentration of 0.01 mg/L) were significantly different.

Most wells sampled for total ammonia were in the forested areas and were underlain by sand/sand and gravel surficial deposits and either carbonate or igneous/metamorphic bedrock types. No significant differences were detected for total ammonia concentrations between land use, surficial-deposit texture, and bedrock categories. In only 1 RHU (F22) were 10 or more samples collected, therefore, no comparisons could be made among RHU's.

Dissolved Ammonia

Surface Water

Sampling frequency was higher and the spatial coverage was more complete for dissolved ammonia than for total ammonia (appendixes 1.3 and 1.4). Sampling sites were most dense around Milwaukee and Green Bay. Only a few samples were collected in the southwestern and northwestern parts of the study unit and in northern Wisconsin. Most samples were collected at downstream, integrator sites. The overall median concentration of dissolved ammonia (as N) was 0.11 mg/L, and the mean concentration was 0.35 mg/L. These concentrations were similar to those for total ammonia except in urban areas, where total ammonia concentrations were higher than those for the dissolved fraction.

Dissolved ammonia concentrations were highest in urban areas and lowest in forested areas (median concentrations of 0.13 and 0.03 mg/L, respectively) (figs. 28 and 43; appendix 4.5). A similar ranking of the concentrations by land use was found for dissolved and total ammonia; however, dissolved ammonia concentrations at urban sites were only slightly higher than those in the other areas, whereas total ammonia concentrations in urban areas were much higher than those in other areas. Median dissolved ammonia concentra-

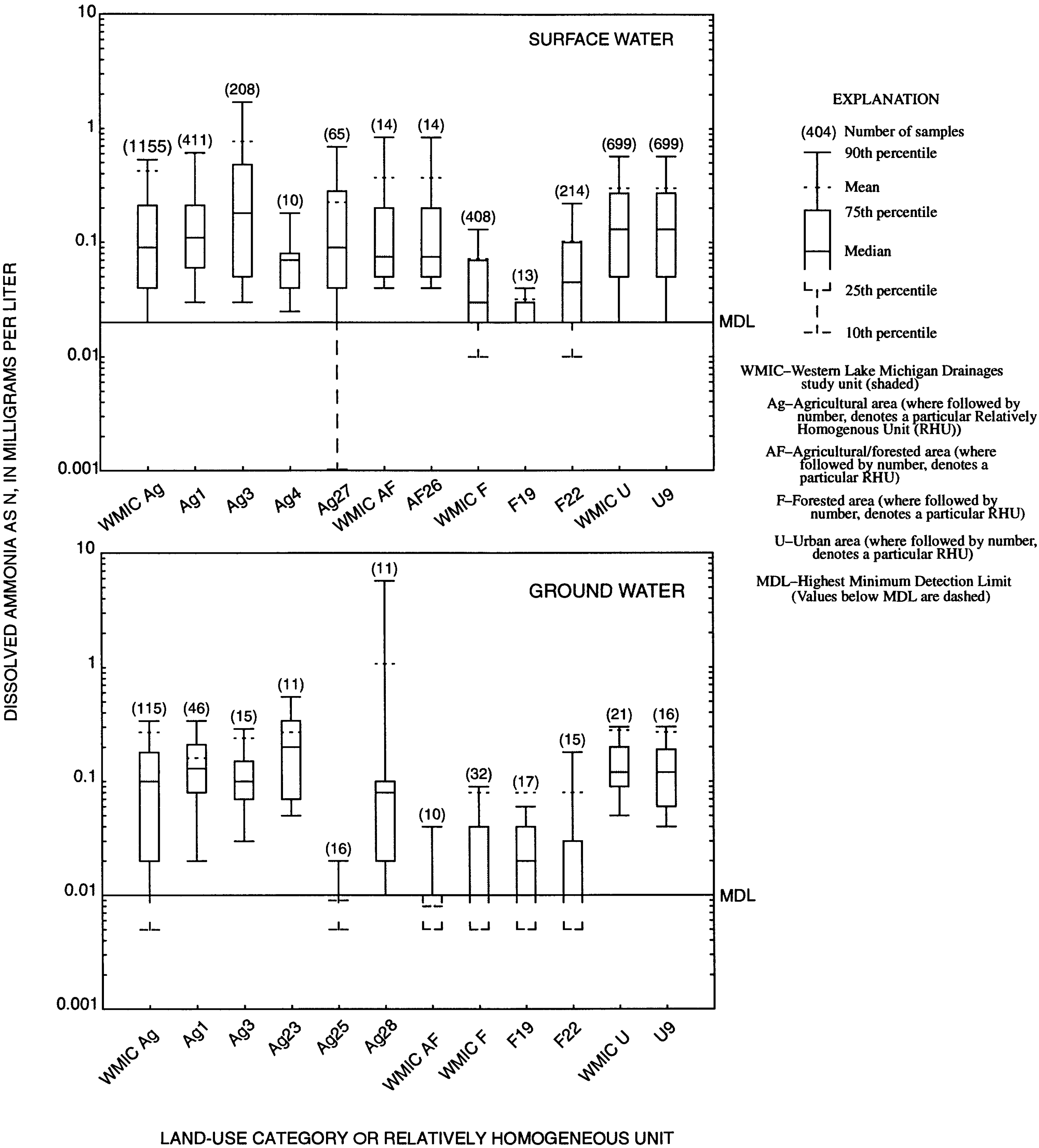


Figure 43. Boxplots of dissolved ammonia concentrations in surface water and ground water, by general land-use category and Relatively Homogenous Unit, Western Lake Michigan Drainages study unit, water years 1971–90.

tions in agricultural and agricultural/forested areas were 0.09 and 0.08 mg/L, respectively. The differences among land-use categories were all statistically significant (urban>agriculture>forest) except for concentrations in agricultural/forested areas, which were not statistically different from those in agricultural or urban areas. For this constituent, the agricultural/forested areas more resembled the agricultural areas than the forested areas.

Dissolved ammonia concentrations in samples collected by the USGS were more similar to those collected by other agencies than for total ammonia (appendix 4.5). However, the median concentration for samples collected by the USGS in agricultural areas (0.05 mg/L) was still lower than that from other agencies (0.10 mg/L). The median concentration for samples collected by the USGS in forested areas (0.04 mg/L) was not significantly different from that of the other agencies (0.03 mg/L). No samples were collected by the USGS in urban or agricultural/forested areas.

Significant seasonality was found in dissolved ammonia concentrations in urban, forested, and agricultural areas (similar to that found for dissolved nitrates for all land uses and for total ammonia in agricultural areas). For all three land-use categories, higher concentrations occurred during the winter than during the summer (concentrations from January through March were significantly higher than those from April through September). The seasonality in concentrations in the forested areas was opposite that found for Kjeldahl nitrogen, which was characterized by higher concentrations in the summer than in the winter. The lower concentrations in dissolved ammonia and dissolved nitrates in the summer can be explained by organisms, use of ammonia and nitrates as a nitrogen source and assimilation of the nitrogen into organic forms. Because ammonia (decreased during the summer) and organic nitrogen (increased during the summer) are included in Kjeldahl nitrogen, little seasonality was observed.

Sufficient numbers of samples were collected in 4 agricultural RHU's (Ag1, Ag3, Ag4, and Ag27) and 2 forested RHU's (F19 and F22) to allow for statistical comparisons (fig. 43). The 4 agricultural RHU's differed in texture of surficial deposit and bedrock type: Ag1, clayey deposits and carbonate bedrock; Ag3, sandy deposits and carbonate bedrock; Ag4, sand and gravel deposits and carbonate bedrock; and Ag27, clay/sand deposits and sandstone bedrock with considerable wetlands. Ag1, Ag3, and Ag4 had similar nitrogen inputs, which were higher than those in Ag27. The concentration in Ag3 was significantly higher than those in Ag1 and Ag27. This result indicates that the difference in texture of surficial deposit may affect dissolved ammonia concentrations in surface water. One possible explanation for these differences is the fact that clay deposits, present in Ag1 and Ag27, have a higher capacity to adsorb ammonia which is positively charged at most ambient pH's. Therefore, ammonia participates in cation exchange and is less readily transported in the dissolved state to streams. The two forested areas differ in forest type: F19, dry forest; and F22, wet forest. Because concentrations were not significantly different, this difference in forest types seems to have had little effect on dissolved ammonia concentrations in surface water. The concentrations in many individual RHU's from different land uses were not significantly different; in other words, several agricultural areas were not significantly different from the urban areas or the agricultural/forested areas. This finding indicates that the differences among land uses was relatively small and that other factors were more influential on dissolved ammonia concentrations than was land use.

Ground Water

Most of the 184 wells sampled for dissolved ammonia were concentrated around Green Bay, Wis., although smaller groups of wells were located along the tributaries of the Wolf River and around the headwaters of the Fox River (appendix 1.4). No wells were sampled for dissolved ammonia in the northern half of the study unit. The overall median concentration of dissolved ammonia was 0.06 mg/L, and the mean concentration was 0.22 mg/L (appendix 4.15). Most of these data came from the NWIS data base (median concentration of 0.05 mg/L from 164 wells) and a few from the GIN data base (median concentration of 0.10 mg/L from 20 wells). No significant differences were detected between these two data bases.

Domestic wells were the most common type of well sampled for dissolved ammonia. No significant differences in concentration were detected among well types except for stock wells, which produced water with significantly lower concentrations of dissolved ammonia than most other well types. Concentrations of dissolved ammonia were significantly higher in wells from the Silurian dolomite aquifer (median of 0.11 mg/L) than in water from the sand and gravel and sandstone aquifers (medians of 0.04 and 0.05 mg/L, respectively). Dissolved ammonia concentrations in water from the basement complex were significantly lower than in water from the other aquifers (median of 0.015 mg/L). Wells sampled for dissolved ammonia were equally distributed over the well-depth categories, and no significant differences in concentration were found among well-depth categories.

At least 10 wells were sampled in each land-use category, the maximum being 115 wells in agricultural areas (fig. 43). Median concentrations were highest in urban areas (0.12 mg/L) and lowest in agricultural/forested areas (0.008 mg/L) (appendix 4.15). Wells in forested areas (median concentration of 0.01 mg/L) and agricultural/forested areas had significantly lower concentrations of dissolved ammonia than did wells in agricultural and urban areas. Dissolved ammonia was a major fraction of the total nitrogen in agricultural and urban areas, but only a minor fraction in agricultural/forested and forested areas (fig. 29).

Most wells sampled for dissolved ammonia were in areas underlain by either clay or sand/sand and gravel surficial deposits. Concentrations were significantly higher in areas of clay deposits (median of 0.12 mg/L) than in areas of sand/sand and gravel deposits (median of 0.01 mg/L). This difference may have been caused by the greater permeability of sand/sand and gravel deposits, which would enhance the downward transport of water and oxygen and enable more oxidation of ammonia to nitrate than in poorly permeable clay deposits.

Most wells were in areas underlain by carbonate bedrock (median concentration of 0.12 mg/L from 84 samples); the remaining bedrock types, in order of decreasing number of wells, were sandstone (median concentration of 0.01 mg/L from 43 samples), igneous/metamorphic (median concentration of 0.008 mg/L from 40 samples) and shale (median concentration of 0.20 mg/L from 11 samples). Dissolved ammonia concentrations were significantly higher in shale and carbonate bedrock areas than in areas underlain by igneous/metamorphic and sandstone bedrock.

Data sets for 8 RHU's were sufficiently large to allow statistical comparisons for dissolved ammonia. Water from the forested RHU's (F19, and F22) generally had significantly lower concentrations than water from the agricultural and urban RHU's (Ag1, Ag3, Ag23, and U9), but concentrations in Ag25 and Ag28 were not significantly different from those in the forested RHU's. These differences correspond to differences in the nitrogen inputs to those land-use categories (fig. 29). The two forested RHU's differ in forest type: F19, dry forest; and F22, wet forest. The fact that concentrations were not significantly different for these two areas indicates that the difference in forest type had little effect on dissolved ammonia concentrations in ground water. Water from Ag25 had significantly lower concentrations than water from Ag1, Ag3, Ag23, Ag28, and U9. Because Ag25 (sandstone bedrock) and Ag3 (carbonate bedrock) differ only in bedrock type, these differences in bedrock may affect dissolved ammonia concentrations, as described in the preceding paragraph. Ag1 (carbonate bedrock) and Ag23 (shale bedrock) also differ only in bedrock type; the absence of significant differences in water quality between these two RHU's is again consistent with the relations suggested in the preceding paragraph.

Phosphorus

Phosphorus is introduced into the WMIC study unit from most of the same sources as for nitrogen: agricultural fertilizers and manures, organic wastes in sewage and industrial effluent, atmospheric deposition, decomposition of organic material, and ambient soils and rocks. In contrast to nitrogen, only a few forms of phosphorus are found in water: organic phosphorus, particulate inorganic phosphates, and dissolved organic and inorganic phosphate. Most particulate phosphorus is present in and on biological material (living and dead) and in mineral phases of soil and rock. Most dissolved phosphorus is present as orthophosphate (also referred to as "dissolved inorganic phosphorus" or "dissolved reactive phosphorus"); lesser amounts are present as low-molecular-weight phosphate esters, as polyphosphates (often originating from detergents), and in association with colloids (Wetzel, 1983). The orthophosphate ion is preferentially adsorbed on the positively charged edges of clay particles. Because of the size of most colloids, all organic and inorganic phosphorus associated with colloids is operationally included in the dissolved fraction.

Phosphorus (in addition to nitrogen) has been applied to farm fields to increase biological productivity; however, excess phosphorus (like nitrogen) has been shown to cause enhanced biological productivity in rivers and also often leads to nuisance macrophyte and algal growth (eutrophication) in downstream lakes and impoundments. Vollenweider (1968) was one of

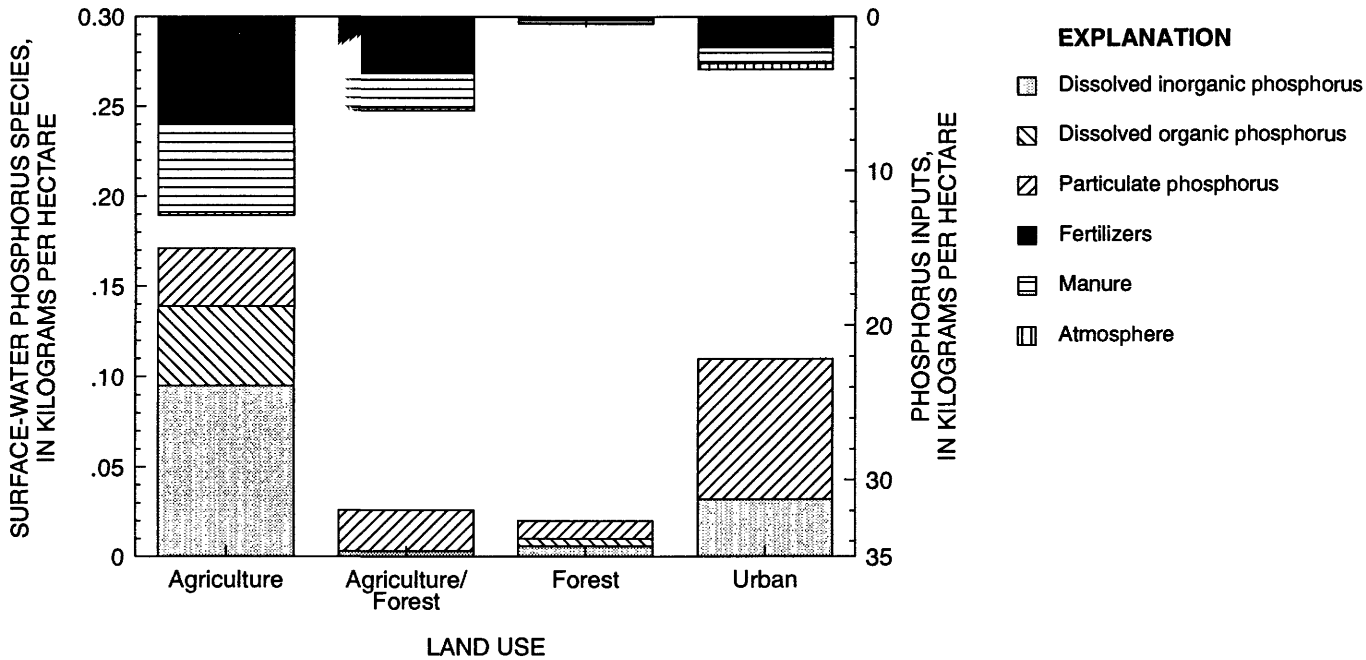


Figure 44. Median concentrations of phosphorus species in surface water (bottom) and phosphorus inputs (top) (fertilizers, manure, and atmosphere) for general land-use categories in the Western Lake Michigan Drainages study unit.

the first to formulate quantitative criteria between phosphorus loading and expected trophic conditions in water bodies. To discourage excessive biotic growth in flowing water, the USEPA has recommended that total phosphorus concentrations (as P) should not exceed 0.1 mg/L (U.S. Environmental Protection Agency, 1986). The median total phosphorus concentration in waters throughout most of the WMIC study unit exceeds this limit.

Total phosphorus was partitioned into its various forms in the following manner: median dissolved organic phosphorus was estimated by subtracting the dissolved inorganic-phosphorus concentration from the median dissolved phosphorus concentration; median particulate phosphorus concentration was estimated by subtracting median dissolved phosphorus concentration from median total phosphorus concentration.

As with nitrogen, the total amount of phosphorus in the surface water of the WMIC study unit coincided with the input of phosphorus applied with the specific land use in the drainage basin. Median concentrations for total phosphorus and each form of phosphorus, and the total inputs of phosphorus for each land use are illustrated in fig. 44. In contrast to nitrogen, atmospheric deposition was usually an insignificant source of phosphorus, except in forested areas. Total phosphorus concentrations mirrored the phosphorus inputs for each land use, an indication that the inputs associated with the various land uses were the primary factor affecting total phosphorus concentrations in the surface water of the WMIC study unit. Median concentrations of total phosphorus were highest in agricultural areas (0.13 mg/L) and lowest in forested areas (0.02 mg/L) (appendix 4.6). The median concentration in urban areas was 0.11 mg/L. Water from urban areas had higher concentrations than expected given the relative magnitude of the external loadings. However, as stated earlier, the estimate of total phosphorus inputs in urban areas was conservative because fertilizers applied to lawns and golf courses were included in total fertilizers and appropriated on the basis of agricultural area. The median total phosphorus concentration in agricultural and urban areas exceeded the 0.1-mg/L limit suggested by the USEPA (1986) to discourage excessive biotic growth. In general, total phosphorus concentrations were lower than total nitrogen concentrations by approximately an order of magnitude.

Dissolved inorganic phosphorus (dissolved reactive phosphorus) and particulate phosphorus were the major forms in urban and agricultural/forested areas, whereas dissolved organic phosphorus was also an important fraction for agricultural and forested areas (fig. 44). In agricultural areas, total phosphorus was present as dissolved inorganic phosphorus (42 percent), dissolved organic phosphorus (34 percent), and particulate phosphorus (25 percent). Particulate phosphorus was the dominant form in agricultural/forested, forested, and urban areas. In agricultural/forested areas, particulate phosphorus accounted for 89 percent of the total phosphorus, and dissolved organic phosphorus accounted for the remaining fraction (11 percent). In forested areas, phosphorus was present as dissolved inorganic (30 percent), dissolved organic (20 percent), and particulate (50 percent) phosphorus. In urban areas, particulate phosphorus accounted for 71 percent of the total, and dissolved inorganic phosphorus accounted for remaining fraction (29 percent).

Because of the small amount of phosphorus data available for ground water, phosphorus could not be partitioned into individual forms for each land-use category. However, total phosphorus concentrations were similar for all land uses and were approximately an order of magnitude less than those in surface water (appendixes 4.6 and 4.16).

Total Phosphorus

For many samples, total phosphorus concentrations as P (parameter code 00665) were not determined, but total phosphorus concentrations as PO_4 (parameter code 71886) were available. These data were converted to total phosphorus as P and used in the statistical analyses.

Surface Water

Of all the forms of phosphorus mentioned previously, total phosphorus was the most frequently sampled for and had the most complete spatial coverage. Surface-water samples analyzed for total phosphorus were collected throughout the study unit but were most dense around Milwaukee and several tributaries to Green Bay, especially the Fox River and Duck Creek (fig. 23). However, only a small number of samples were collected in the southwestern and northwestern parts of the study unit and in northern Wisconsin. More samples were available for headwater, indicator areas than for any other constituent; however, many RHU's were still not adequately sampled to permit their inclusion in statistical analyses. The overall median concentration of total phosphorus (as P) was 0.16 mg/L and the mean concentration was 0.64 mg/L. Both concentrations exceeded the 0.1-mg/L suggested limit.

Total phosphorus concentrations were highest in agricultural areas and lowest in forested areas; median concentrations were 0.13 and 0.02 mg/L, respectively (figs. 44 and 45; appendix 4.6). Median concentrations in forested areas were at the 0.02-mg/L MDL. The differences among land-use categories were all statistically significant (agriculture > urban > agriculture/forest > forest). The differences in concentrations coincided well with the differences in the total phosphorus inputs for these land uses (fig. 44). The median concentration for samples collected in the agriculture/forest area (0.03 mg/L) was similar to that from the forested area; however, the mean concentrations were much different (14.5 and 0.15 mg/L, respectively) because of a few very high concentrations measured in AF20 (appendix 4.6). There was no apparent error that caused these very high concentrations; therefore, these data were not omitted from the statistical analyses. However, these very high concentrations indicate further sampling in this area is needed. Concentrations exceeding the 0.1-mg/L suggested limit were commonly found in all land-use categories except forested areas.

Median concentrations for all land-use categories within the WMIC study unit were less than the NAC's for their respective land uses (fig. 45; appendix 4.6) (Smith and others, 1993). The NAC for total phosphorus in agricultural areas was 0.23 mg/L, whereas the median concentration within the WMIC was 0.13 mg/L. In urban areas, the NAC for total phosphorus was 0.20 mg/L, whereas the median concentration within the WMIC was 0.11 mg/L. In forested areas, the NAC for total phosphorus was 0.05 mg/L, whereas for the WMIC, it was 0.02 mg/L.

Concentrations in samples collected by the USGS were similar to those collected by other agencies for all land uses except in agricultural areas (appendix 4.6). The median concentration for samples collected by the USGS in agricultural areas was 0.21 mg/L, whereas the median for other agencies was 0.13 mg/L. The reason for this significant difference may have been that many of the samples collected by the USGS were during high flows as part of chemical-load studies, whereas most samples collected by other agencies were collected as part of synoptic surveys and routine monitoring. The median concentrations in forested areas were identical for both groups. Few or no sam-

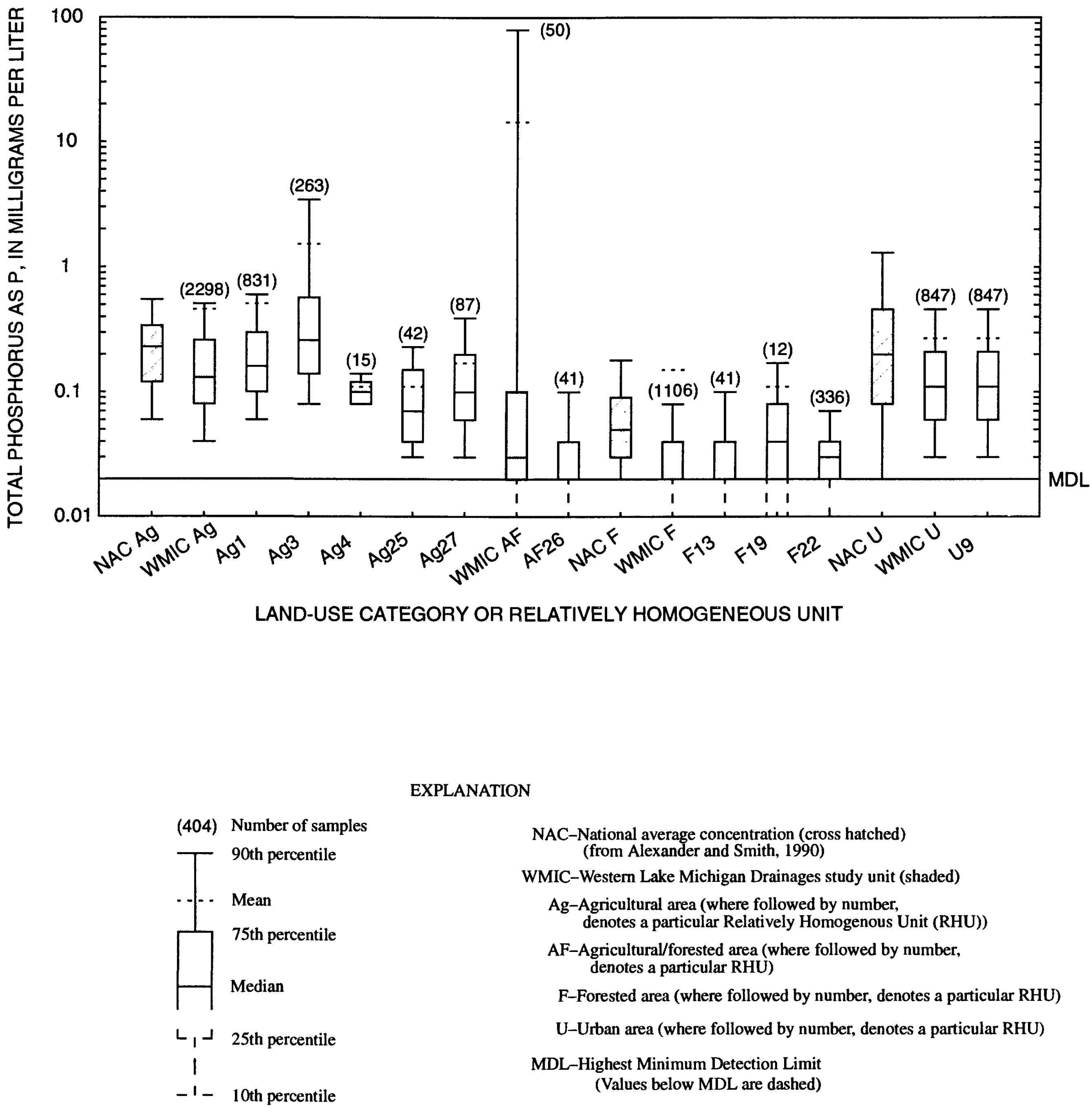


Figure 45. Boxplots of total phosphorus concentrations in surface water, by National land-use category, general land-use category and Relatively Homogenous Unit in the Western Lake Michigan Drainages study unit, water years 1971–90.

ples were collected by the USGS in urban and agricultural/forested areas.

Significant seasonality was found in total phosphorus concentrations in agricultural areas, and slight seasonality was found in forested areas. For agricultural areas, median summer concentrations were higher than median winter concentrations (concentrations during June–September were significantly higher than concentrations during October–January). No seasonality was observed in urban areas.

Because many samples were collected in indicator areas, comparisons could be made among several RHU's. Ten or more samples were collected in five agricultural areas with different deposits and bedrock types: Ag1, clayey deposits and carbonate bedrock; Ag3, sandy deposits and carbonate bedrock; and Ag4, sand and gravel deposits and carbonate bedrock; Ag25, sandy deposits and sandstone bedrock; and Ag27, clay/sand deposits and sandstone bedrock, but mixed with wetland areas. The only difference among Ag1, Ag3, and Ag4 is the type of surficial deposits; phosphorus inputs to all three areas were similar. Total phosphorus concentrations were significantly higher in Ag3 than Ag1, an indication that the difference between clayey and sandy surficial deposits affected total phosphorus concentrations in surface water. This difference may be caused by differences in biological communities, which were not examined. Because only a few samples were collected in Ag4 and because of the small difference in concentrations, no statistically significant difference was found between Ag3 and Ag4. The only difference between Ag3 and Ag25 is the bedrock type; application rates of phosphorus in both areas were similar. Total phosphorus concentrations were significantly higher in Ag3 than Ag25, an indication that surface water in areas of carbonate bedrock had higher concentrations of total phosphorus than in areas of sandstone bedrock. This relation may have been the result of lower concentrations of phosphorus in sandstones than in carbonates and corresponding rates of phosphorus release to surface water.

Ten or more samples were collected in three forested RHU's: F13, F19, and F22. Two of these areas differ only in the type of forest: F19, dry forest and F22, wet forest. Because concentrations were not significantly different, the results indicate that these forest types (wet as opposed to dry) had little effect on total phosphorus concentrations in surface water. F13 is not directly comparable because it has two components that differ from each of the other two RHU's. Comparisons among RHU's with different land use showed that total phosphorus concentrations in several RHU's were not significantly different. For example, the lower concentrations in Ag25 were not significantly different from concentrations in U9 or F19.

Omernick and others (1988) did a similar spatial comparison for lakes in Wisconsin, Michigan, and Minnesota. Total phosphorus concentrations in lakes among different land uses, soil types, bedrock types, potential vegetation zones, ecoregions, and land-resource regions were compared. This analysis indicated higher total phosphorus concentrations in lakes in agricultural areas than in forested areas, similar to results found during this study for streams. In their analysis, areas with similar total phosphorus concentrations were individually described with respect to each of the ancillary-data layers. However, the effects of the individual components (strata) could not be distinguished, because each of the defined lake areas had various combinations of the components, unlike RHU's.

Ground Water

Most of the wells sampled for total phosphorus were in the northwestern part of the study unit (fig. 23). In addition, a small grouping of wells was near the headwaters of the Fox River, and a widely spaced group of wells was located throughout Upper Michigan. Few samples were collected in the central and eastern parts of the study unit. The overall median total phosphorus concentration was 0.01 mg/L, and the mean was 0.03 mg/L (appendix 4.16). This median and mean were lower than concentrations in surface water by approximately one order of magnitude. Almost all of these data were stored in the NWIS data base and most samples were from domestic wells. Median concentrations were 0.10 mg/L for each of the four aquifers and thus were not significantly different. Wells sampled for total phosphorus were equally distributed over the well-depth categories; again, no significant differences were detected.

Of the 128 wells sampled for total phosphorus, 75 were in the forested areas and 30 were in agricultural areas. Median concentrations ranged from 0.01 mg/L in agricultural/forested areas to 0.06 mg/L in urban areas (appendix 4.16). No significant differences were detected between land-use categories. More than 75 percent of the wells were in areas underlain by sand/sand and gravel surficial deposits and more than half of the wells were in areas underlain by igneous/metamorphic bedrock. No significant differences were detected among surficial-deposit or bedrock types.

In only 2 RHU's were 10 or more samples collected for total phosphorus determinations: Ag25 and F22. Concentrations in these two RHU's were also not significantly different.

Dissolved Phosphorus

Surface Water

Surface-water samples were infrequently analyzed for dissolved phosphorus, and the spatial coverage of the sampled sites was very limited. Water samples were collected only at the NASQAN sites, at Duck Creek near Green Bay, and at a few tributaries to the Wolf River (appendix 1.5). Very little information was available for most of the study unit. The overall median concentration of dissolved phosphorus (as P) was 0.03 mg/L, and the mean concentration was 0.06 mg/L (appendix 4.7).

Dissolved phosphorus concentrations were highest in agricultural areas and lowest in forested areas; median concentrations were 0.10 and 0.01 mg/L, respectively (figs. 44 and 46; appendix 4.7). Median concentrations in forested areas were at the 0.01-mg/L MDL. No samples were collected in agricultural/forested areas. The differences among land-use categories were all statistically significant (agriculture>urban>forest). These differences in concentration were similar to those found for total phosphorus and coincide well with the total phosphorus inputs for these land uses (fig. 44).

Concentrations in samples collected by the USGS could be compared only with those in samples from other agencies for agricultural areas (appendix 4.7). Concentrations in samples collected by the USGS were significantly greater than those in samples collected by MMSD (the only other agency analyzing for dissolved phosphorus), 0.12 mg/L and 0.08 mg/L, respectively. However, the median concentration from MMSD data was based on only one sampling location. Data were insufficient to test for seasonal changes in concentration.

Because of the small number of samples in indicator areas, comparisons could be made among only 3 RHU's: one agricultural (Ag1), one forested (F22), and one urban (U9). Concentrations in all three RHU's were significantly different, and their median concentrations were similar in order to those for general land use (Ag1>U9>F22).

Ground Water

Only 108 wells were sampled for dissolved phosphorus and were primarily near the city of Green Bay and around the headwaters of the Wolf River (appendix 1.5). Therefore, dissolved phosphorus information was unavailable for most of the study unit. The overall median concentration of dissolved phosphorus was at the 0.01-mg/L MDL, and the mean concentration was 0.02 mg/L (appendix 4.17). All the data were retrieved from the NWIS data base. Most of the wells sampled were either domestic or public-supply wells. No significant differences were detected among well types. Wells finished in the basement complex and sand and gravel aquifers (median concentrations of 0.02 and 0.01 mg/L, respectively) had significantly higher concentrations than those finished in the sandstone aquifer (median concentration of 0.008 mg/L), which in turn had significantly higher concentrations than those finished in the Silurian dolomite aquifer (median concentration of 0.005 mg/L). No significant differences were detected with well depth.

The number of wells sampled by land-use category ranged from 49 in agricultural areas to 8 in agricultural/forested areas. Median concentrations were highest in agricultural/forested areas (0.04 mg/L) and lowest in agricultural and urban areas (0.005 mg/L, which was one half of the MDL). Concentrations of dissolved phosphorus were significantly higher in forested areas (median concentration of 0.02 mg/L) than in agricultural and urban areas. These differences among land uses were opposite those found for surface water. Concentrations in agricultural/forested areas were not significantly different from those among other land-use categories.

About 92 percent of the wells sampled for dissolved phosphorus were in areas underlain by clay or sand/sand and gravel surficial deposits. Median concentrations were significantly higher for sand/sand and gravel surficial deposits (0.02 mg/L) than for clay deposits (0.005 mg/L, less than the MDL).

Median concentrations of dissolved phosphorus were higher in igneous/metamorphic and sandstone bedrock areas (0.02 mg/L) than in carbonate and shale bedrock areas (0.005, less than the MDL). Concentrations in igneous/metamorphic areas were significantly

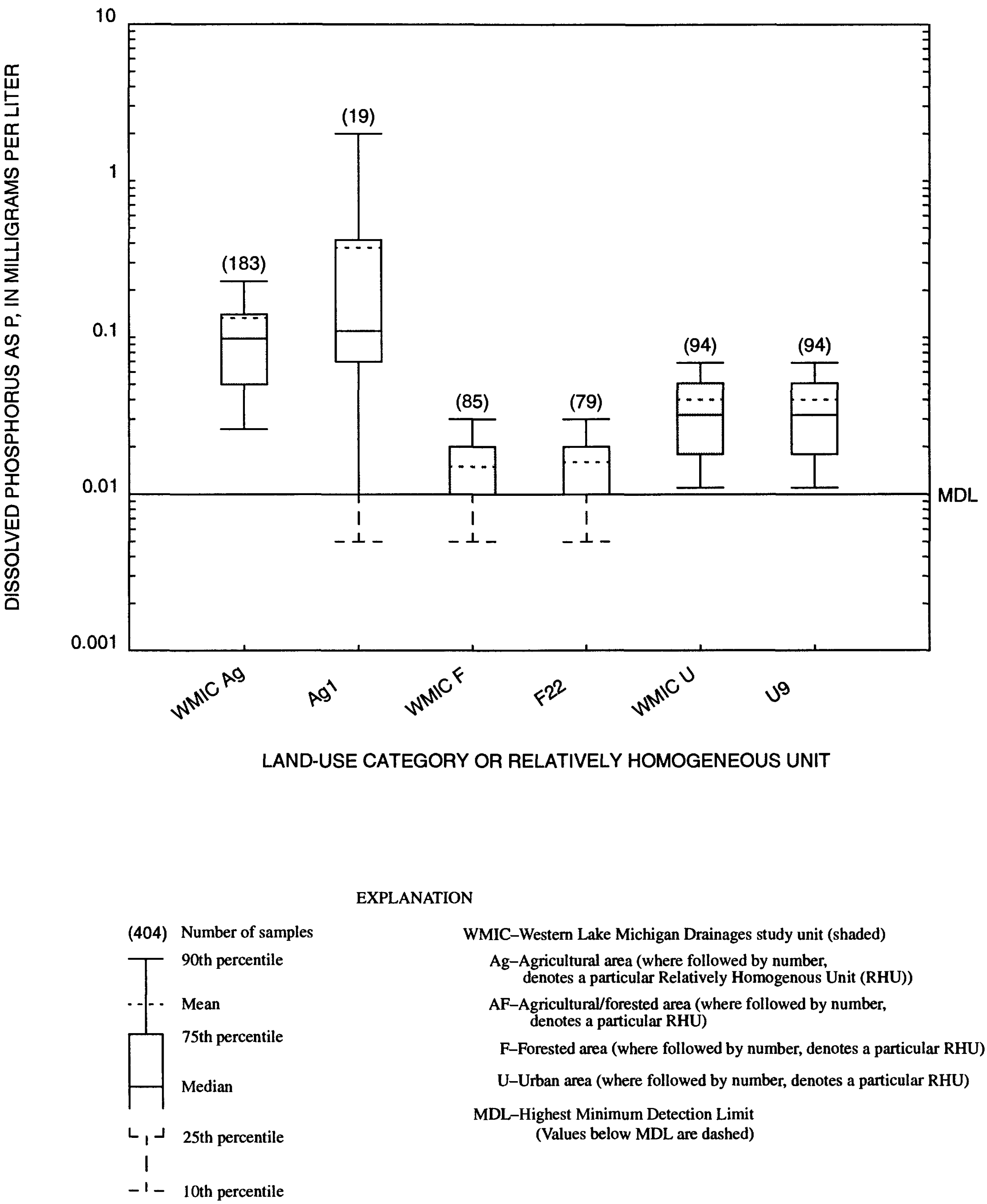


Figure 46. Boxplots of dissolved phosphorus concentrations in surface water, by general land-use category and Relatively Homogenous Unit, Western Lake Michigan Drainages study unit, water years 1971–90.

higher than in carbonate and shale bedrock areas. Concentrations in sandstone areas were significantly higher than those in carbonate bedrock areas.

Because of the small number of samples in indicator areas, comparisons could be made among only 3 RHU's: one agricultural (Ag1) and two forested (F19 and F22). Concentrations in the two forested areas, which differed only in forest type, were not significantly different, an indication that this difference in forest type had little effect on dissolved phosphorus concentrations in ground water. Wells sampled in F22 had significantly higher concentrations than those sampled in Ag1; however, concentrations in F19 were not significantly different from those in Ag1.

Total Orthophosphate

Surface Water

Surface-water samples analyzed for total orthophosphate were mainly collected in Upper Michigan, primarily around Escanaba, Mich., and along the Menominee River and its headwaters; samples were also collected at a few sites scattered around Wisconsin (appendix 1.6). Data were unavailable for most of the study unit. The overall median concentration of total orthophosphate (as P) was 0.01 mg/L, and the mean concentration was 0.06 mg/L (appendix 4.8).

Total orthophosphate concentrations were highest in agricultural areas and lowest in forested areas; median concentrations were 0.09 and 0.01 mg/L, respectively (fig. 47; appendix 4.8). Median concentrations in forested areas were below the MDL. No samples were collected in urban areas. Concentrations in agricultural areas were significantly greater than those in forested areas. Concentrations in agricultural/forested areas (median concentration of 0.03 mg/L) were significantly higher than those in forested areas but not significantly different from those in agricultural areas. The difference in concentrations coincided well with the differences in total phosphorus applied for these land uses (fig. 44). Median concentrations in agricultural/forested areas were intermediate to those found in agricultural and forested areas. However, only 14 samples were collected in agricultural/forested areas.

Samples collected by the USGS could be compared with samples collected by other agencies only for agricultural and forested areas (appendix 4.8). Median concentrations in samples collected by the USGS in agricultural areas were greater than those in samples collected by other agencies, 0.16 and 0.08 mg/L, respectively; however, the differences in concentration were not statistically significant. Median concentrations in forested areas were identical. No seasonality was found for total orthophosphate; however, only a small amount of data was available.

In only 5 RHU's were 10 or more samples collected: 2 agricultural areas (Ag1 and Ag27), 1 agricultural/forested area (AF26), and 2 forested areas (F13 and F22). The two agricultural sites differed in surficial-deposit type, bedrock type, and amount of wetland: hence any comparison that singles out one of these factors would be difficult. Concentrations in water from these two agricultural areas were not significantly different. The two forested areas primarily differed in bedrock type (F13, carbonate; F22, igneous/metamorphic). Concentrations in water from the two forested areas were not significantly different, an indication that the difference in bedrock did not affect total orthophosphate concentrations. Comparisons among RHU's with different land use demonstrated that total orthophosphate concentrations in all agricultural RHU's were significantly higher than those in forested RHU's. Concentrations in the agricultural/forested RHU (AF26) were not significantly different from those in the agricultural or forested RHU's.

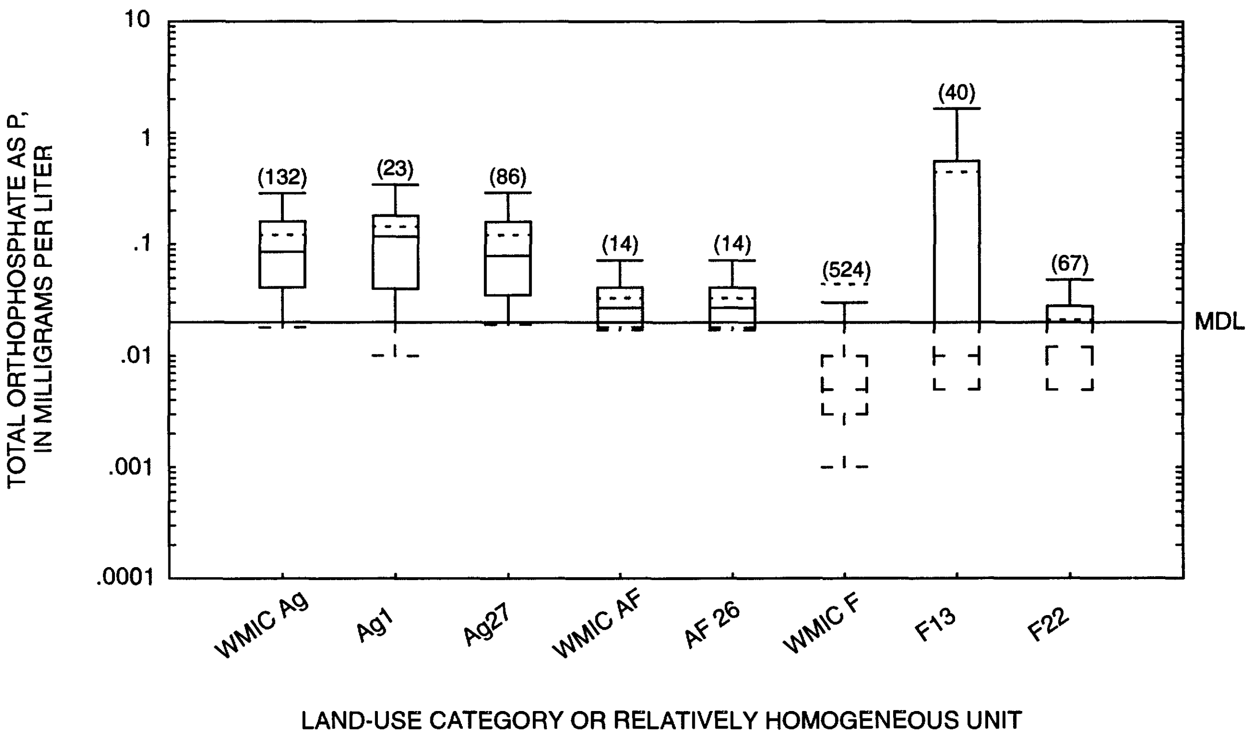
Ground Water

Only 27 wells were sampled for total orthophosphate and all but 1 were in Upper Michigan (appendix 1.6). NWIS was the only data base that contained total orthophosphate concentration data, and at least 75 percent of the listed concentrations were below the 0.01-mg/L MDL (appendix 4.18). Almost all the wells were of unknown water use (26 of 27), finished in the sandstone aquifer, and more than 70 m deep. No significant differences were detected in concentrations by well type, aquifer, well depth, land use, surficial deposit, bedrock, or RHU.

Dissolved Orthophosphate

Surface Water

Dissolved orthophosphate (dissolved reactive phosphorus) was second only to total phosphorus in number of analyses; however, the gaps in the spatial coverage that were previously mentioned for total



EXPLANATION

(404) Number of samples

90th percentile

Mean

75th percentile

Median

25th percentile

10th percentile

WMIC–Western Lake Michigan Drainages study unit (shaded)

Ag–Agricultural area (where followed by number, denotes a particular Relatively Homogenous Unit (RHU))

AF–Agricultural/forested area (where followed by number, denotes a particular RHU)

F–Forested area (where followed by number, denotes a particular RHU)

U–Urban area (where followed by number, denotes a particular RHU)

MDL–Highest Minimum Detection Limit (Values below MDL are dashed)

Figure 47. Boxplots of total orthophosphate concentrations in surface water, by general land-use category and Relatively Homogenous Unit, Western Lake Michigan Drainages study unit, water years 1971–90.

phosphorus in Upper Michigan, northern Wisconsin, and the southwest part of the study unit were evident for this constituent as well. Sites where dissolved orthophosphate was sampled for were most dense around Milwaukee, Wis., and several tributaries to Green Bay, especially the Fox River and Duck Creek (appendix 1.7). Only a small number of samples were available for headwater, indicator sites. The overall median concentration of dissolved orthophosphate (as P) was 0.045 mg/L, and the mean concentration was 0.20 mg/L (appendix 4.9).

Dissolved orthophosphate concentrations were highest in agricultural areas and lowest in forested and agricultural/forested areas; median concentrations were 0.05, 0.006, and 0.003 mg/L, respectively (fig. 48; appendix 4.9). Median concentrations in forested and agricultural/forested areas were below the 0.01-mg/L MDL. The differences among land-use categories were all statistically significant (agriculture>urban>forest> agriculture/forest). These relations were similar to those found for total orthophosphate and coincided well with the differences in total phosphorus input for these land uses, except for agricultural/forested areas, where concentrations were lower than expected (fig. 44). For this constituent, the agricultural/forested areas resembled the forested areas more than they did the agricultural areas; however, only 30 samples were collected in agricultural/forested areas. In all land-use categories except agriculture/forest, concentrations for dissolved orthophosphate commonly exceeded the 0.1-mg/L suggested limit for total phosphorus.

Concentrations of dissolved orthophosphate in samples collected by the USGS in agricultural areas (median concentration of 0.09 mg/L) were significantly higher than those collected by other agencies (median concentration of 0.05 mg/L). This difference, again, may have resulted from collection of the USGS samples during high flows. The median concentrations in forested and agricultural/forested areas were both below the MDL. No seasonality was found in dissolved orthophosphate concentrations in any land-use category.

In 7 RHU's, 10 or more samples were collected: 4 agricultural (Ag1, Ag3, Ag4, and Ag25), 1 forested (F22), 1 urban (U9), and 1 agricultural/forested (AF26). Comparisons could be made primarily among the four agricultural RHU's, which differed in surficial deposit and bedrock types: Ag1, clayey deposits and carbonate bedrock; Ag3, sandy deposits and carbonate bedrock; Ag4, sand and gravel deposits and carbonate bedrock; and Ag25, sandy deposits and sandstone bedrock. All four areas had similar phosphorus inputs. The only difference among Ag1, Ag3, and Ag4 is the type of surficial deposits. Dissolved orthophosphate concentrations (as for total phosphorus) were significantly higher in Ag3 than in Ag1, an indication that the difference between clayey and sandy surficial deposits caused differences in dissolved orthophosphate concentrations. This difference in concentrations may be the result of differences in biological communities, which were not examined. Owing to the small number of samples in Ag4 and the small difference in concentrations, no statistical difference was found between Ag3 and Ag4. The only difference between Ag3 and Ag25 is bedrock type. Dissolved orthophosphate concentrations, again as for total phosphorus, were significantly higher in Ag3 than in Ag25, an indication that surface water in areas underlain with carbonate bedrock had higher concentrations than in areas underlain by sandstone bedrock. Sandstones, in general, contain lower concentrations of phosphorus than do carbonates and therefore may release less phosphorus to surface water (Wetzel, 1983).

Comparisons among RHU's having different land uses demonstrated that water from all agricultural and urban RHU's had significantly higher dissolved orthophosphate concentrations than forested and agricultural/forested RHU's. Concentrations in agricultural areas Ag3 and Ag1 were significantly higher than those in Ag25 and U9; however, concentrations in Ag4 were not significantly different from those in any other agricultural or urban RHU. Concentrations in the forested RHU (F22) were not significantly different from those in the agricultural/forested RHU (AF26).

Ground Water

Only 9 wells were sampled for dissolved orthophosphate in the WMIC study unit (appendix 1.7). These were spread out over the southern half of the study unit, although a few were clustered near the headwaters of the Wolf River. The overall median concentration was 0.02 mg/L, and the mean was 0.04 mg/L (appendix 4.19). Because such a small amount of data was available for ground water, no statistical tests for assessing differences in concentration among well type, aquifer, well-depth, or land-use categories were performed.

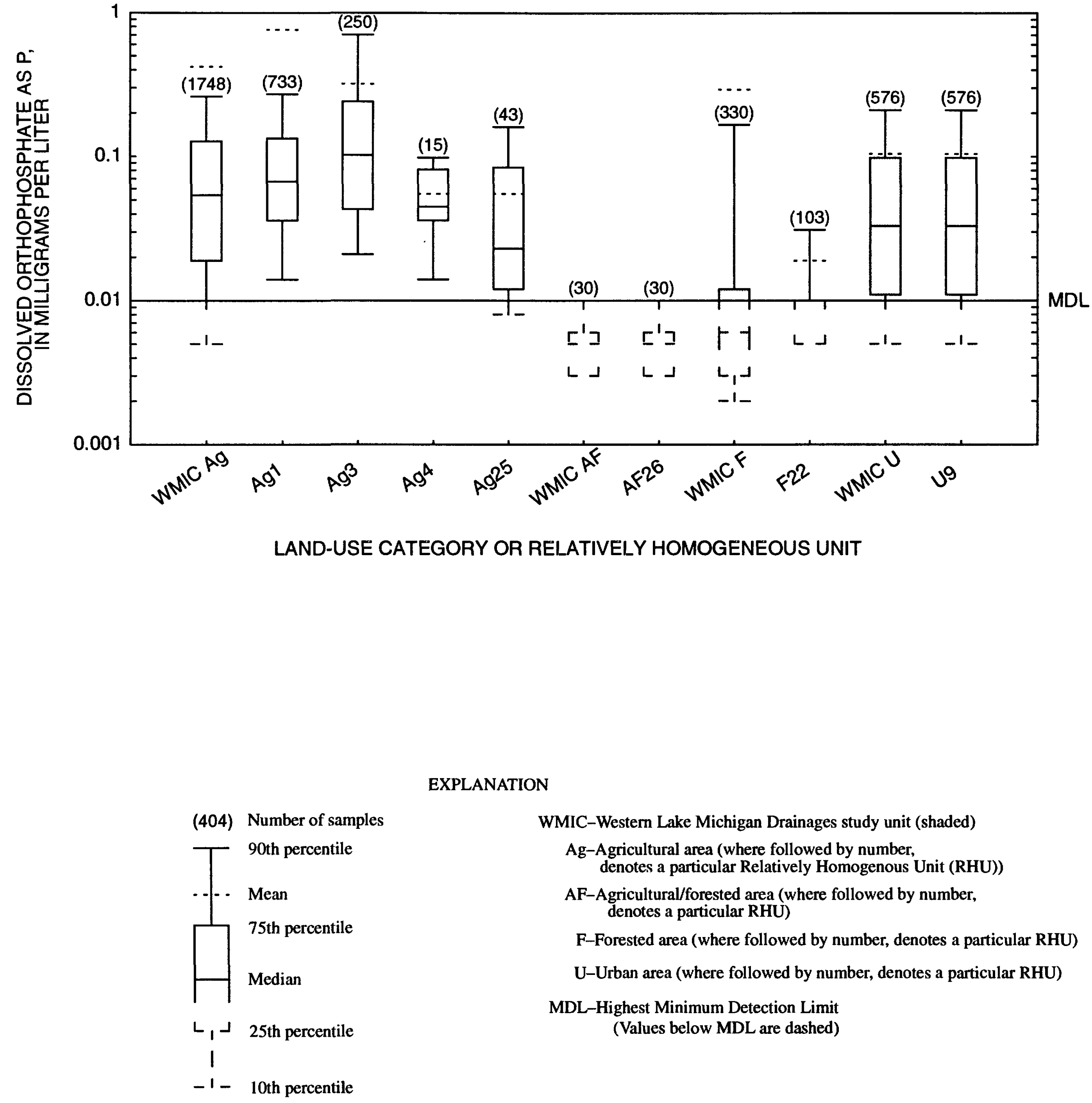


Figure 48. Boxplots of dissolved orthophosphate concentrations in surface water, by general land-use category and Relatively Homogenous Unit, Western Lake Michigan Drainages study unit, water years 1971–90.

SUSPENDED-SEDIMENT CONCENTRATIONS

Suspended sediment in streams affects the biological community and plays a major role in the transport of various chemical constituents. Soil erosion produces the fine particles required for macrophyte growth; however, in excess, suspended sediment can (1) reduce the penetration of light and limit macrophyte and algal growth; (2) reduce water clarity and cause problems for visual predators; and (3) increase the deposition of fine sediments and cover the large bed materials required for invertebrate habitat and fish spawning. Suspended sediment is generally composed of inorganic material; however, organic material can be a significant fraction, especially in agricultural areas. Decomposition of organically enriched sediment can reduce the dissolved oxygen concentration in a stream, making specific reaches uninhabitable by many fish and invertebrates. In addition, various nutrients, trace elements, and organic compounds are commonly adsorbed to the inorganic material. Therefore, the transport of suspended sediment can be an important factor in the movement and fate of many chemicals in the environment, and the presence of suspended sediment can limit the use of the water for domestic water supplies (Rinella and others, 1992). Erosion and the accompanying high concentrations of suspended sediment have been identified as primary water-quality concerns throughout the WMIC study unit. With the control of point sources of pollution in the study unit, much of the present effort in improving water quality focuses on nonpoint-source pollutants, such as soil erosion.

Surface-water samples analyzed for suspended sediment were collected primarily at downstream, integrator sites; sampling sites were most dense around Milwaukee and the rivers flowing toward Milwaukee (fig. 24). Additional sites were located on the Fox and Wolf Rivers and near where most large rivers discharge into Green Bay and Lake Michigan. Most of these sites were downstream from one or more dams, which may have significantly affected suspended-sediment concentrations. Only a small amount of data was available for headwater, indicator areas. At most of the sites for which data are available, suspended-sediment information was collected for a short time in the 1970's, but use of the sites has since been discontinued. Suspended-sediment data were collected by the USGS only; other agencies analyze primarily for suspended solids. The overall median concentration of suspended sediment was 23.0 mg/L, and the mean concentration was 285.1 mg/L (appendix 4.10).

No seasonality was observed in suspended-sediment concentrations. Higher concentrations, anticipated to occur during the spring high-flow periods (especially in agricultural areas), were not observed. The lack of seasonality in suspended-sediment concentrations may have been the result of dams upstream from the sampling locations, which decreased the water velocity required to maintain the sediment in suspension.

Total suspended-sediment concentrations were highest in urban areas and lowest in forested areas; median concentrations were 148.0 and 4.0 mg/L, respectively (fig. 49; appendix 4.10). Contrary to what was expected, suspended-sediment concentrations were significantly higher in urban areas than in agricultural areas (median concentration of 25.0 mg/L). The median concentration in agricultural/forested areas was 18.0 mg/L, but only five samples were collected in this area. The differences among land-use categories were significant (urban>agriculture>forest), except for agricultural/forested areas, which were significantly different only from urban areas. The high concentrations in urban areas may have been caused by construction activities and washoff of particulate material from streets during storms.

Concentrations of suspended sediment within the WMIC study unit were quite different from the NAC's for all land uses (fig. 49; appendix 4.10) (Smith and others, 1993). Suspended-sediment concentrations in the study unit were less than the NAC in agricultural areas (median concentrations of 25.0 and 131.0 mg/L, respectively) and in forested areas (median concentrations of 4.0 and 19.0 mg/L, respectively). However, concentrations in urban areas in the study unit were much higher than the NAC (median concentrations 148.0 and 25.0 mg/L, respectively).

Because of the small number of samples in indicator areas, concentrations can be compared for only 4 RHU's: 2 agricultural (Ag1 and Ag3), 1 forested (F22), and 1 urban (U9). The two agricultural areas differ only in texture of surficial deposit: Ag1, clayey deposits and Ag3, sandy deposits. Suspended-sediment concentrations were significantly higher in Ag1 than Ag3, an indication that the difference in clayey and sandy surficial deposits affected suspended-sediment concentrations. This difference may result from greater erodibility of clayey deposits compared with sandy

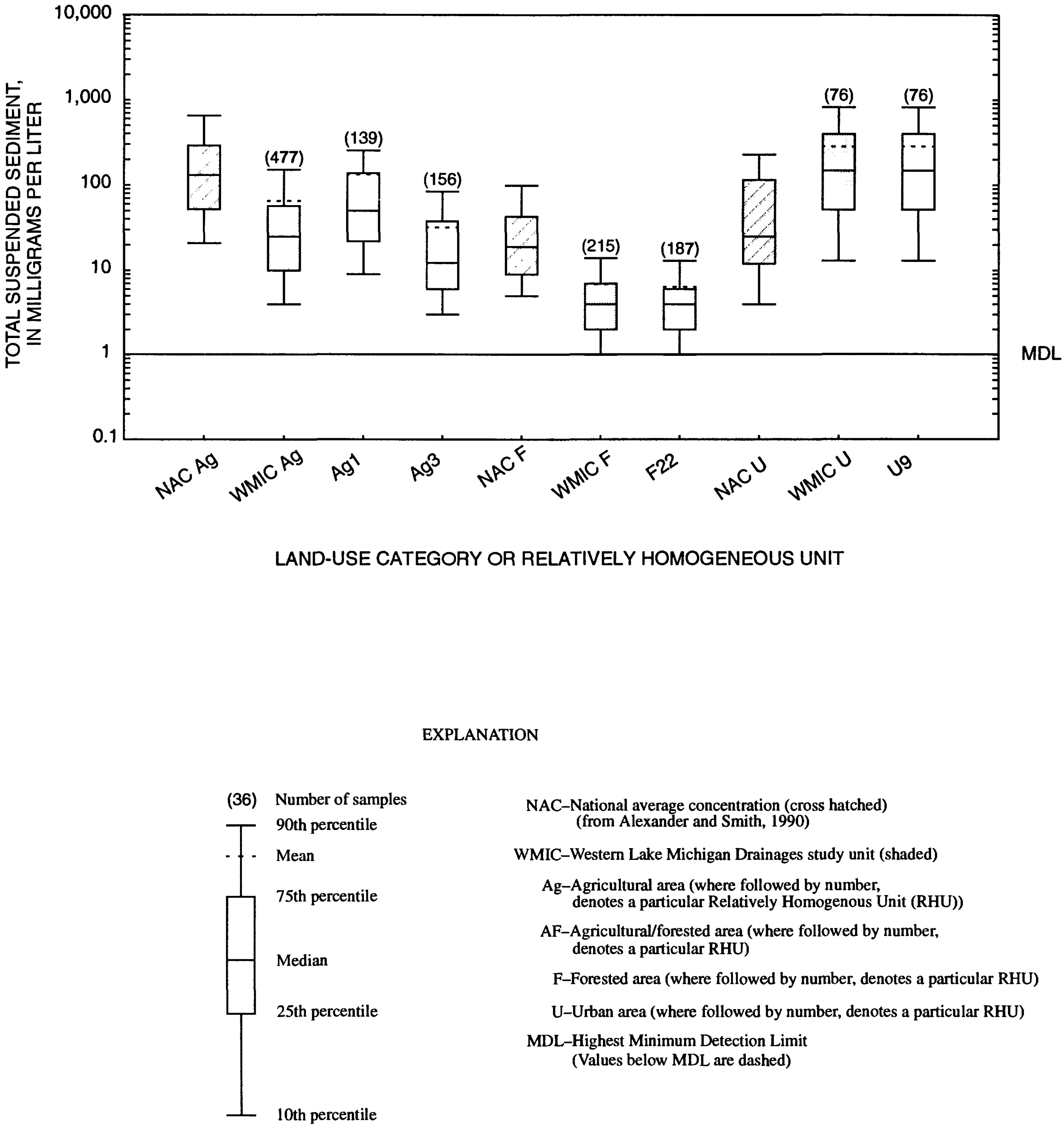


Figure 49. Boxplots showing total suspended sediment concentrations for surface water, by National land-use category, general land-use category and Relatively Homogenous Unit in the Western Lake Michigan Drainages study unit, water years 1971–90.

deposits and (or) the tendency for clay particles to remain in suspension longer than larger sand particles. The concentrations in the urban RHU (U9) were significantly higher than those in both agricultural RHU's (Ag1 and Ag3), which in turn were significantly higher than those in the forested RHU (F22).

RELATION OF CONSTITUENT CONCENTRATION TO STREAMFLOW

Constituent-concentration data and accompanying streamflow data were available from the seven NASQAN sites (fig. 24) for suspended sediment and all the nitrogen and phosphorus species previously described in this report except total orthophosphate. All of these sites were sampled fairly uniformly over all months and deciles of flow (appendixes 2 and 3). At four of these sites, dams or reservoirs upstream from the sampling sites affected the concentration-streamflow relations: Escanaba (1), Menominee (4), Fox (8), and Milwaukee (10) Rivers. Four of the NASQAN sites represented predominantly forested areas: Escanaba (1), Ford (2), Popple (3), and Menominee (4) Rivers. The Fox (8) and Milwaukee (10) Rivers represent mixed agricultural, urban, and forested areas, and the Manitowoc River (9) represents predominantly agricultural areas. In addition to these sites, concentration and accompanying streamflow data were also available for total phosphorus and suspended sediment at Silver Creek (5), White Creek (6), and Green Lake Inlet (7). These sites drain small, heavily farmed basins and were established to estimate loads of selected nutrients. Therefore, these sites were sampled more frequently during high flows, especially during spring. Total ammonia data and accompanying streamflow data were also available at White Creek (6).

In general, only weak relations, if any, were found between concentration and streamflow for any nitrogen constituent. Nitrate plus nitrate concentrations decreased with increased flow in forested areas (1, 2, and 4); however, no relation was observed for the Popple River (3). Concentrations increased slightly with increased flow at the Manitowoc River (9) (an agricultural site) and the Fox River (8) (a mixed agricultural, forested, and urban site). No definite relation was found at the Milwaukee River (10) (a mixed agricultural and urban site). Opposite trends were found for Kjeldahl nitrogen. Concentrations in forested areas (1, 2, 3, and 4) increased with increased streamflow; otherwise concentrations either decreased (8) or did not change consistently with increased streamflow (9 and 10). Total and dissolved ammonia concentrations increased slightly with increased flow in predominantly agricultural areas (6, 8, and 9); however, concentrations did not change consistently with flow in the forested areas (1, 2, 3, and 4) or in the Milwaukee River (10).

As with the nitrogen species, only weak relations, if any, were found between concentration and streamflow for any phosphorus constituent. Total phosphorus concentrations increased slightly with increased flow in agricultural areas (5, 6, 7, and 9); however, no relations were found in the forested areas (1, 2, 3, and 4) or in the Milwaukee River (10). Concentrations decreased with increased flow at the Fox River (8) (a mixed agricultural, forested, and urban site). Relations of concentrations and streamflow are shown for the Escanaba River (1), Fox River (8), Green Lake Inlet (7), and Manitowoc River (9) Rivers in figure 50. No relations between dissolved phosphorus and total and dissolved orthophosphate concentration and streamflow were found. Concentrations of most phosphorus species were near the detection limit for all forested areas.

Total suspended-sediment concentrations demonstrated a weak but positive relation with streamflow for all of these sites. Relations of concentrations and streamflow are shown for the Escanaba River (1), Menominee River (4), Green Lake Inlet (7), and Fox River (8) in figure 51.

Flow adjustments are commonly made before data are examined for trends in water quality. Because of the weak relations with streamflow, compensation (adjustment) in nitrogen and phosphorus concentrations for flow should have little effect on the detection of trends. Therefore, these data indicate that trends can also be examined without much bias, at sites for which no streamflow information is available. For suspended-sediment concentrations, however, a consistent relation with streamflow was found; therefore, concentrations should be adjusted for variable flow before trend analyses are done. The weak relations between concentration and streamflow for all nutrient species and suspended sediment (a weakness that may have been partly the result of upstream dams) would cause considerable uncertainty in load estimations made by use of regression-type approaches.

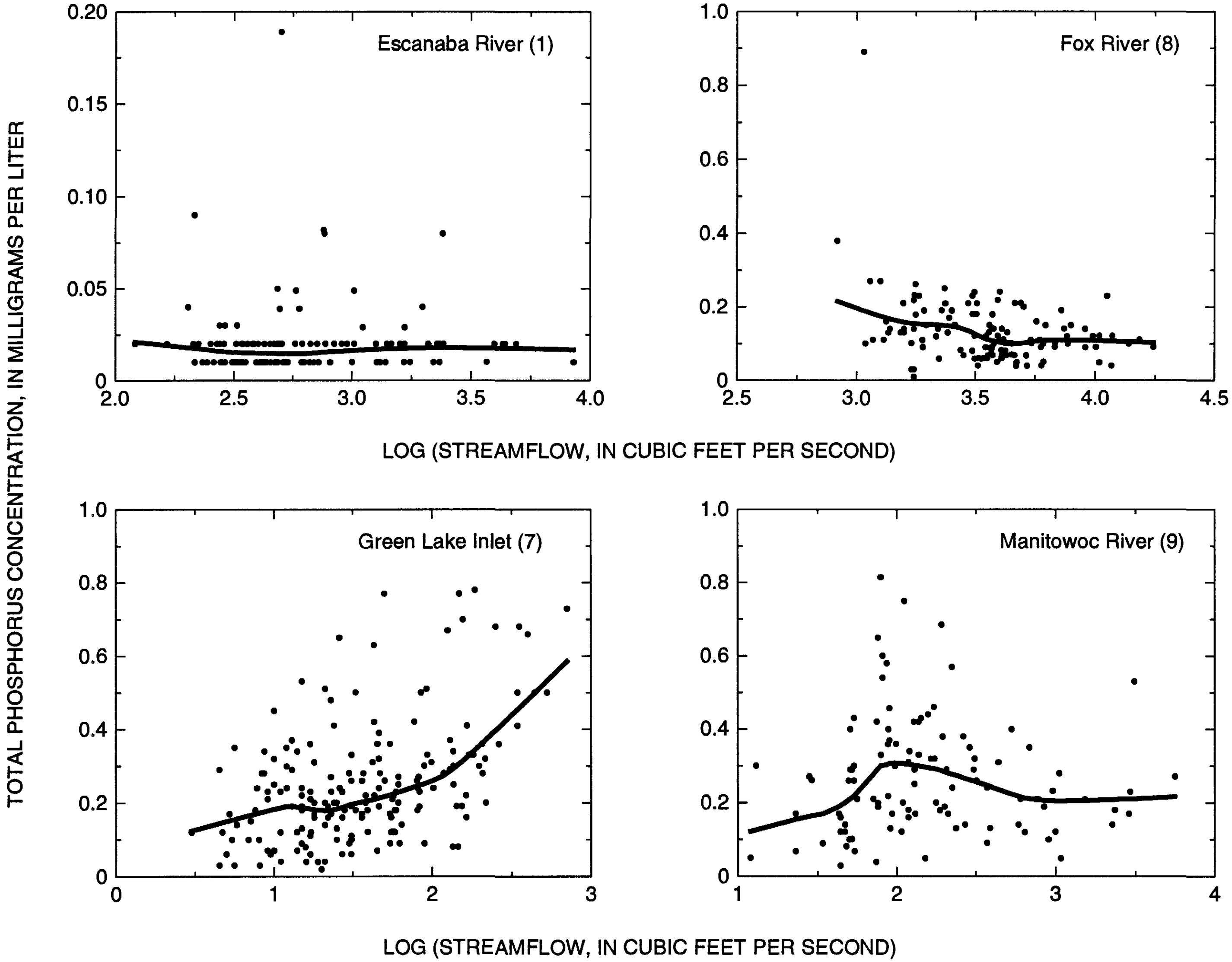


Figure 50. Total phosphorus concentration as a function of streamflow for selected sites in the Western Lake Michigan Drainages study unit, water years 1971–90. [The lowess smooth is plotted through the data. River locations (identification numbers are in parentheses) are shown in figure 24.]

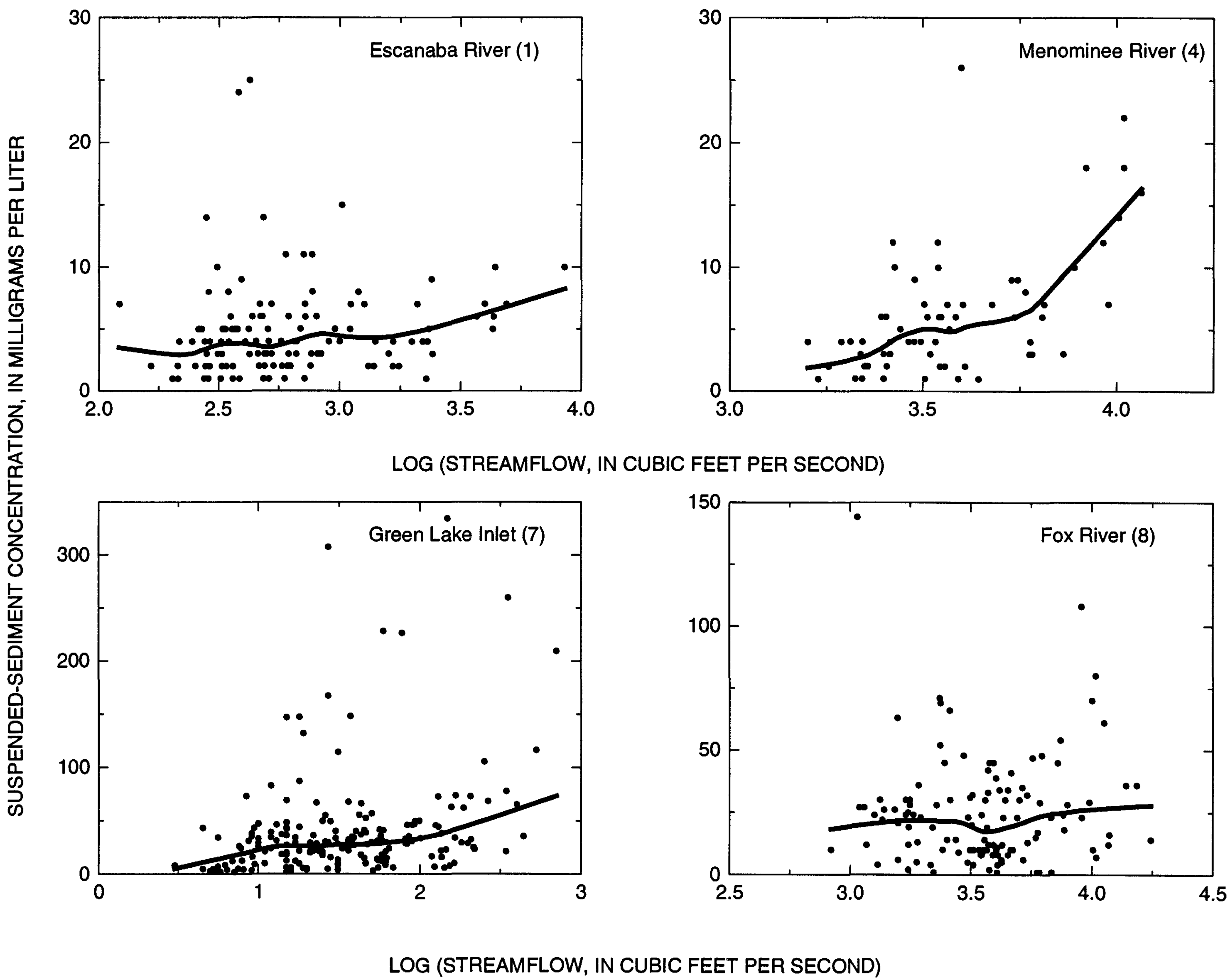


Figure 51. Suspended-sediment concentration as a function of streamflow for selected sites in the Western Lake Michigan Drainages study unit, water years 1971–90. [The lowess smooth is plotted through the data. River locations (identification number are in parentheses) are shown in figure 24.]

TRANSPORT OF SEDIMENT AND NUTRIENTS IN THE WESTERN LAKE MICHIGAN DRAINAGES

Nutrients and suspended sediment are essential for algal and macrophyte growth in aquatic environments; but in sufficiently high concentrations, these constituents can adversely affect water quality. Runoff and erosion and the accompanying high transport (loading) of nutrients and suspended sediment have been identified as primary water-quality concerns throughout the WMIC study unit, especially in Lake Winnebago, and downstream from the study unit in Lake Michigan and Green Bay. With the belief that point sources of pollution in the study unit are under control, much of the current effort in improving water quality focuses on quantifying and reducing nonpoint source loading, such as that associated with runoff and soil erosion.

Constituent transport models were used to estimate the annual export rates of total phosphorus, suspended sediment, total Kjeldahl nitrogen, and dissolved nitrite plus nitrate from six major river basins [(Escanaba River (1), Ford River (2), Menominee River (4), Fox River (8), Manitowoc River (9), and Milwaukee River (10)], which represent greater than 63 percent of the study unit, and two smaller indicator rivers [Popple River (3), and White Creek (5)]. Locations of all the sites are shown in fig. 24. These sites were part of the National Stream-Quality Accounting Network (NASQAN) sites (except White Creek), and have sufficient data to represent all seasons and all flow regimes. Nitrogen data were not available for White Creek. These load estimates are used to quantify the total loads of nutrient and suspended sediment exported from these basins, compare the input of nutrients to the quantity exported, estimate the transport from the entire WMIC study unit, and determine if the point sources of nutrients are truly minor contributors in these selected river basins and the entire study unit. These results can then be used to help aid regional water-resource managers and policymakers in prioritizing where further actions are needed.

The constituent-transport models were based on the relations between constituent load and two variables: stream discharge (Q, in cubic feet per second) and time of the year (T, in radians) (Cohn and others, 1989). The general form of the model was

$$\log(\text{Daily Load}) = a + b(\log(Q) - c) + d(\log(Q) - c)^2 + e(\sin(T)) + f(\cos(T)). \qquad (1)$$

Equation 1 was calibrated by use of multiple regression analyses between daily loads (estimated by multiplying daily average discharges by instantaneous concentrations) and daily average discharges, Q, and the time of the year, T. A, b, c, d, e, and f are calibration coefficients that are specific to the river and the constituent being modeled. Each calibration procedure used all of the available data for each site from water years 1971–90. All load estimates and export rates for nutrients and suspended sediment were estimated for 11 years (1980–90), except for White Creek (1983–88), and Menominee River (1980–85). These estimates were used to determine the average annual export, and the annual export during a wet year (1986, the year of the highest streamflows throughout the study unit) and a dry year (1988, the year of the lowest streamflows throughout the study unit).

Nutrient Input

The total inputs of phosphorus and nitrogen into each of the eight basins are summarized in tables 20 and 21 and are shown in figures 52 and 53. The percentage of agricultural land in each basin also is indicated in these figures. The total input of phosphorus directly relates to the percentage of agriculture in the basin; more than 20 kg/ha was applied annually into areas completely in agriculture (White Creek), less than 1 kg/ha applied annually in forested areas, and intermediate amounts were applied in mixed areas. Almost all the phosphorus input into each area was from agricultural applications, except in isolated forested areas where the atmospheric deposition was small, but nevertheless a major phosphorus source. Point sources of phosphorus in all these basins were relatively small; most of the major inputs were very near river mouths or directly into Green Bay or Lake Michigan.

Nutrient inputs into the six major river basins (reference basins) were used to extrapolate the total input of nutrients into the entire study unit. Nutrient inputs into areas not included in the six major basins from each nonpoint source were estimated by (1) determining how much of the remaining area resembled, in terms of similar land usė and surficial deposits, the area of each of the six reference basins; (2) estimating the total area that each reference basin represents (the

Table 20. Average annual total phosphorus inputs and outputs from nonpoint sources in selected drainage basins within the Western Lake Michigan Drainages study unit and the entire study unit

[kg, kilograms; kg/ha, kilograms per hectare; average runoff loads were estimated for water years 1980–90 and for the wettest (1986) and driest (1988) years during the period]

Basin	Annual inputs (kg/ha)						Annual outputs				Percentage of inputs exported			Effective-area factor
	Fertilizer	Manure	Atmospheric deposition	Other nonpoint	Point sources	Total phosphorus	Average total (kg)	Average (kg/ha)	Wet year (kg/ha)	Dry year (kg/ha)	Average	Wet year	Dry year	
Escanaba	0.57	0.33	0.05	0	0	0.95	13,700	0.06	0.08	0.05	6.4	8.1	5.0	2.40
Ford	.35	0.19	.05	0	0	.59	7,700	.07	.11	.05	11.0	19.2	8.1	2.31
Fox	5.01	3.59	.20	.01	.08	8.87	474,900	.30	.43	.18	3.4	4.8	2.0	1.13
Menominee[1]	.33	0.21	.05	0	.01	.60	97,900	.10	.09	.09	16.1	14.7	14.9	1.59
Manitowoc	6.73	7.22	.20	0	.01	14.15	63,300	.48	1.09	.17	3.4	7.7	1.2	4.67
Milwaukee	6.43	5.14	.20	0	.04	11.82	71,400	.40	.68	.23	3.4	5.8	2.0	1.72
Popple River	.08	.09	.05	0	0	.22	2,700	.06	.08	.03	28.8	37.7	13.2	0
White Creek[2]	11.09	8.83	.20	0	0	20.12	2,500	3.13	4.47	.44	15.5	22.2	2.2	0
WMIC[3]	3.11	2.53	.13	0	.08	5.85	1,161,000	.23	.36	.13	3.9	6.2	2.3	

[1]Based on load estimates from Oct. 1979 through Sept. 1985; the 1982 water year was used as the dry year.

[2]Based on load estimates from Oct. 1982 through June 1988; dry year based on monthly loads from July 1987 to June 1988.

[3]Average load per hectare for the entire study unit, based on extrapolated loads from these basins by use of the effective-area factors.

Table 21. Average annual total nitrogen inputs and outputs from nonpoint sources in selected drainage basins within the Western Lake Michigan Drainages study unit and the entire study unit

[kg, kilograms; kg/ha, kilograms per hectare; N/A, data not available; average runoff loads were estimated for water years 1980–90 and for the wettest (1986) and driest (1988) years during the period]

Basin	Annual inputs (kg/ha)							Annual outputs				Percentage of inputs exported			Effective-area factor
	Fertilizer	Manure	Fixation	Atmospheric deposition	Other nonpoint	Point sources	Total nitrogen	Total average (kg)	Average (kg/ha)	Wet year (kg/ha)	Dry year (kg/ha)	Average	Wet year	Dry year	
Escanaba	2.32	1.45	11.18	7.31	0	0	22.25	542,400	2.40	2.96	2.00	10.8	13.3	9.0	2.40
Ford	1.42	0.91	12.81	7.85	0	0	22.94	268,900	2.27	3.15	1.65	9.9	13.7	7.2	2.31
Fox	21.11	17.71	21.71	8.41	.10	.36	69.38	7,070,000	4.52	6.60	3.15	6.5	9.5	4.5	1.13
Menominee[1]	1.35	1.08	12.74	7.05	.01	.03	22.25	2,647,400	2.62	3.42	2.33	11.8	15.4	10.5	1.59
Manitowoc	28.35	39.52	27.85	9.07	.08	.03	104.09	949,400	7.17	13.63	3.95	6.9	13.1	3.8	4.67
Milwaukee	27.11	25.94	22.41	10.40	.03	.02	85.91	1,529,900	8.58	13.75	7.60	10.0	16.0	8.8	1.72
Popple River	0.33	.43	10.59	6.66	0	0	18.00	84,300	1.96	2.89	1.10	10.9	16.0	8.8	0
White Creek[2]	46.76	36.16	33.00	9.17	0	0	125.09	N/A	N/A	N/A	N/A	N/A	N/A	N/A	0
WMIC[3]	13.09	13.00	17.99	8.03	.06	.54	52.70	21,186,000	4.14	6.31	3.05	7.9	12.0	5.8	

[1]Based on load estimates from Oct. 1979 through Sept. 1985; the 1982 water year was used as the dry year.

[2]No nitrogen data available.

[3]Average load per hectare for the entire study unit, based on extrapolated loads from these basins by use of the effective-area factors.

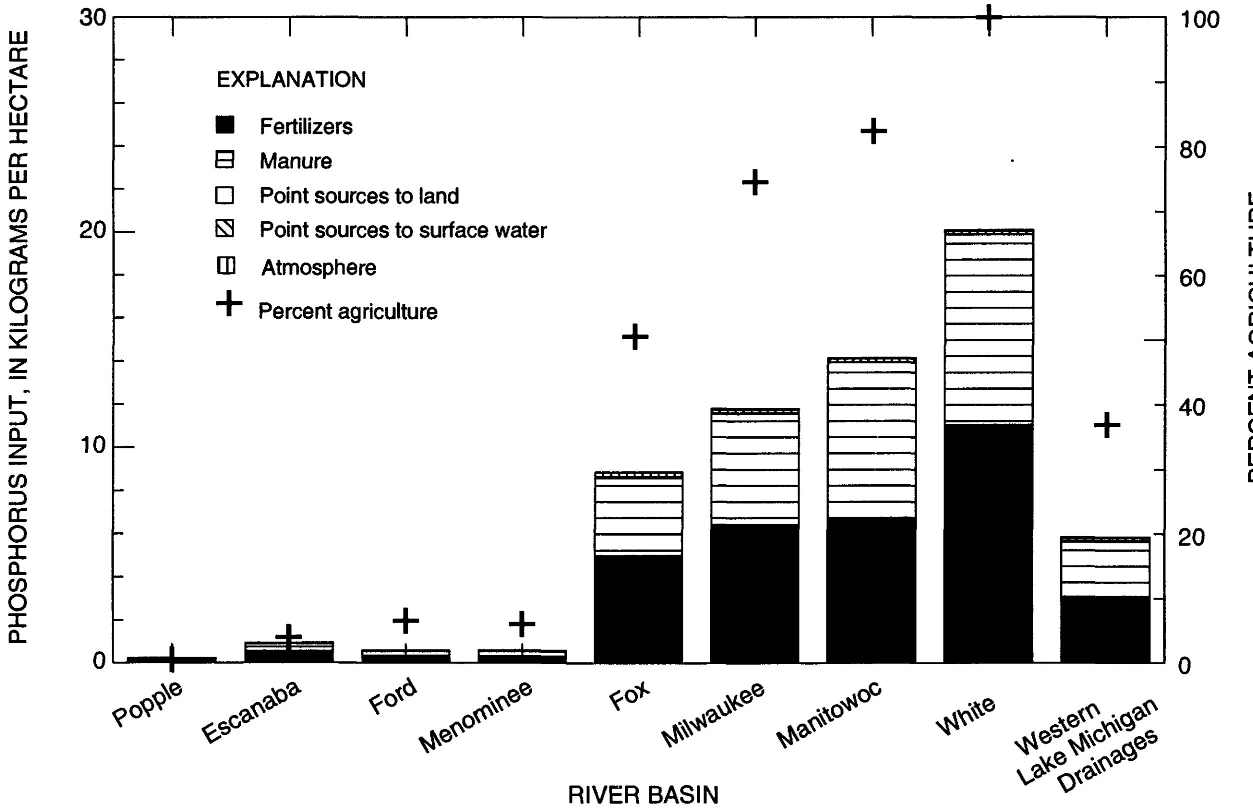


Figure 52. Average annual phosphorus inputs into selected river basins and the Western Lake Michigan Drainages study unit. [Percent of agricultural land in the basin is indicated.]

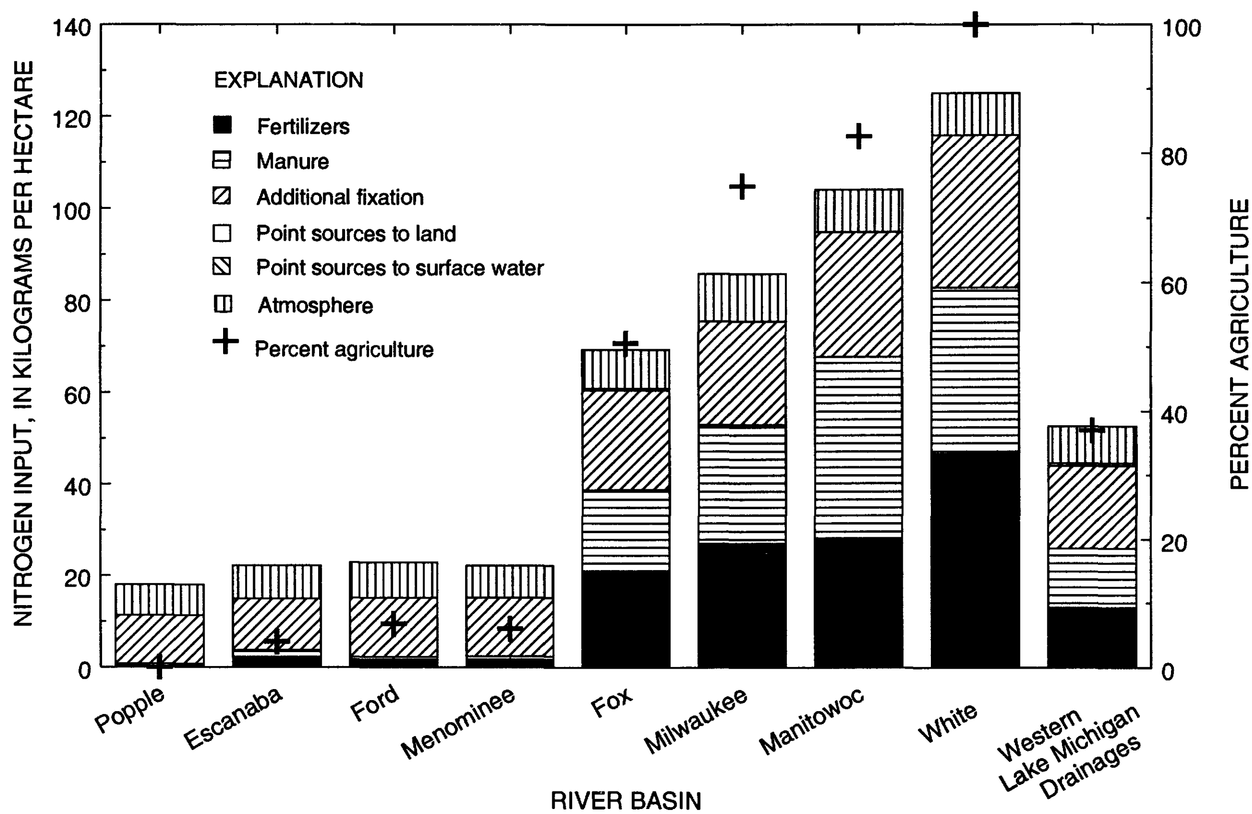


Figure 53. Average annual nitrogen inputs into selected river basins and the Western Lake Michigan Drainages study unit. [Percent of agricultural land in the basins is indicated.]

drainage area of the reference river plus any unmonitored areas with similar land uses and surficial deposits); (3) computing the ratio of the total area each river represents to the area of that reference basin, referred to here as the "effective-area factor" (given in tables 20 and 21); (4) multiplying the estimated input rate of nutrients into each reference basin by the product of the effective-area factor and the area of the reference basin; (5) summing the products of (4); and (6) converting the sum back into a rate by dividing the final sum by the area of the study unit. Therefore, nutrient inputs into each of the six major rivers are used to estimate the total input into an area larger than its own drainage basin. For example, the input into the Escanaba River was used to estimate the total input into an area 2.4 times the size of its own basin. Additional nutrients from point sources directly input to surface water and to land (also referred to as "other nonpoint inputs") not included in the six major basins were quantified from the WDNR data base (described earlier). For the entire study unit, greater than 96 percent of the total input of phosphorus comes from fertilizers and manure; point sources contribute only about 1.3 percent of the total input.

The total inputs of nitrogen, as was the case for phosphorus, were directly related to the percentage of agriculture in the basins. More than 125 kg/ha was input annually to areas completely in agriculture (White Creek), less than 25 kg/ha input annually to forested areas, and intermediate amounts input in mixed areas. Most nitrogen, like phosphorus, was input for agricultural purposes; however, nitrogen was input at much higher rates. Annual input rates of nitrogen from additional fixation (10 to 33 kg/ha, the additional input not incorporated in the manure rates) and atmospheric deposition (approximately 8 kg/ha throughout the study unit) were much more significant sources than for phosphorus. Fixation and atmospheric contributions were the major sources of nitrogen input to the forested areas. Point sources of nitrogen were again relatively small compared to nonpoint sources of nitrogen. Nitrogen input to the entire study unit was estimated in a manner similar to that for phosphorus. Total nitrogen input for the entire study unit was fairly evenly divided among fertilizers, manure, fixation, and atmospheric contributions. Point sources contributed only about 1 percent of the total; but, as with phosphorus, point-source contributors of nitrogen can be important in localized areas.

Nutrient and Suspended-Sediment Export

Phosphorus

Total phosphorus export from each of the individual basins and from the entire study unit is summarized in table 20 and shown in figure 54 (along with phosphorus input to these areas). Phosphorus export appears to be directly related to land use and the amount of phosphorus input to the basins; phosphorus export per unit area from agricultural areas is much higher than that from forested areas. No data were available for completely urbanized areas. The average annual total phosphorus exported from a basin ranged from more than 3 kg/ha in small agricultural basins (White Creek) to approximately 0.3 to 0.5 kg/ha in large agricultural areas (Fox, Milwaukee, and Manitowoc Rivers) to less than 0.1 kg/ha in forested areas of any size (Escanaba, Ford, Menominee, and Popple Rivers). During wet years, these exports increased significantly, especially in the Manitowoc River Basin, where the annual load more than doubled. During dry years, phosphorus export was significantly reduced in all agricultural areas and small forested areas; however, export from large forested areas was not significantly reduced. Export from small basins appears to be the most variable from year to year. The reduced loads and variability in the large agricultural basins compared to those in the small agricultural basin may be due to sediment deposition in reservoirs or lakes intersecting the rivers, especially the Fox and Milwaukee Rivers.

Panuska and Lillie (1995) compiled total phosphorus export rates from studies done throughout Wisconsin. These studies concentrated mostly on small basins (less than 20,000 ha), smaller than most of those examined in this analysis. For forested areas, they found the average annual export of total phosphorus to be approximately 0.1 kg/ha, which agrees with that found for the WMIC study unit. For agricultural areas, they found the annual export of phosphorus to range from 0.2 to 3.0 kg/ha; however, in a few cases, export rates were greater than the 3 kg/ha estimated in this study for White Creek.

Although the absolute amount of phosphorus exported was higher from agricultural areas than from forested areas, the forested areas exported relatively more of the input phosphorus than did agricultural areas. In large agricultural areas, only about 3 percent of the total phosphorus input into the basin was exported, whereas 6 to 28 percent was exported from

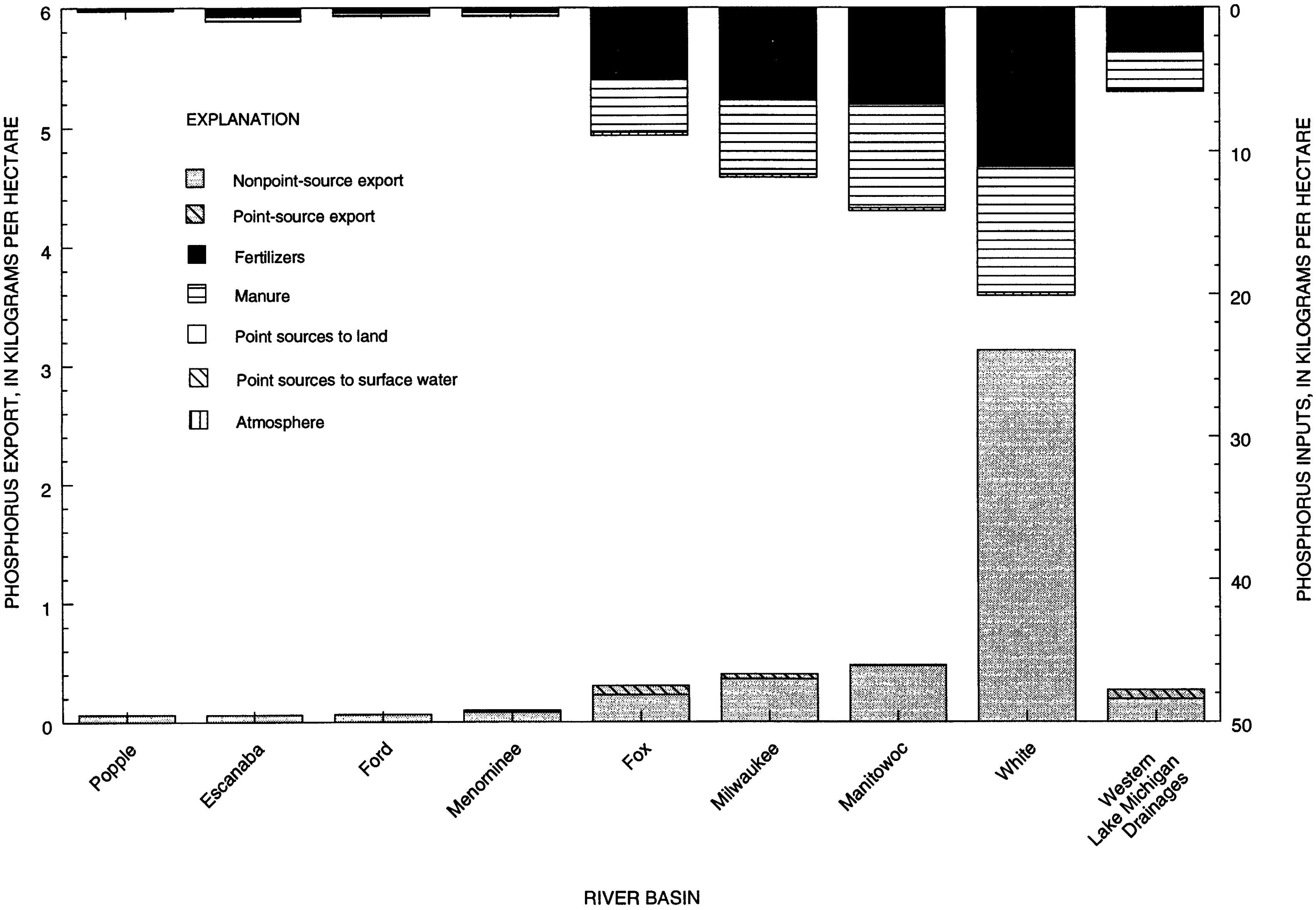


Figure 54. Average annual phosphorus exports from (bottom) and imports into (top) selected basins and the Western Lake Michigan Drainages study unit.

forested areas. However, during most years, small agricultural basins can export 15 to 20 percent of the total phosphorus added. The smaller percentage of phosphorus loss in agricultural areas may be due to much of the added phosphorus being incorporated into milk products and into crops that were later harvested.

Loads from the six major river basins were used to extrapolate the total load exported from nonpoint sources throughout the entire study unit. The loads from unmonitored areas were estimated by multiplying the measured load of each reference river by the effective-area factor and summing the products. Therefore, each of the six major rivers is used to estimate the total load from an area larger than its own drainage basin. The smaller indicator rivers were used to describe variability within these larger basins and describe loads from smaller, more homogeneous areas.

From these export rates, the effective-area factors, and the point-source inputs, the total export of phosphorus can be estimated by any one of three methods, which differ in the assumptions that are made concerning the transport or export of phosphorus from point sources. The three assumptions for point sources are the following: (1) assume that all point sources can be treated as nonpoint sources; (2) assume that only point sources that discharge directly to Lake Michigan and Green Bay are considered as point sources (in other words, 100 percent of that input into Green Bay and Lake Michigan is exported); and (3) assume that 100 percent of all point-source inputs are exported out of the study unit.

In the first method, point-source inputs are completely incorporated into the export rates previously described; therefore, the total export from the study unit is obtained by multiplying the loads from the reference basins by the effective-area factors and summing (tables 20 and 21). By this method, there would be an average annual export of approximately 1,161,000 kg of total phosphorus into Lake Michigan and Green Bay, which is approximately 4 percent of the total amount of phosphorus input (tables 20 and 22). The overall annual export rate for the entire study unit would be 0.23 kg/ha. This estimate increases by about 60 percent (to 0.36 kg/ha) in wet years and decreases by about 42 percent (to 0.13 kg/ha) in dry years. By this method, point sources would contribute at a ratio similar to that of the inputs, or in other words, point sources accounted for 1.3 percent of the input and therefore should account for 1.3 percent of the export (rounded off to a rate of 0 kg/ha in table 22). This small percentage clearly underestimates the importance of point sources. Approximately 80 percent of this total load comes from the southern half of the study unit, which is dominated by agriculture.

In the second method, point-sources contributors (except those directly discharging into Lake Michigan and Green Bay) are treated as nonpoint sources and are incorporated into the export rates previously described. Therefore, the total export is obtained by multiplying the basin loads by the effective-area factors and summing, then adding the point-source loads directly input into Lake Michigan and Green Bay. By this method, there would be an average annual export of total phosphorus of approximately 1,370,600 kg from the WMIC study unit (table 22). The overall annual export rate would be 0.27 kg/ha (0.23 kg/ha contributed by nonpoint sources plus 0.04 kg/ha contributed by point sources). This method treats all point sources not directly discharging into Lake Michigan and Green Bay as nonpoint sources and contribute at a rate proportional to the inputs. Therefore, point sources within the basins (which now represent only 0.05 percent of the total input) contribute only 0.05 percent of the nonpoint contribution and point sources directly to Lake Michigan and Green Bay contribute 0.04 kg/ha. By this method, point sources (almost entirely discharging directly into Green Bay and Lake Michigan) would contribute 16 percent of the total export.

In the third method, 100 percent of all of the point sources are treated as being exported from the study unit; therefore, the overall export rates for each reference basin must be reduced by the amount of point sources within each basin. The total export from nonpoint sources is computed by multiplying the nonpoint-source export rates for each basin (computed by subtracting the input rates for all of the point sources from the total export rate in table 20) by the effective-area factors and summing. This results in an export of 985,300 kg. To this sum is added 100 percent of the point-source export (382,300 kg). By this method, in an average year, approximately 1,367,600 kg of total phosphorus would be exported out of the WMIC study unit, and the overall annual export rate would be 0.27 kg/ha (0.19 kg/ha from nonpoint sources plus 0.08 kg/ha from point sources) (table 22). By this method, point sources would contribute 28 percent of the total export.

Therefore, the average annual export of phosphorus from the WMIC study unit should be between 1,161,000 to 1,370,600 kg. Overall, point sources, in

Table 22. Extrapolation of total phosphorus loads from selected basins to that exported from the Western Lake Michigan Drainages study unit and allocation of loads to those contributed by point and nonpoint sources

[kg, kilograms; kg/ha, kilograms per hectare; --, not applicable; average runoff loads were estimated for water year 1980–90 and for the wettest (1986) and driest (1988) years during the period]

Basin, additional sources, or computational treatment of point sources	Total average annual export		Allocation of annual load						Effective-area factor
	(kg)	(kg/ha)	Point sources (kg)	Point sources (kg/ha)	Nonpoint sources (kg)	Nonpoint sources (kg/ha) Average	Wet year	Dry year	
Escanaba	13,700	0.06	0	0	13,700	0.06	0.08	0.05	2.40
Ford	7,700	.07	0	0	7,700	.07	.11	.05	2.31
Fox	474,900	.30	121,700	.08	353,200	.23	.35	.10	1.13
Menominee	97,900	.10	13,000	.01	84,900	.08	.08	.08	1.59
Manitowoc	63,300	.48	1,000	.01	62,200	.47	1.08	.16	4.67
Milwaukee	71,400	.40	7,400	.04	64,000	.36	.64	.19	1.72
Additional sources in study unit			29,600	.02	--	--			--
Additional sources to Green Bay or Lake Michigan			209,700	.04	--	--			--
Extrapolation to the entire study unit									
All point sources treated as nonpoint sources	1,161,000	0.23	14,900	0	1,146,100	0.22	0.36	0.13	--
Point sources to Lake Michigan and Green Bay treated as point sources; remainder treated as nonpoint sources	1,370,600	.27	216,400	.04	1,154,200	.23	.37	.13	--
All point sources treated as point sources	1,367,600	.27	382,300	.08	985,300	.19	.33	.10	--

the worst case (100 percent exported), could contribute as much as 28 percent, and in a very dry year contribute about 44 percent (0.08 kg/ha from point sources and 0.10 kg/ha from nonpoint sources); however, not all the phosphorus from point sources is exported. These estimates are based on nonpoint-source data from 1980–90 and point-source estimates for 1992. Sager (Wisconsin Department of Natural Resources, 1993) estimated that annual point-source loads of phosphorus in the Fox River basin decreased from 430,000 kg in 1970 to 110,000 kg in 1990. Similar reductions in phosphorus are expected to have occurred in most other major sewage-treatment plants, such as that in Milwaukee. Therefore, the total load of phosphorus leaving the WMIC study unit is believed to have been significantly higher around 1970 (the beginning of this study).

This approach can be used to estimate the total export from a single basin, such as from the Fox River Basin, and to determine how important point and nonpoint sources are for a specific basin. The load of phosphorus leaving the Fox River Basin represents approximately 40 percent of the total load of phosphorus leaving the entire WMIC study unit. Based on the assumptions described above, the average annual load of phosphorus from the Fox River into Green Bay should be between 500,000 kg (all point sources treated as nonpoint sources), 530,000 kg (100 percent of all point sources are exported), and 605,000 kg (all point sources upstream of Wrightstown, Wis., treated as nonpoint sources and all point sources downstream of Wrightstown treated as point sources). Sager (Wisconsin Department of Natural Resources, 1993) estimated the annual export of phosphorus from the Fox River to be 700,000 kg in 1990. In this study, point sources in the worst case (100 percent exported) were found to contribute as much as 30 percent of the average annual load from the Fox River in an average year and almost 42 percent in a very dry year. Sager estimated that point sources contribute 110,000 kg or 16 percent of the total annual export. In this study, nonpoint sources were estimated to contribute from 370,000 kg (all point sources treated as point sources) to 493,000 kg (only point sources discharging directly to Green Bay treated as point sources). Sager estimated the average annual nonpoint-source export of phosphorus from the Fox River to be 590,000 kg.

Nitrogen

Total nitrogen export from each of the individual basins and from the entire study unit is summarized in table 21 and shown in figure 55 (along with nitrogen input to these areas). Nitrogen export, like phosphorus export, appears to be directly related to land use and the amount of nitrogen input into the basins: agricultural areas export much more nitrogen per unit area than forested areas. No data were available for completely urbanized areas. The average annual export of total nitrogen from the basins ranged from about 2 kg/ha in forested areas to more than 8 kg/ha in agricultural areas. No data were available to determine whether the high phosphorus export rates in small agricultural areas, such as White Creek, also occurs for nitrogen. During wet years, these export rates increased significantly, especially in agricultural areas. During dry years, nitrogen export was significantly reduced in all agricultural areas and small forested areas; however, export rates remained similar for large forested areas.

Although the absolute amount of nitrogen export was higher from agricultural areas than from forested areas, relatively more of the nitrogen that was input to the forested areas was exported out of the basins. In large agricultural areas (Fox, Manitowoc, and Milwaukee Rivers), 6 to 10 percent of the total nitrogen input to the basin was exported, whereas 10 to 12 percent was exported from forested areas (Escanaba, Ford, and Menominee Rivers). The smaller percentage of nitrogen loss from agricultural areas may again be due to incorporation of the added nitrogen into milk products and into crops that were later harvested.

By use of the same three methods for computing the export of point sources loads of phosphorus, the total export of nitrogen from the study unit was estimated. If all point sources were treated as nonpoint sources and were completely incorporated into the export rates previously described, then, the average annual export of total nitrogen to Lake Michigan and Green Bay would be 21,181,000 kg. This is approximately 8 percent of the total nitrogen input (tables 21 and 23) and is about 20 times the amount of exported phosphorus. The average annual export rate for the entire study unit would be 4.14 kg/ha. This estimate increases by about 50 percent (to 6.31 kg/ha) in wet years and decreases by about 25 percent (to 3.05 kg/ha) in dry years (table 21). If point sources contribute at a ratio similar to that of the inputs and then they should account for 1.02 percent of the export (0.04 kg/ha).

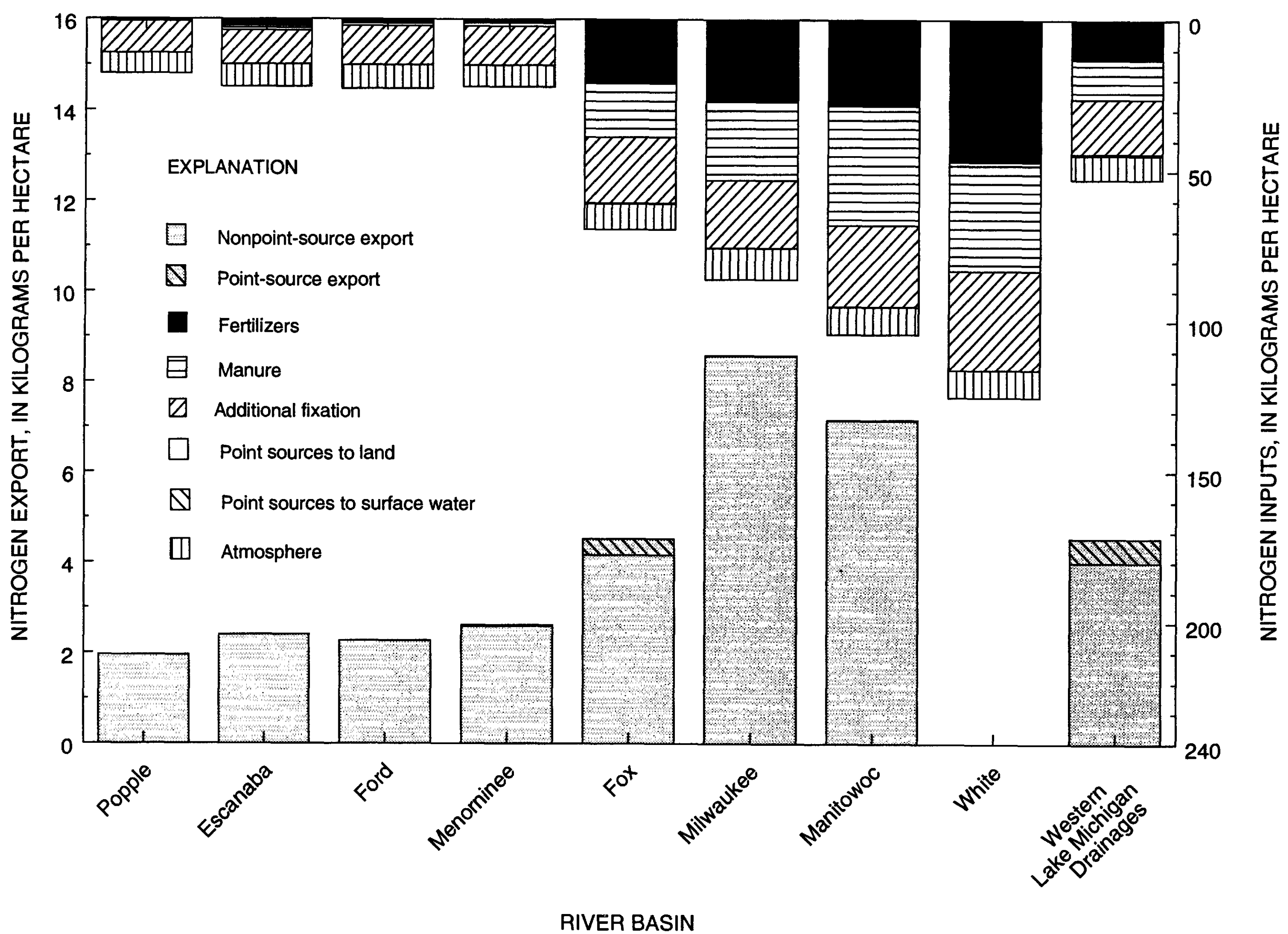


Figure 55. Average annual nitrogen exports from (bottom) and imports into (top) selected basins and the Western Lake Michigan Drainages study unit.

Table 23. Extrapolation of total nitrogen loads from selected basins and additional sources to that exported from the Western Lake Michigan Drainages study unit and allocation of loads to those contributed by point and nonpoint sources

[kg, kilograms; kg/ha, kilograms per hectare; --, not applicable; average runoff loads were estimated for water years 1980–90 and for the wettest (1986) and driest (1988) years during the period]

Basin, additional sources, or computational treatment of point sources	Total average annual export		Allocation of annual load						Effective area factor
	(kg)	(kg/ha)	Point sources (kg)	Point sources (kg/ha)	Nonpoint sources (kg)	Nonpoint sources (kg/ha) Average	Wet year	Dry year	
Escanaba	542,400	2.40	0	0	542,400	2.40	2.96	2.00	2.40
Ford	268,900	2.27	0	0	268,900	2.27	3.15	1.65	2.31
Fox	7,070,000	4.52	686,267	.44	6,384,000	4.08	6.16	2.71	1.13
Menominee	2,647,400	2.62	30,700	.03	2,616,700	2.59	3.39	2.30	1.59
Manitowoc	949,400	7.17	3,700	.03	945,700	7.14	13.60	3.92	4.67
Milwaukee	1,529,900	8.58	3,700	.02	1,526,100	8.56	13.73	7.58	1.72
Additional sources in study unit			218,500	.12	--	--			--
Additional sources to Green Bay or Lake Michigan			1,921,400	.38	--	--			--
Extrapolation to the entire study unit									
All point sources treated as nonpoint sources	21,186,100	4.14	215,200	.04	20,971,000	4.10	6.27	3.01	--
Point sources to Lake Michigan and Green Bay treated as point sources; remainder treated as nonpoint sources	23,107,600	4.52	1,986,000	.39	21,121,600	4.13	6.30	3.04	--
All point sources treated as point sources	23,219,300	4.54	2,736,600	.54	20,482,800	4.01	6.15	2.89	--

Table 24. Extrapolation of total suspended-sediment export from selected drainage basins to that exported from the Western Lake Michigan Drainages study unit

[kg, kilograms; kg/ha, kilograms per hectare; average runoff loads were estimated for water years 1980–90 and for the wettest (1986) and driest (1988) years during the period]

Basin	Annual export				Effective-area factor
	Total average year (kg)	Average year (kg/ha)	Wet year (kg/ha)	Dry year (kg/ha)	
Escanaba	4,011,000	17.8	23.3	15.1	2.40
Ford	5,789,000	48.9	146.9	37.2	2.31
Fox	143,707,000	91.9	156.9	40.5	1.13
Menominee[1]	24,568,000	24.3	33.6	22.3	1.59
Manitowoc	38,377,000	289.6	906.2	100.8	4.67
Milwaukee	23,976,000	134.5	316.4	78.2	1.72
Popple River	870,000	20.2	27.4	11.2	0
White Creek	7,257,000	9,070.7	16,531.4	414.8	0
WMIC[2]	444,911,000	87.0	203.7	41.5	

[1]Based only on load estimates from Oct. 1979 through Sept. 1985; water year 1982 was used as the dry year.

[2]Average load per hectare for the entire study unit, based on loads only from these basins extrapolated by use of the effective-area factors.

Approximately 70 percent of this total load comes from the southern half of the study unit, which is dominated by agriculture.

If point sources other than those discharging directly to Lake Michigan and Green Bay are treated as nonpoint sources and are incorporated into the export rates previously described, then the average annual export of nitrogen from the WMIC study unit would be 23,107,600 kg (table 23). The overall annual export rate would be 4.52 kg/ha. Allocation of the overall annual export rate would be 4.13 kg/ha from nonpoint sources and 0.39 kg/ha from point sources (0.38 kg/ha directly added to Lake Michigan and Green Bay plus 0.01 kg/ha from point sources within the basin). By this method, point sources (almost entirely discharging directly into Green Bay and Lake Michigan) would contribute 9 percent of the total export.

If all point-source inputs are treated as point sources and are exported from the study unit, the average annual export of nitrogen from the WMIC study unit would be 23,219,300 kg and the overall annual export rate would be 4.54 kg/ha (4.01 kg/ha from nonpoint sources and 0.54 kg/ha from point sources) (table 23). By this method, point sources would contribute 12 percent of the total export.

The average annual export of nitrogen from the WMIC study unit is estimated to be between 21,186,100 to 23,219,300 kg. Point sources, in the worst case (100 percent exported) could contribute as much as 12 percent of the total load in an average year and about 16 percent in a very dry year (0.54 kg/ha from point sources and 2.89 kg/ha from nonpoint sources). Nonpoint sources contribute approximately 21,000,000 kg regardless of the selected assumptions.

Suspended Sediment

Total suspended sediment exported from each of the individual basins and from the entire study unit is summarized in table 24. Suspended-sediment export appears to be directly related to land use and the texture of surficial deposits: agricultural areas, especially areas with clay deposits, export more sediment than forested areas. No data were available for completely urbanized areas. The average annual export of suspended sediment ranged from more than 9,000 kg/ha in small agricultural basins (White Creek), to 100–300 kg/ha in larger agricultural basins, to less than 50 kg/ha in forested basins of any size. During wet years, these exports increased significantly, in several cases by a factor of 3. During dry years, sediment export was significantly reduced in all agricultural areas and small forested areas; however, export from large forested areas remained about the same (similar to phosphorus and nitrogen). Export of suspended sediment from small basins appears to be extremely variable from year to year, especially for agricultural basins.

Hindall's (1976) estimates of sediment yields from streams throughout Wisconsin were generally less than those estimated here. He estimated the average annual yield for the Milwaukee River at Milwaukee to be 30 kg/ha and the average annual yield for the Popple River near Fence to be 12 kg/ha; estimates based on the 1971–90 data examined in this study are 135 and 20 kg/ha, respectively.

Average annual export of suspended sediment to Lake Michigan and Green Bay is estimated to be approximately 445,000,000 kg (table 24). This estimate increases by more than a factor of 2 in wet years and decreases by about 50 percent in dry years. Approximately 75 to 90 percent of the total load comes from the southern half of the study unit, which is dominated by agriculture. The export rates in table 24 can be used to estimate the total export from individual basins, such as from the entire Fox River Basin. The estimated average annual export of suspended sediment from the mouth of the Fox River is 151,000,000 kg (extrapolation of the load estimated at Wrightstown, which represents 95.42 percent of the entire basin to that exported from the mouth in Green Bay), or about 34 percent of the total load leaving the entire WMIC study unit.

TRENDS IN WATER QUALITY

Trends or long-term changes in water quality were examined for suspended sediment and for nitrogen and phosphorus species, except dissolved nitrite, total orthophosphate, and total ammonia at the eight sites for which export rates were estimated. Changes in water quality were examined over two periods: water years 1980–90 (table 25) and the entire length of the individual records, ending in 1990 (table 26). Commonly, concentrations of suspended sediment and various nutrients are strongly related to streamflow. Therefore, to facilitate detection of trends, the time series of each constituent was adjusted to remove the effects of discharge by first relating discharge to concentration by use of the LOWESS method (Helsel and Hirsch, 1992) and then subtracting the LOWESS value, estimated for each discharge, from each point in the original time series. In the LOWESS method, a smoothing coefficient ("f" value) of 0.5 has been found to capture the basic concentration-flow relations at many stream-gaging stations (Lanfear and Alexander, 1990); therefore, 0.5 was used here. LOWESS smooths (using a smoothing coefficient of 0.5) are included in the time-series plots throughout this section to smooth the original time series and allow trends to be more easily observed. The PT2 statistical and graphic package (K.J. Lanfear, U.S. Geological Survey, written commun., 1993) was used to flow adjust the time-series data, test for significant trends in the flow-adjusted data. Within PT2, seasonal Kendall tests (Crawford and others, 1983) were used to determine whether statistically significant monotonic time trends were present in the flow-adjusted constituent concentrations.

A few time series included a large proportion of samples at or below detection limits and were unable to be flow adjusted; therefore, the trend analyses for these time series were based on non-flow-adjusted concentrations and identified in tables 25 and 26. Trend analyses were performed on flow-adjusted concentrations, whenever possible; however, similar results would be anticipated for most non-flow-adjusted concentrations, except suspended sediment, because only weak relationships were found between concentration and discharge.

No trends were found in dissolved nitrite plus nitrate concentrations at any of the sites examined (fig. 56). Smith and others (1987), in contrast, found increases in dissolved nitrite plus nitrate concentrations for many rivers in the midwestern United States for the period 1974–81. However, few data were available for the WMIC study unit before 1979.

In general, Kjeldahl nitrogen concentrations increased at most of the sites, except for the Menominee River (water years 1978–86) and the Milwaukee River (water years 1973–90) (fig. 57). The upward trend in Kjeldahl nitrogen concentration was significant ($\rho < 0.10$) for the Ford River (water years 1974–90), Fox River (water years 1974–90), Manitowoc River (water years 1979–90), and Milwaukee River (water years 1980–90). The increase in Kjeldahl nitro-

Table 25. Summary of statistical results for trend analyses, Western Lake Michigan Drainages study unit, water years 1980–90
[NT, trend test could not be done; ρ, probability; all slopes are given in μg/L per year]

Basin	Nitrite plus nitrate, dissolved		Kjeldahl nitrogen, total		Ammonia, dissolved		Phosphorus, total		Phosphorus, dissolved		Orthophosphate, dissolved		Suspended sediment	
	Slope	ρ	Slope	ρ	Slope	ρ	Slope	ρ	Slope	ρ	Slope	ρ	Slope	ρ
Escanaba River	0	0.92	+1.4	0.90	0[1]	0.67	0[1]	0.58	0[1]	0.93	0[1]	0.16	0[1]	0.90
Ford River	0	1.00	+22.9	.06	0	.92	0	.25	0[1]	.21	NT	NT	-44.8	.64
Popple River	0	.21	+12.3	.20	-1.7	.14	0	.93	0[1]	.23	0[1]	.68	+137.0	.06
Menominee River	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
Fox River	0	.83	+31.8	.26	+1.2	.42	+1.0	.73	-2.0	.09	NT	NT	+816.5	.29
Manitowoc River	0	.08	+32.3	.12	-.6	.93	+5.4	.55	-4.8	.30	-.2	.96	+994.3	.53
Milwaukee River	0	.11	+2.8	.10	0	1.0	-2.1	.37	-6.1	.00	0	.32	+190.2	.47
White Creek	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT

[1]Trend test performed on non-flow adjusted data.

Table 26. Summary of statistical results for trend analyses, Western Lake Michigan Drainages study unit, for the entire period of record, as specified
[NT, trend test could not be done; ρ, probability; all slopes are given in μg/L per year]

Basin	Nitrite plus nitrate, dissolved		Kjeldahl nitrogen, total		Ammonia, dissolved		Phosphorus, total		Phosphorus, dissolved		Orthophosphate, dissolved		Suspended sediment	
	Slope	ρ	Slope	ρ	Slope	ρ	Slope	ρ	Slope	ρ	Slope	ρ	Slope	ρ
Escanaba River (1974–90)	0	0.77[1]	+5.0	0.19	0	0.11[2]	0[3]	0.95	0[3]	.23[4]	0[3]	0.16[5]	+31.8	0.54
Ford River (1974–90)	0	1.00[1]	+16.0	.01	0	.93[1]	0[3]	.59	0[3]	.41[4]	0[3]	.62[6]	+37.0	.40
Popple River (1971–90)	0	.09[1]	+12.3	.20[5]	-1.7	.14[5]	-.4	.09	NT	NT[7]	NT	NT[1]	-62.0	.25
Menominee River (1977–86)	0	.91[8]	-16.4	.32[9]	+.1	.36[8]	+.2	.24	0[3]	.41	0[3]	1.00[10]	-45.4	.87
Fox River (1974–90)	0	.88[1]	+25.6	.02	+.4	.73[1]	-2.1	.13	-2.7	.00[4]	NT	NT[5]	+573.9	.13
Manitowoc River (1979–90)	0	.12[1]	+39.7	.02	-.9	.80[1]	+4.4	.54	-3.6	.28	-.2	.96[5]	NT	NT[11]
Milwaukee River (1973–90)	0	.13[1]	-13.0	.36	0	.79[1]	-3.3	.04	-4.2	.00[4]	0	.32[5]	+459.5	.12[7]
White Creek (1981–86)	NT	NT	NT	NT	NT	NT	-5.1	.34	NT	NT	NT	NT	+972.3	.81

[1]1979–90.
[2]1978–90.
[3]Trend test only performed on non-flow adjusted data.
[4]1977–90.
[5]1980–90.
[6]1981–90.
[7]1971–90.
[8]1979–86.
[9]1978–86.
[10]1981–86.
[11]1972–90.

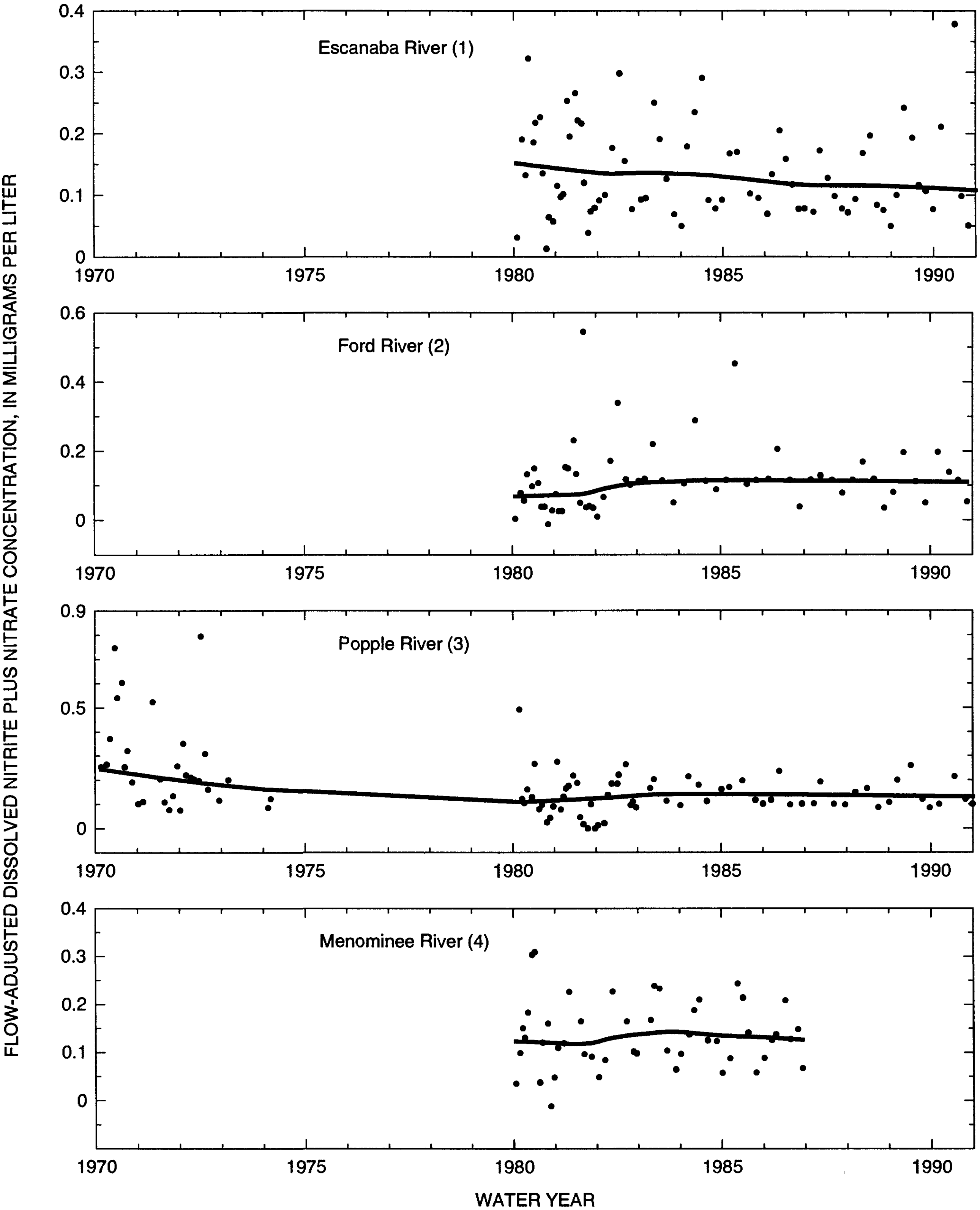


Figure 56. Flow-adjusted dissolved nitrite plus nitrate concentrations at selected sites in the Western Lake Michigan Drainages study unit. [The lowess smooth is plotted through the data. River locations (identification numbers are in parentheses) are shown in figure 24.]

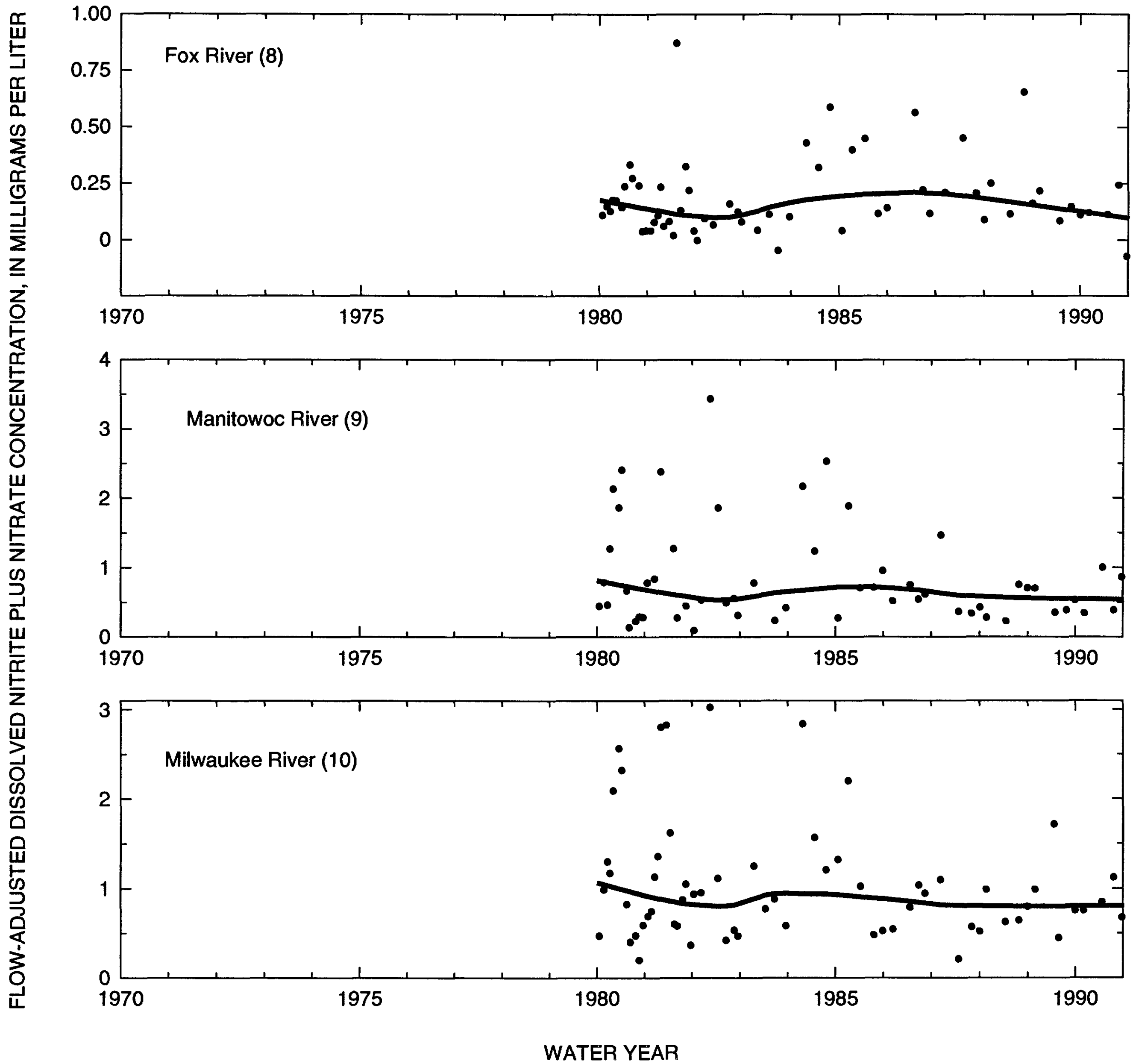


Figure 56. Flow-adjusted dissolved nitrite plus nitrate concentrations at selected sites in the Western Lake Michigan Drainages study unit—Continued.

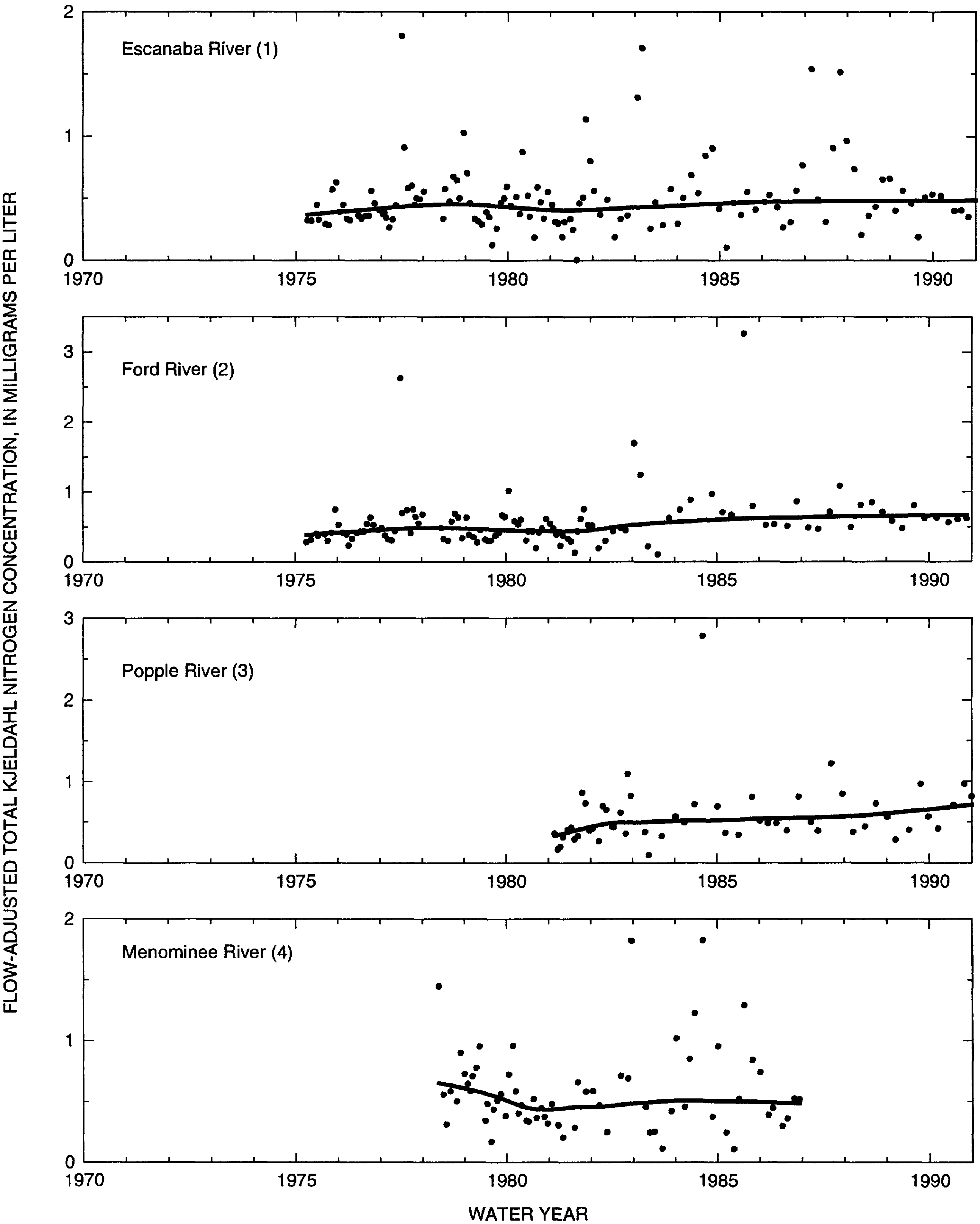


Figure 57. Flow-adjusted Kjeldahl nitrogen concentrations at selected sites in the Western Lake Michigan Drainages study unit. [The lowess smooth is plotted through the data. River locations (identification numbers are in parentheses) are shown in figure 24.]

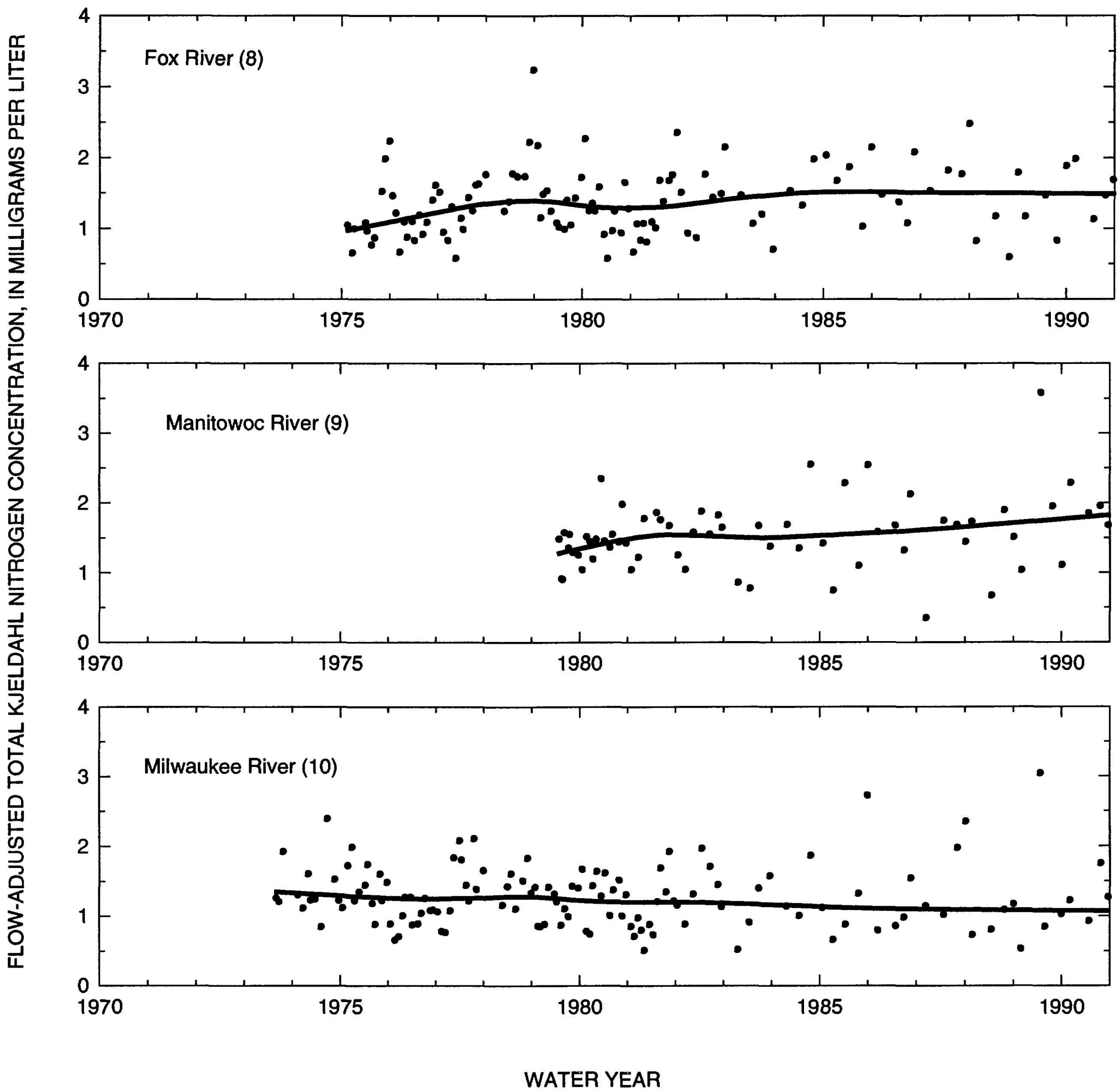


Figure 57. Flow-adjusted Kjeldahl nitrogen concentrations at selected sites in the Western Lake Michigan Drainages study unit—Continued.

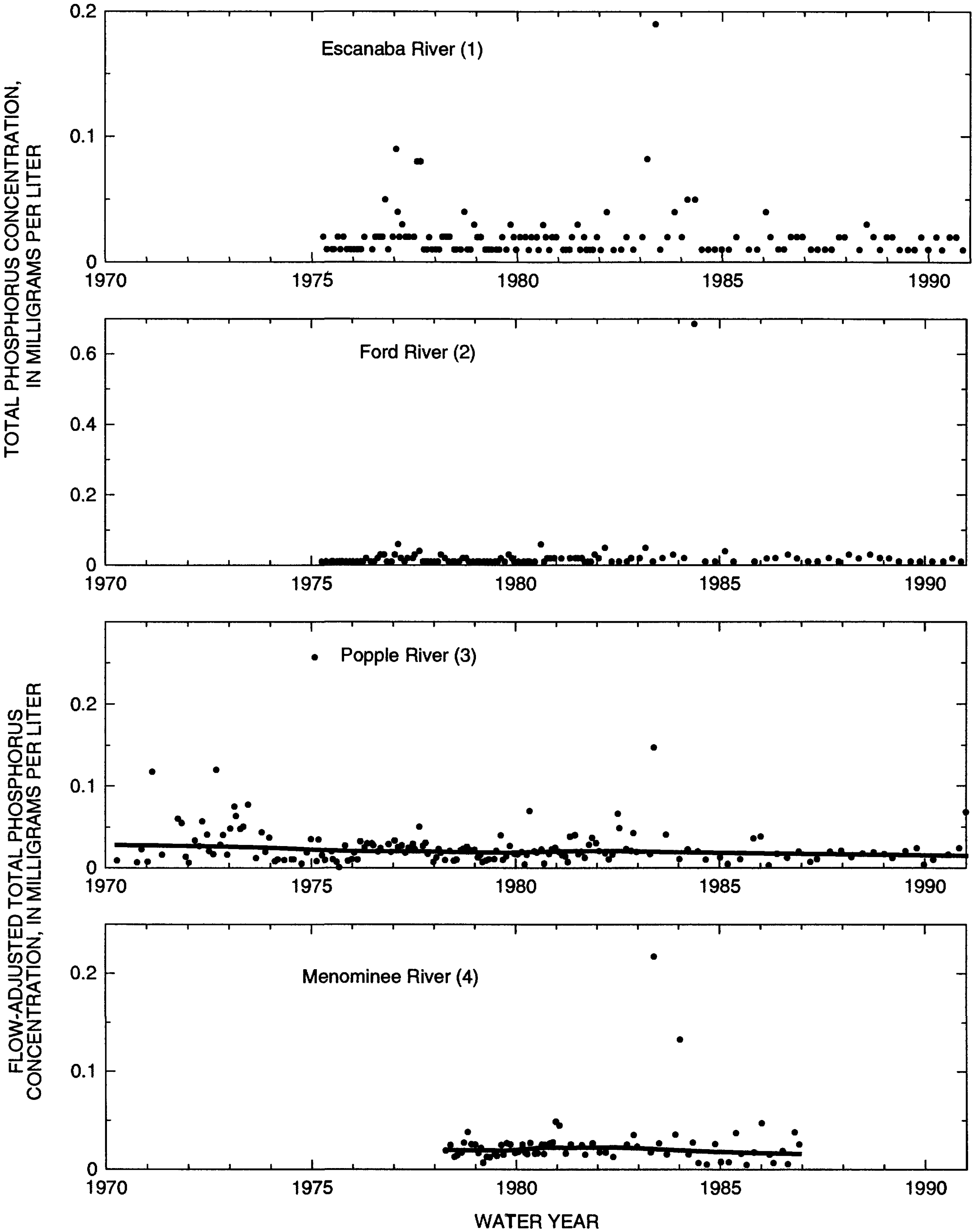


Figure 58. Flow-adjusted total phosphorus concentrations at selected sites in the Western Lake Michigan Drainages study unit. [The lowess smooth is plotted through the data. Total phosphorus concentrations for the Escanaba and Ford Rivers were unable to be flow adjusted and therefore no lowess smooth was plotted. River locations (identification numbers are in parentheses) are shown in figure 24.]

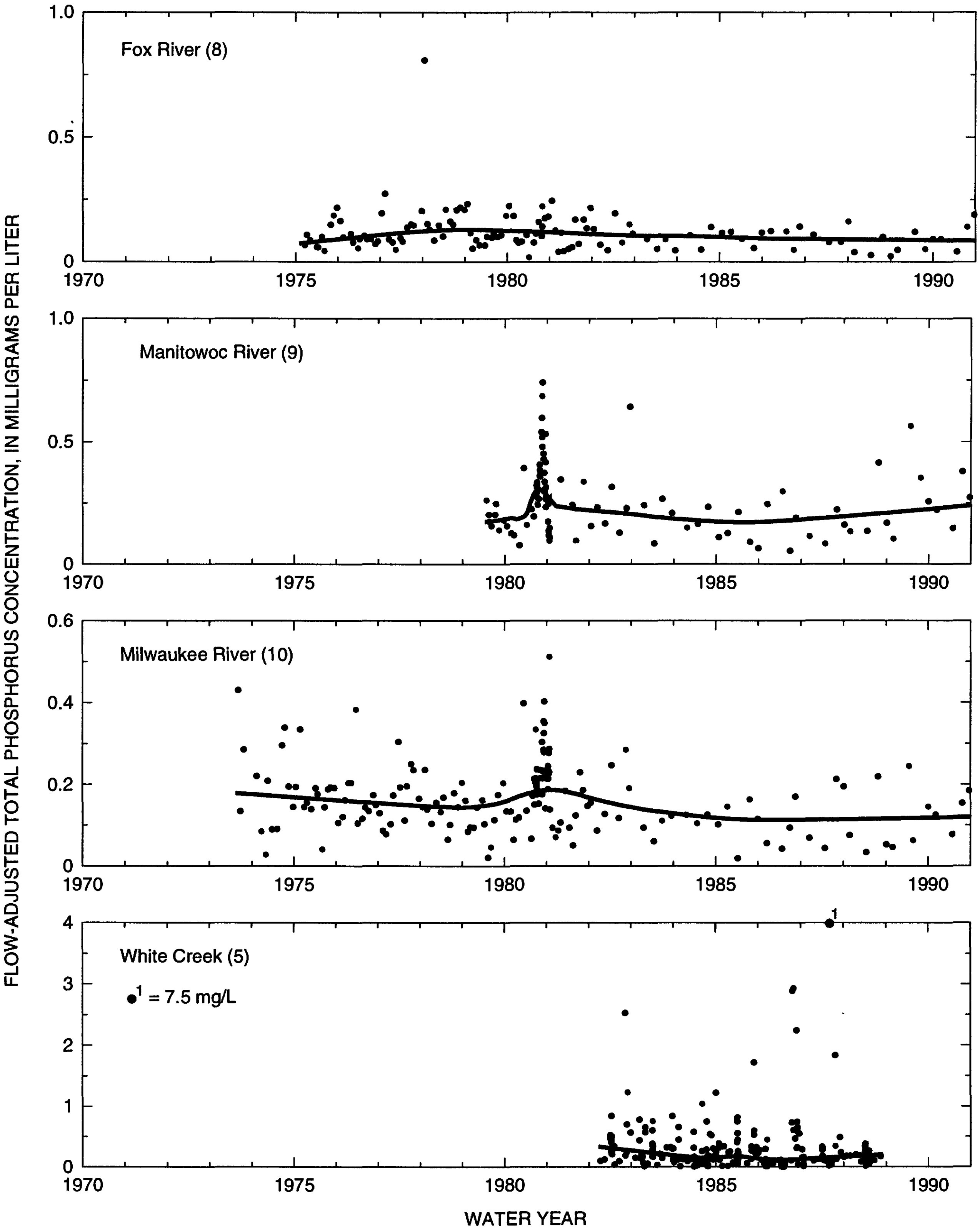


Figure 58. Flow-adjusted total phosphorus concentrations at selected sites in the Western Lake Michigan Drainages study unit—Continued.

gen concentrations in association with no change in dissolved nitrite plus nitrate concentrations indicates an increase in total nitrogen concentrations in rivers draining these areas.

Dissolved ammonia concentrations decreased in the Popple and Manitowoc Rivers and increased in the Fox and Menominee Rivers, although no significant changes were observed.

Changes in total phosphorus concentrations formed no consistent pattern across the study unit (fig. 58). During 1980–90, little change was detected. However, when the 1971–79 data were included, significant downward trends were found in concentrations in the Popple River ($\rho < 0.10$), Milwaukee River ($\rho < 0.05$), and Fox River ($\rho < 0.15$). A period of unusually high total phosphorus concentrations in the Manitowoc and Milwaukee Rivers occurred around 1981, although no unusual climatic or hydrologic conditions were noted during this period (see "Climate" and "Surface-water Hydrology" sections). Significant downward trends were found in dissolved phosphorus concentrations for the Fox River (1980–90, $\rho < 0.10$; 1974–90, $\rho < 0.05$) and the Milwaukee River (1980–90 and 1973–90, $\rho < 0.05$). A similar downward trend was found in dissolved orthophosphate concentrations, but the trends in the time series were not statistically significant.

The downward trends in phosphorus concentrations and, ultimately, phosphorus exports, which were most significant in the southern part of the study unit, may have been caused by the reduction in phosphorus in detergents and improvements in sewage-treatment facilities. Sager (Wisconsin Department of Natural Resources, 1993) estimated that point-source loads of phosphorus in the Fox River Basin decreased from 430,000 kg in 1970 to 110,000 kg in 1990. This downward trend is consistent with that found by Smith and others (1987) for the 1974–81 period for sites in the Great Lakes region. Concentrations of the phosphorus species in the Escanaba and Ford Rivers were already near detection limits throughout the period.

During 1980–90, suspended-sediment concentrations increased or remained unchanged at all of the sites, except the Ford River; however, the only significant ($\rho < 0.10$) increase occurred in the Popple River (table 25). When the 1971–79 data were included, the increases in the southern half of the study unit (agricultural and urban areas) became more significant (table 26). Concentrations at one of the forested sites, Popple River, significantly increased during the 1980–90 ($\rho < 0.10$), but the trend over the entire 1971–90 period was downward, indicating a possible long-term cycle in concentrations. No periods of unusually high or low concentrations were found for suspended sediment; however, a few very high concentrations were noted in each time series and were not necessarily measured during high flows. The increases in suspended-sediment concentrations were not detected by Smith and others (1987) in this region.

SUMMARY AND CONCLUSIONS

One of the goals of this report was to describe the amount and extent of available nutrient and suspended-sediment data for the WMIC study unit. Surface- and ground-water samples analyzed for these constituents were collected throughout the study unit; but, in general, sampling sites were most dense near the major metropolitan areas of Milwaukee and Green Bay, near the Fox and Wolf Rivers, and near the mouths of the large rivers entering Green Bay and Lake Michigan. Relatively few surface-water samples were collected from headwater, indicator areas, especially in southwestern and northwestern parts of the study unit and especially for dissolved nitrite, dissolved and total orthophosphate, and suspended sediment. Ground-water samples analyzed for dissolved nitrite plus nitrate, the most extensively determined constituent, were collected throughout the southern two-thirds of the study unit; however, samples analyzed for other constituents were much more limited in coverage, especially samples for total ammonia, total and dissolved phosphorus, and total orthophosphate, which were collected primarily in the northern one-third of the study unit.

At most surface-water monitoring sites, samples for nutrients and suspended sediment were collected relatively uniformly throughout the year and throughout the range of streamflows. However, at sites sampled to estimate loads, samples were collected at highest frequency during high flows, especially during spring runoff and summer storms. At sites that were part of large synoptic studies, sampling was concentrated during summer. Ground-water sites were generally sampled only once during the entire period.

Nutrient concentrations in surface water were very weakly related to streamflow, if at all; however, a weak positive relation was found for suspended-sediment concentrations. The weakness of these relations may have been the result of upstream dams. Therefore, compensating (adjusting) nitrogen and phosphorus concentrations for variable flow when conducting trend analyses should have little effect on the data, and examination of raw and adjusted concentrations should yield similar results. Suspended-sediment concentrations had a consistent relation to daily streamflow and therefore should be adjusted for flow before trend analyses are done.

Land use was the primary factor affecting nutrient concentrations in the surface water of the WMIC study unit. Total concentrations of nitrogen and phosphorus were directly related to the input of nutrients associated with the specific land use in the drainage basins, and concentrations decreased in the following order: agriculture>agriculture/forest>urban>forest. The differences in phosphorus concentrations in rivers in forested and agricultural areas were similar to those found for lakes in Wisconsin and Michigan by Omernick and others (1988).

Dissolved nitrate and organic nitrogen were the two primary forms of nitrogen in the surface water of all general land-use categories, except urban, where ammonia was also an important fraction. Concentrations of both nitrate (represented by nitrite plus nitrate) and organic nitrogen (represented by Kjeldahl nitrogen) decreased in the following order: agriculture>urban>forest. Concentrations of total and dissolved ammonia and dissolved nitrite were highest in urban areas, moderate in agricultural areas, and lowest in forested areas.

Nitrogen concentrations in ground water also were related to land use; however, well depth and the texture of surficial deposits also were important factors. The land use determines how much nitrogen is applied in an area. The texture of surficial deposits determines how much of the nitrogen makes it to the water table. Generally, nitrogen concentrations in ground water were higher in areas of agriculture and agriculture/forest with sandy or sand and gravel surficial deposits where nitrogen was mainly in the form of dissolved nitrate. Dissolved nitrate concentrations were inversely related to well depth. Dissolved ammonia was also an important fraction in urban and agricultural areas, and organic forms and particulate ammonia were important fractions in forested areas.

Concentrations of nitrogen species were compared among RHU's to determine whether differences in land use, texture of surficial deposit, and bedrock type effect surface-water quality. No statistically significant differences were detected between RHU's of similar land use for nitrite plus nitrate, Kjeldahl nitrogen, and total ammonia in surface water. However, available data indicated a significant difference between dissolved nitrite and dissolved ammonia concentrations in rivers surrounded by agriculture on sandy deposits and those surrounded by agriculture on clayey deposits. One possible explanation for this difference is that clayey deposits preferentially adsorb ammonia, which is positively charged at most ambient pH's. Therefore, ammonia participates in cation exchange and may be less readily transferred to streams than other nitrogen species.

In ground-water samples, only dissolved nitrate plus nitrate and dissolved ammonia concentrations were significantly different among RHU's. These differences appeared to be caused by differences in land use and the texture of the surficial deposits. Nitrogen applications on permeable surficial deposits resulted in high nitrate plus nitrate concentrations in ground water, whereas applications on areas with clayey surficial deposits resulted in high dissolved ammonia concentrations.

With regard to surface-water/ground-water interactions, only dissolved nitrate plus nitrate concentrations could be examined because data were insufficient for other constituents. Agricultural areas with clayey surficial deposits (low permeability) had high concentrations in surface water and low concentrations in ground water. This pattern was expected in areas where the surface-runoff rates were high and the ground-water recharge rates were low. Areas underlain by sand/sand and gravel deposits (high permeability) had high concentrations in surface water and in ground water. This pattern was expected where the ground-water recharge rate was high and a significant part of annual streamflow was derived from ground-water discharge.

Distinct seasonality was observed in nitrate plus nitrate and dissolved ammonia concentrations in surface water. Higher dissolved ammonia and lower dissolved nitrate plus nitrate concentrations occurred during winter and early spring than during summer. This seasonality can be explained by the uptake of ammonia and nitrates by aquatic organisms and the subsequent assimilation of these nitrogen species into combined organic forms during summer.

During 1971–90, no significant ($\rho < 0.10$) trends were found in dissolved nitrate plus nitrate concentrations. In general, Kjeldahl nitrogen concentrations increased at almost all of the sites examined; however, this upward trend was significant ($\rho < 0.15$) only for the

Ford, Fox, and Manitowoc Rivers. The increase in Kjeldahl nitrogen concentrations in association with no change in dissolved nitrite plus nitrate concentrations indicates an increase in total nitrogen concentrations in rivers draining these areas.

Nitrate plus nitrate concentrations in the surface water of agricultural and urban areas were similar to the "national average" surface-water concentrations (NAC) for these land uses, but were lower than the NAC for forested areas. Dissolved nitrate plus nitrate concentrations exceeding the USEPA 10-mg/L MCL for dissolved nitrite plus nitrate were found only in agricultural areas. Only two samples from mixed (downstream, integrator) land-use areas exceeded the 1-mg/L MCL for dissolved nitrite.

Dissolved inorganic phosphorus (dissolved reactive phosphorus) and particulate phosphorus were the primary forms of phosphorus in the surface water for all land use categories, except agriculture, where dissolved organic phosphorus also was an important fraction. Concentrations of total orthophosphate, and dissolved orthophosphate decreased in the following order: agriculture>urban>forest. Concentrations in forested regions were usually near the detection limits for all phosphorus constituents. The scarcity of phosphorus data precluded the partitioning of phosphorus for each general land-use category for ground water.

Total phosphorus concentrations in surface water appear to be higher in areas of sandy surficial deposits than in areas of clayey deposits. This difference may be caused by preferential adsorption of phosphates onto the positively charged edges of clay particles, resulting in a higher retention of total phosphorus. Total phosphorus concentrations were also significantly higher in areas of carbonate bedrock than in areas of sandstone bedrock. This relation may have been the result of higher phosphorus concentrations in carbonates than in sandstones, resulting in larger phosphorus release to the surface water.

Dissolved phosphorus concentrations in surface water were highest in agricultural areas, moderate in urban areas and lowest in forested areas; however insufficient data precluded examining the effects of surficial deposits and bedrock. Dissolved phosphorus was the only phosphorus constituent in ground water for which sufficient data were available to be examined in detail. In general, ground water in forested and agricultural/forested areas had higher dissolved phosphorus concentrations than did ground water in urban and agricultural areas, and ground water in areas of sand/sand and gravel surficial deposits had higher concentrations than that in areas of clay.

No statistical differences in concentrations of phosphorus species in surface water were detected among RHU's of similar land use for dissolved phosphorus, dissolved inorganic phosphorus, and total orthophosphate. Dissolved orthophosphate concentrations (similar to total phosphorus) were significantly higher in areas of sandy deposits than in areas of clayey deposits and were significantly higher in areas of carbonate bedrock than in areas of sandstone bedrock.

Significant seasonality was found in total phosphorus concentrations in agricultural areas, but only slight seasonality was found in forested areas, where higher concentrations occurred during summer than during winter.

Analysis of data from 1980 to 1990 revealed few changes in total phosphorus concentrations across the study unit; however, when the 1971–79 data were included, significant ($\rho < 0.10$) downward trends in concentrations were found for the Popple and Milwaukee Rivers. Significant ($\rho < 0.01$) downward trends were also found in dissolved phosphorus concentrations for the Fox and Milwaukee Rivers. Similar downward trends were found in dissolved orthophosphate concentrations, but these were not statistically significant. The downward trend in phosphorus concentrations, which were most significant in the southern part of the study unit, may have been caused by the reduction in phosphorus in detergents and by improvements in sewage-treatment facilities.

Concentrations exceeding the 0.1-mg/L suggested limit for total phosphorus were commonly found in all land-use categories except forested areas, where total phosphorus concentrations only sporadically exceeded this limit. Median concentrations for all land-use categories were less than the NAC for the respective land uses.

Suspended-sediment concentrations in surface water decreased in the following order: urban>agriculture>forest. Concentrations in agricultural/forested areas were not significantly different from those in agricultural or forested areas. Contrary to what was anticipated, suspended-sediment concentrations were significantly higher in urban areas than in agricultural areas and may have been caused by construction activities and washoff of particulate material from streets during storms. Suspended-sediment concentrations were much less than the NAC in agricultural areas and in forested areas. These differences may have been a result of dams on most of the rivers upstream from the monitored locations. However, suspended-sediment concentrations in urban areas were much higher than the NAC. Suspended-sediment concentrations were significantly higher in areas of clayey deposits than in areas of sandy deposits. This difference may result from the greater erodibility of the clayey deposits compared with sandy deposits and (or) the tendency for clay particles to remain in suspension longer than larger sand particles.

During 1980–90, suspended-sediment concentrations increased or remained unchanged at all of the sites, except the Ford River; however, the only significant ($\rho < 0.10$) increase occurred in the Popple River. When the 1971–79 data were included, the increases in the southern half of the study unit (agricultural and urban areas) became more significant, but the increase in the Popple River was no longer apparent.

The total export of phosphorus, nitrogen, and suspended sediment was directly related to land use: the agricultural areas in the southern half of the study unit contributed approximately 80 percent of the total load of phosphorus, 70 percent of the total load of nitrogen, and 75 to 90 percent of the suspended sediment. Although point sources of nutrients have been significantly controlled, point sources of phosphorus may still contribute a significant proportion of the total export, especially during dry years in the Fox and Milwaukee River Basins.

IMPLICATIONS FOR FUTURE DATA COLLECTION AND ANALYSES

Two of the primary purposes of this report were to provide information to assist in designing the sampling components of the intensive phase of the WMIC study unit and to provide preliminary conclusions that can be validated or invalidated and hypotheses that can be tested by use of data collected during the intensive phase.

The primary surface-water sampling component of NAWQA is the routine sampling of basic fixed sites (BFS). There are two types of BFS: indicator sites, whose drainage basins are completely contained within one RHU, and integrator sites, whose drainage basins are composed of more than one RHU. These sites will be sampled for nutrients, suspended sediment, and major ions for at least 2 years. Because only small amounts of historical data were available for indicator areas, eight indicator sites and only three integrator sites were chosen as BFS. Four BFS were chosen to represent agricultural RHU's: Ag1, Ag2, Ag3 and Ag23 (fig. 18, and reference figure at the end of this report). Sites in Ag1 (Duck Creek) and Ag3 (North Branch of the Milwaukee River) will be used to validate or invalidate the differences in constituent concentrations between areas of clayey and sandy deposits. In addition, Ag2 (Pensaukee River) was chosen to determine if loamy deposits have a demonstrable affect on water quality compared to agricultural land use on other deposit types. Ag23 (East River) is similar to Duck Creek in that both have clayey deposits, but Ag23 is underlain by shale bedrock, whereas Ag1 is underlain by carbonate bedrock. Water quality in Ag1 and Ag23 will be compared to determine whether these differences in bedrock affect surface-water quality. One agricultural/forested site (AF20, Tomorrow River) was chosen to determine if the water quality in areas with this mixed land use was significantly different from agricultural and forested areas. This site is important because only a small amount of historical data were available to describe this type of area. Two forested sites were chosen to represent relatively pristine conditions and to examine the effects of forest type: F16 (Peshekee River, in a dry forested area) and F22 (Popple River, in a wet forested area). In addition, sampling the Peshekee River (F16) will provide information in the far northern part of the study unit, where almost no historical data were available. Sampling the Popple River (F22), in contrast, will extend the long-term data set in a relatively pristine area. One site, U9 (Lincoln Creek), was chosen to represent urban conditions.

Three integrator sites were chosen to represent the diverse conditions throughout the study unit, as well as the major contributors of nutrient and suspended sediment to Green Bay and Lake Michigan. The Milwaukee River at Milwaukee represents a combination of agricultural and urban influences. The Fox River at the mouth in Green Bay represents a combination of forest, agricultural, and urban influences. The Menominee River near McAllister in contrast, represents forested conditions.

The three ground-water sampling components in the WMIC NAWQA study are land-use surveys, flowpath studies, and study-unit surveys. Two land-use surveys will be done in Ag3 and AF20/AF26 combined to examine how agricultural land use affects the quality of shallow ground water. Ag3 was chosen because of its relatively permeable surficial deposits. AF20 and AF26 were chosen to determine whether the high dissolved nitrate plus nitrate concentrations in the historical data were truly indicative of these areas. A flow-path study will be done in the North Branch of the Milwaukee River Basin (Ag3, sandy surficial deposits). The purpose of this study is to examine changes in nutrients and pesticides along a ground-water flow path in an agriculture setting. The purpose of the study-unit survey is to describe the quality of ground water in the major aquifers of the WMIC study unit. The first phase of this study will be to examine the water quality in the sandstone aquifer.

The data collected from these sites will allow the NAWQA program to improve the description of water quality in the WMIC study unit; to validate or invalidate the preliminary conclusions based on retrospective data; to refine the understanding of the relations among geology, land use, and water quality; and to detect long-term changes in water quality.

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APPENDIXES 1–3

Appendix 1. Location of surface- and ground-water sites in the Western Lake Michigan Drainages study unit sampled during water years 1971–90 for:

Symbols in this series of maps represent the following types of sites:

Study unit boundary

△ U.S. Geological Survey site

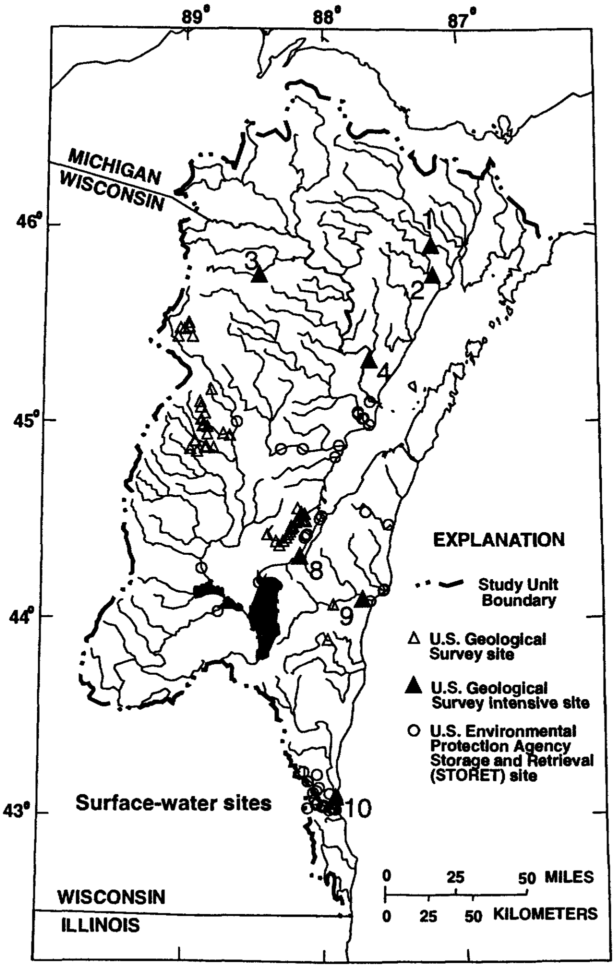
▲ U.S. Geological Survey intensive site
(River names of the numbered U.S. Geological Survey Intensive sites are given on page 49 of the text.)

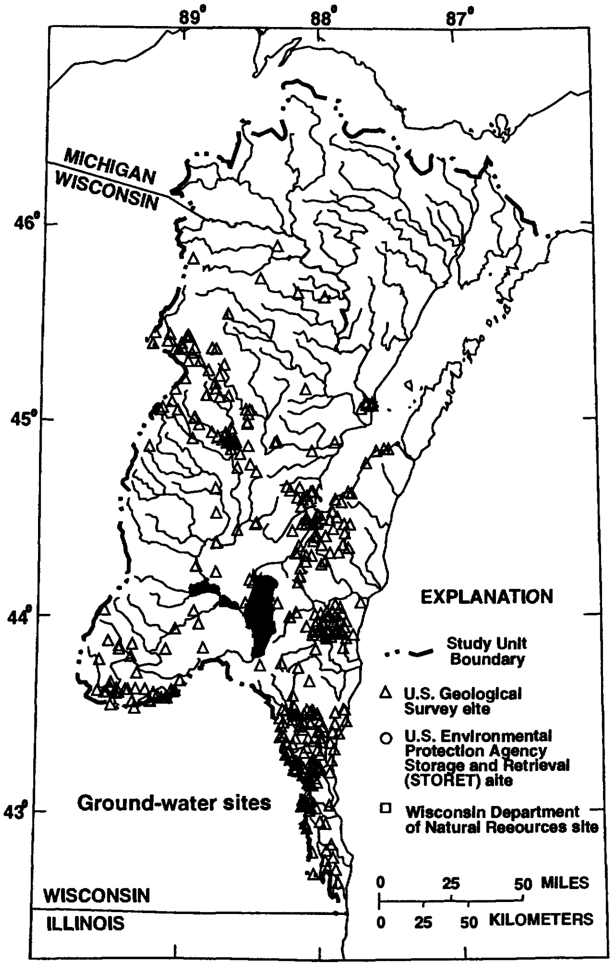
○ U.S. Environmental Protection Agency Storage and Retrieval (STORET) site

□ Wisconsin Department of Natural Resources site

Appendix 1.1. Location of surface- and ground-water sites in the Western Lake Michigan Drainages study unit sampled during water years 1971–90 for: dissolved nitrite

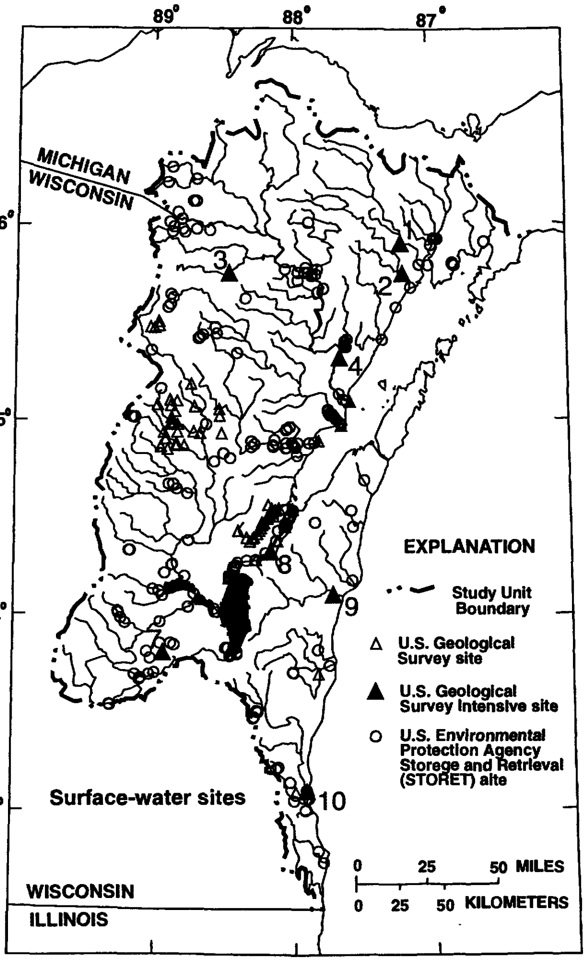
[Explanation of map symbols is given on the first page of this appendix.]

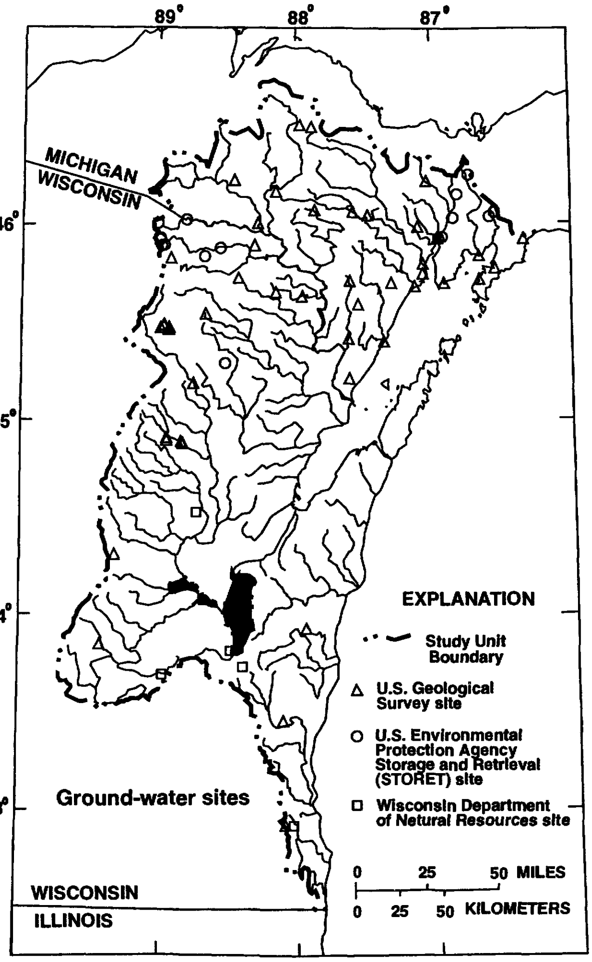




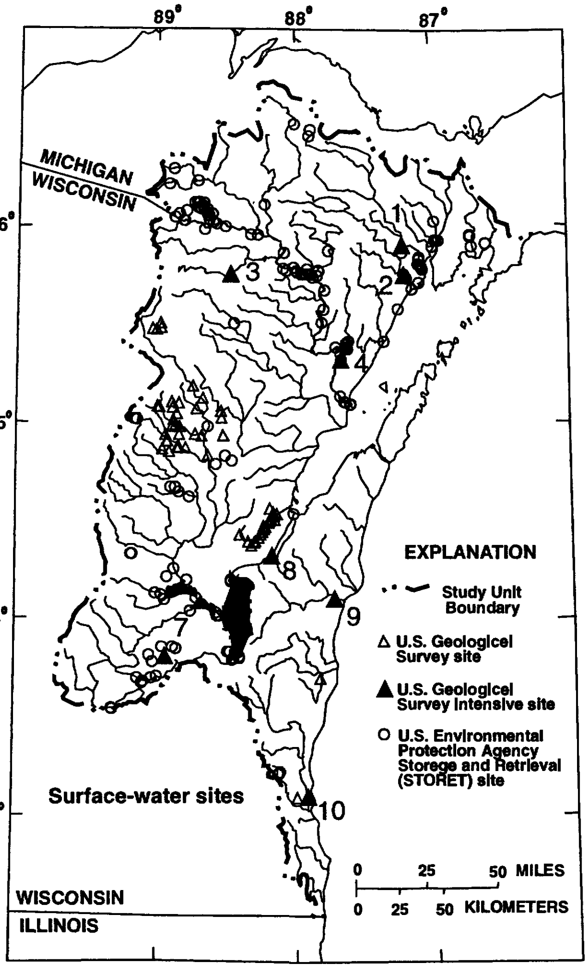
Appendix 1.2. Location of surface- and ground-water sites in the Western Lake Michigan Drainages study unit sampled during water years 1971–90 for: Total Kjeldahl nitrogen (ammonia plus organics)

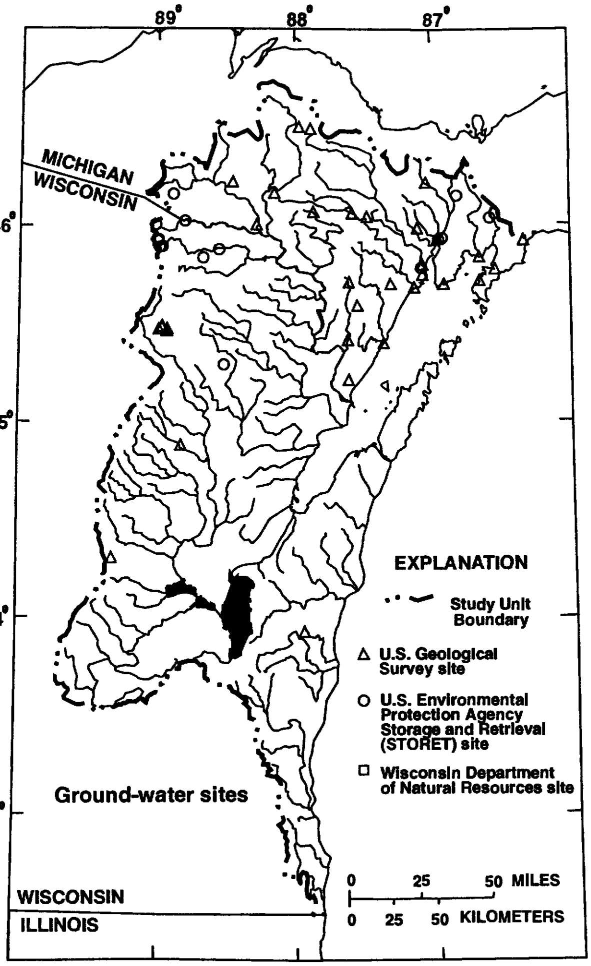
[Explanation of map symbols is given on the first page of this appendix.]



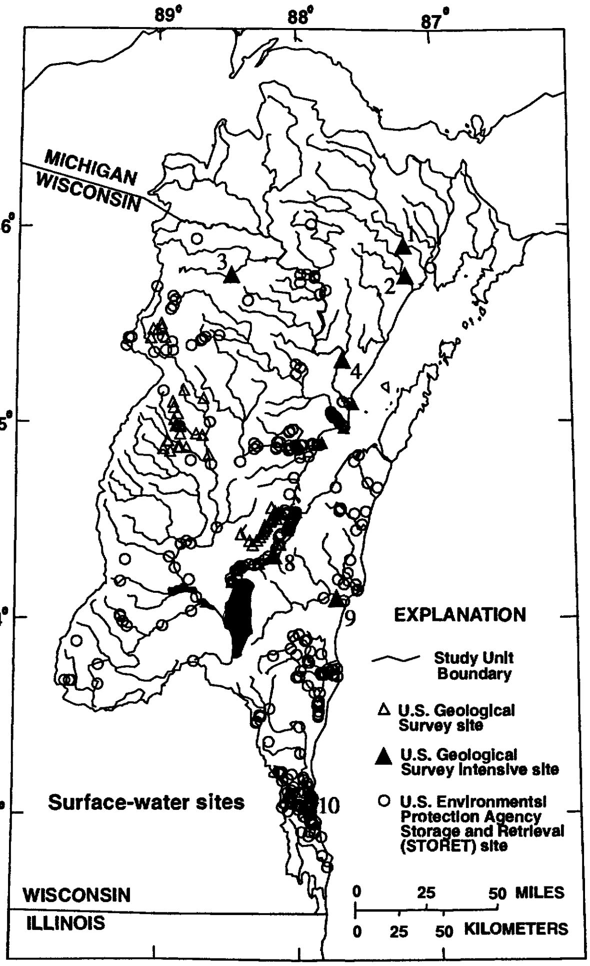


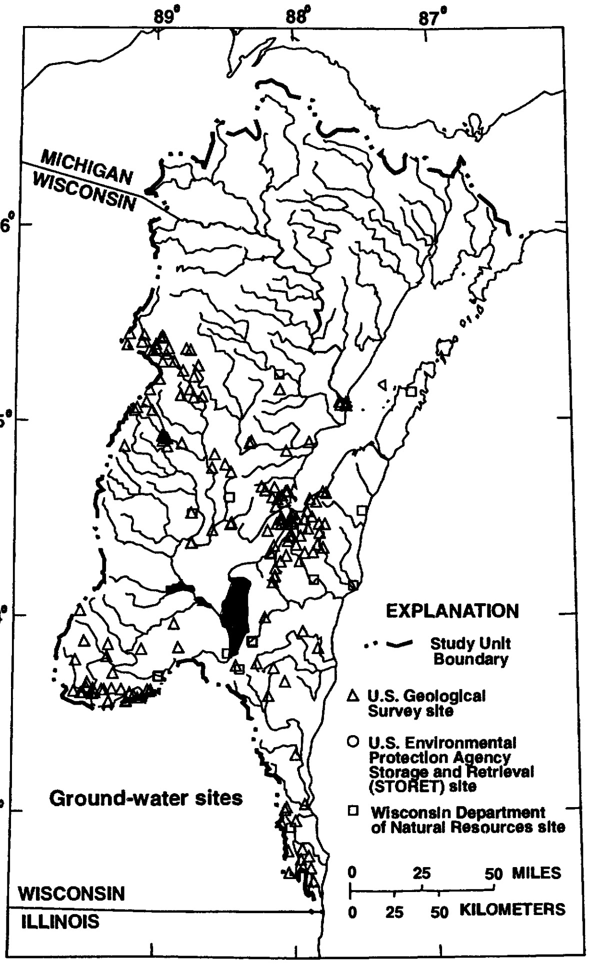
Appendix 1.3. Location of surface- and ground-water sites in the Western Lake Michigan Drainages study unit sampled during water years 1971–90 for: total ammonia
[Explanation of map symbols is given on the first page of this appendix.]





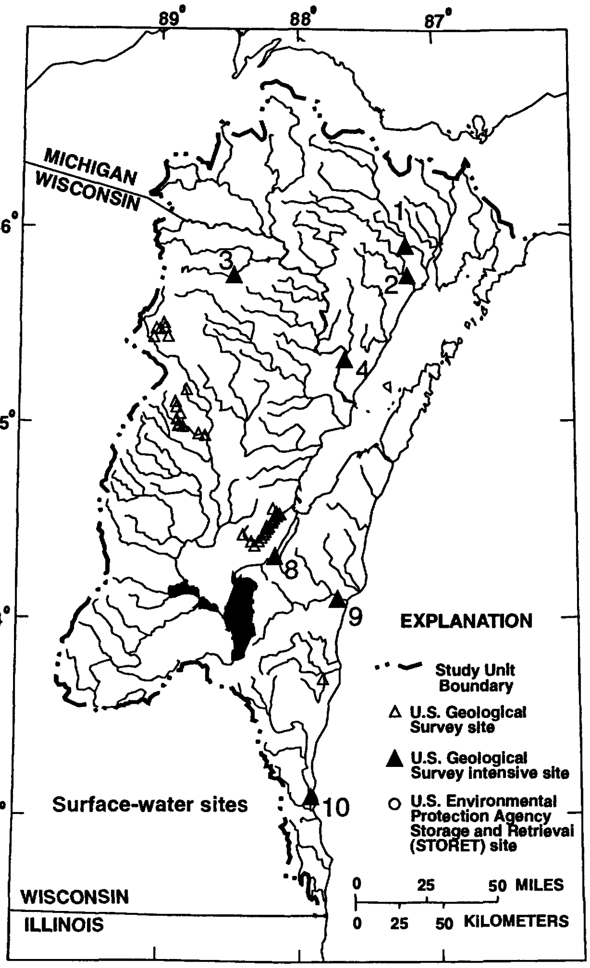
Appendix 1.4. Location of surface- and ground-water sites in the Western Lake Michigan Drainages study unit sampled during water years 1971–90 for: dissolved ammonia
[Explanation of map symbols is given on the first page of this appendix.]

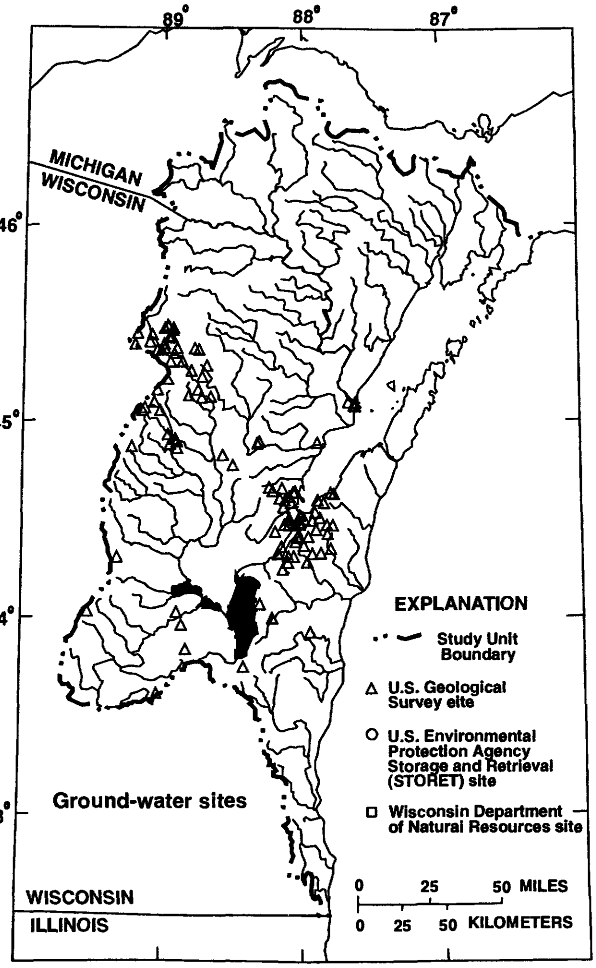




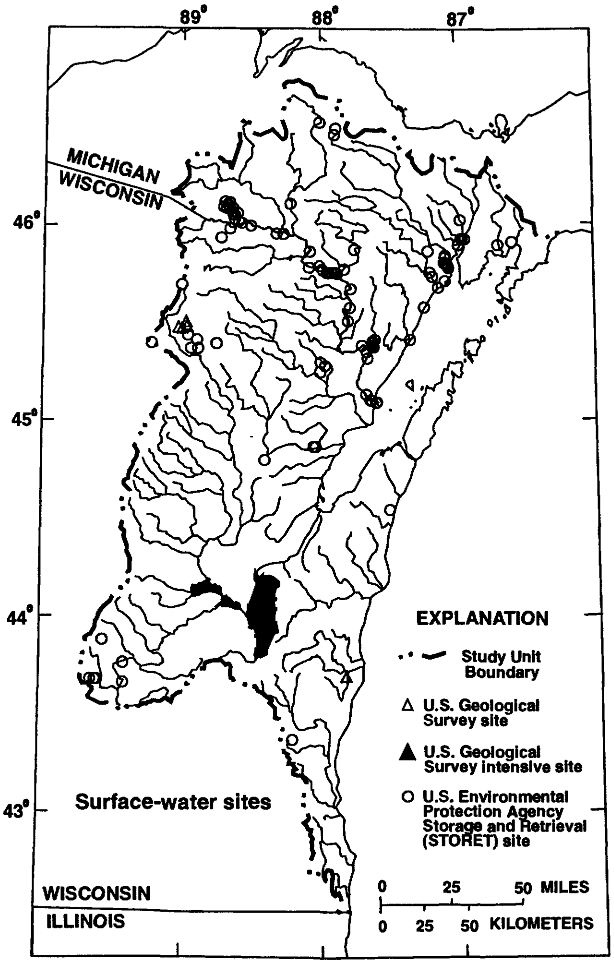
Appendix 1.5. Location of surface- and ground-water sites in the Western Lake Michigan Drainages study unit sampled during water years 1971–90 for: dissolved phosphorus

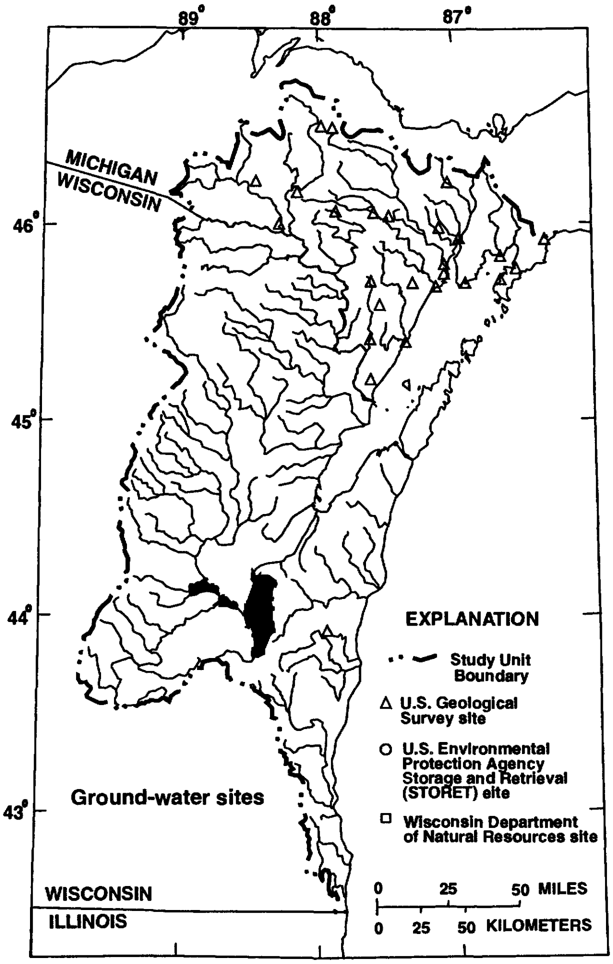
[Explanation of map symbols is given on the first page of this appendix.]



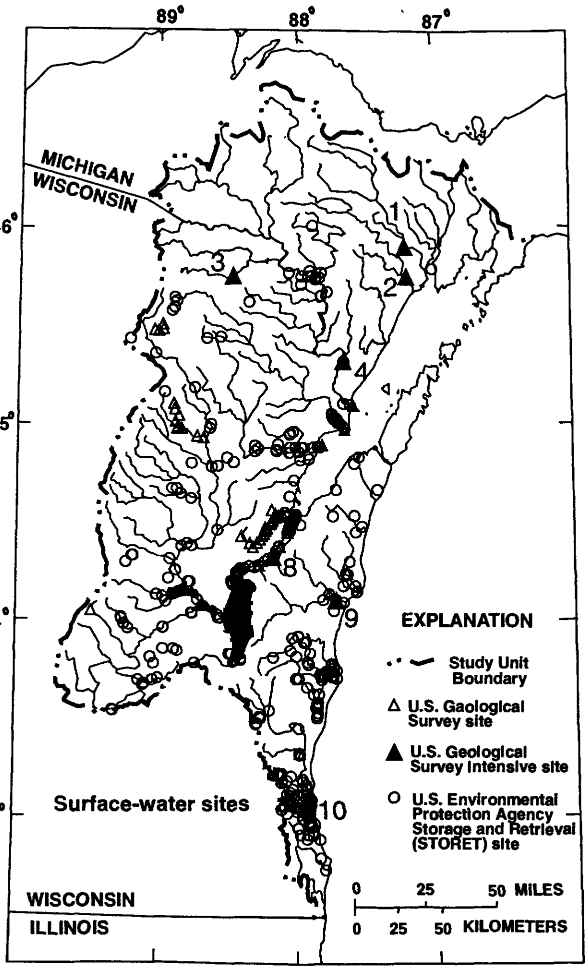


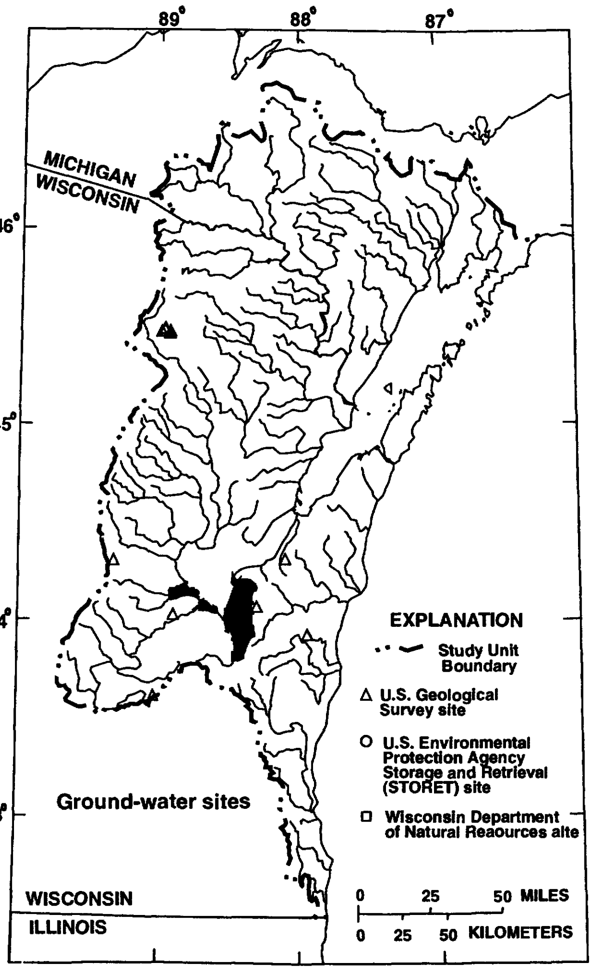
Appendix 1.6. Location of surface- and ground-water sites in the Western Lake Michigan Drainages study unit sampled during water years 1971–90 for: total orthophosphate
[Explanation of map symbols is given on the first page of this appendix.]





Appendix 1.7. Location of surface- and ground-water sites in the Western Lake Michigan Drainages study unit sampled during water years 1971–90 for: dissolved orthophosphate
[Explanation of map symbols is given on the first page of this appendix.]





Appendix 2.1. Monthly distribution of samples collected throughout the Western Lake Michigan Drainages study unit and at 10 surface-water sites, water years 1971–90, for determination of dissolved nitrite plus nitrate

[site locations shown in figure 24]

Site (site number)	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
All sites	542	720	1,331	1,066	961	1,593	1,458	1,725	991	793	731	547
Escanaba River (1)	7	2	9	7	7	8	5	7	7	6	7	5
Ford River (2)	10	3	3	8	6	3	10	2	4	7	5	2
Fox River (8)	3	2	10	2	5	8	4	8	5	4	6	5
Green Lake Inlet (7)	0	0	0	0	0	0	0	0	0	0	0	0
Manitowoc River (9)	3	1	10	2	5	7	4	7	5	3	6	4
Menominee River (4)	6	3	3	4	5	3	5	3	5	1	6	3
Milwaukee River (10)	3	2	11	3	5	8	4	8	6	4	6	5
Popple River (3)	7	6	8	5	7	9	5	9	7	5	13	5
Silver Creek (6)	0	0	0	0	0	0	0	0	0	0	0	0
White Creek (5)	0	0	0	0	0	0	0	0	0	0	0	0

Appendix 2.2. Monthly distribution of samples collected throughout the Western Lake Michigan Drainages study unit and at 10 surface-water sites, water years 1971–90, for determination of dissolved nitrite

[site locations shown in figure 24]

Site (site number)	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
All sites	44	36	105	64	111	115	136	169	84	67	63	37
Escanaba River (1)	2	1	4	3	2	4	1	4	1	3	2	3
Ford River (2)	4	1	0	3	2	0	5	0	0	4	1	0
Fox River (8)	0	0	5	0	1	4	1	3	1	2	3	0
Green Lake Inlet (7)	0	0	0	0	0	0	0	0	0	0	0	0
Manitowoc River (9)	0	0	5	0	1	4	1	3	1	2	3	0
Menominee River (4)	0	0	1	1	0	1	0	1	0	0	1	1
Milwaukee River (10)	0	0	5	1	1	4	1	2	2	2	3	0
Popple River (3)	2	1	2	1	1	3	0	4	1	0	5	0
Silver Creek (6)	0	0	0	0	0	0	0	0	0	0	0	0
White Creek (5)	0	0	0	0	0	0	0	0	0	0	0	0

Appendix 2.3. Monthly distribution of samples collected throughout the Western Lake Michigan Drainages study unit and at 10 surface-water sites, water years 1971–90, for determination of total Kjeldahl nitrogen (ammonia plus organics)
[site locations shown in figure 24]

Site (site number)	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
All sites	330	292	458	498	621	681	814	852	643	530	513	319
Escanaba River (1)	10	7	16	11	11	12	11	12	12	9	9	9
Ford River (2)	14	8	8	11	10	7	16	7	8	10	8	6
Fox River (8)	7	7	16	7	9	13	9	13	8	8	10	9
Green Lake Inlet (7)	0	0	0	0	0	0	0	0	0	0	0	0
Manitowoc River (9)	3	1	11	4	6	9	5	8	5	3	6	4
Menominee River (4)	8	5	5	6	6	5	7	5	7	2	7	4
Milwaukee River (10)	9	8	16	10	11	13	10	13	10	9	11	10
Popple River (3)	5	4	5	2	5	6	2	6	5	1	9	3
Silver Creek (6)	0	0	0	0	0	0	0	0	0	0	0	0
White Creek (5)	0	0	0	0	0	0	0	0	0	3	3	0

Appendix 2.4. Monthly distribution of samples collected throughout the Western Lake Michigan Drainages study unit and at 10 surface-water sites, water years 1971–90, for determination of total ammonia
[site locations shown in figure 24]

Site (site number)	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
All sites	221	281	474	444	496	510	465	764	424	379	374	259
Escanaba River (1)	6	4	9	7	6	7	6	7	5	4	6	6
Ford River (2)	8	5	4	7	6	3	10	2	4	7	5	3
Fox River (8)	4	4	9	4	5	8	5	7	6	6	7	3
Green Lake Inlet (7)	0	0	0	0	0	0	0	0	0	0	0	0
Manitowoc River (9)	2	1	7	4	4	7	4	5	4	3	5	1
Menominee River (4)	4	3	4	5	4	4	4	4	4	2	4	4
Milwaukee River (10)	4	4	9	5	5	7	5	6	7	6	7	4
Popple River (3)	4	3	4	2	3	5	2	6	2	1	7	2
Silver Creek (6)	0	0	0	0	0	0	0	0	0	0	0	0
White Creek (5)	12	90	170	56	29	55	69	75	49	19	45	36

Appendix 2.5. Monthly distribution of samples collected throughout the Western Lake Michigan Drainages study unit and at 10 surface-water sites, water years 1971–90, for determination of dissolved ammonia
[site locations shown in figure 24]

Site (site number)	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
All sites	573	732	1,329	1,059	936	1,574	1,462	1,719	986	802	736	581
Escanaba River (1)	6	3	9	6	6	8	5	6	6	5	6	6
Ford River (2)	10	3	3	7	5	3	9	2	3	7	5	2
Fox River (8)	3	2	10	2	5	8	4	8	4	4	6	5
Green Lake Inlet (7)	0	0	0	0	0	0	0	0	0	0	0	0
Manitowoc River (9)	3	1	10	2	5	7	4	7	4	3	6	4
Menominee River (4)	6	3	3	4	5	3	5	3	5	1	6	3
Milwaukee River (10)	3	2	11	3	5	7	4	7	5	4	6	5
Popple River (3)	5	4	5	2	5	5	2	6	5	1	9	3
Silver Creek (6)	0	0	0	0	0	0	0	0	0	0	0	0
White Creek (5)	0	0	0	0	0	0	0	0	0	0	0	0

Appendix 2.6. Monthly distribution of samples collected throughout the Western Lake Michigan Drainages study unit and at 10 surface-water sites, water years 1971–90, for determination of total phosphorus
[site locations shown in figure 24]

Site (site number)	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
All sites	842	1,144	2,191	1,851	1,842	2,557	2,434	3,042	1,945	1,402	1,285	878
Escanaba River (1)	11	7	15	11	11	12	11	12	12	9	10	9
Ford River (2)	15	8	8	11	10	7	16	7	8	11	9	6
Fox River (8)	7	7	16	7	11	15	9	13	9	9	12	10
Green Lake Inlet (7)	6	5	35	16	15	34	20	23	16	8	7	1
Manitowoc River (9)	3	1	11	4	9	21	13	20	12	3	6	4
Menominee River (4)	8	5	5	6	9	5	7	5	7	2	7	5
Milwaukee River (10)	9	8	16	10	18	21	15	22	22	9	12	11
Popple River (3)	15	14	14	11	12	14	12	16	13	11	18	11
Silver Creek (6)	4	15	125	57	66	54	56	60	69	20	22	3
White Creek (5)	12	88	166	54	29	52	71	73	49	20	47	37

Appendix 2.7. Monthly distribution of samples collected throughout the Western Lake Michigan Drainages study unit and at 10 surface-water sites, water years 1971–90, for determination of dissolved phosphorus
[site locations shown in figure 24]

Site (site number)	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
All sites	81	61	171	173	258	232	233	254	205	186	203	111
Escanaba River (1)	8	4	13	9	8	9	7	9	8	7	8	6
Ford River (2)	12	5	5	10	7	4	13	4	5	7	7	3
Fox River (8)	5	4	5	2	5	6	2	6	5	2	9	3
Green Lake Inlet (7)	8	5	5	6	7	5	7	5	7	2	7	5
Manitowoc River (9)	3	1	11	4	9	21	13	20	12	3	6	4
Menominee River (4)	4	4	13	5	7	9	6	9	8	6	8	7
Milwaukee River (10)	5	4	12	4	7	10	6	10	7	6	8	7
Popple River (3)	0	0	0	0	0	0	0	0	0	0	0	0
Silver Creek (6)	0	0	0	0	0	0	0	0	0	0	0	0
White Creek (5)	0	0	0	0	0	0	0	0	0	0	0	0

Appendix 2.8. Monthly distribution of samples collected throughout the Western Lake Michigan Drainages study unit and at 10 surface-water sites, water years 1971–90, for determination of dissolved orthophosphate
[site locations shown in figure 24]

Site (site number)	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
All sites	607	807	1,458	1,248	1,197	1,729	1,595	1,947	1,152	860	724	604
Escanaba River (1)	4	1	7	5	4	6	4	5	3	5	4	3
Ford River (2)	8	1	1	5	3	1	8	0	1	5	3	0
Fox River (8)	4	3	4	2	4	5	1	5	5	0	8	2
Green Lake Inlet (7)	4	2	2	2	3	2	3	2	3	0	4	2
Manitowoc River (9)	1	0	9	0	6	17	10	18	9	2	4	3
Menominee River (4)	1	0	9	1	9	11	7	14	14	2	4	3
Milwaukee River (10)	1	0	8	0	4	8	2	6	2	2	4	3
Popple River (3)	0	0	0	0	0	0	0	0	0	0	0	0
Silver Creek (6)	0	0	0	0	0	0	0	0	0	0	0	0
White Creek (5)	0	0	0	0	0	0	0	0	0	0	0	0

Appendix 2.9. Monthly distribution of samples collected throughout the Western Lake Michigan Drainages study unit and at 10 surface-water sites, water years 1971–90, for determination of suspended sediment
[site locations shown in figure 24]

Site (site number)	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
All sites	469	594	1,422	1,100	969	1,103	1,076	1,179	1,038	781	788	503
Escanaba River (1)	10	7	16	11	11	12	11	12	12	9	10	6
Ford River (2)	13	8	8	12	10	7	16	7	8	11	9	5
Fox River (8)	34	34	74	105	51	41	36	35	35	29	38	27
Green Lake Inlet (7)	8	4	5	6	7	5	6	5	7	2	7	5
Manitowoc River (9)	4	3	17	4	7	10	8	15	6	5	9	4
Menominee River (4)	9	8	19	13	17	17	14	30	14	10	14	11
Milwaukee River (10)	7	6	15	7	10	13	9	32	9	9	10	10
Popple River (3)	5	4	45	21	18	34	22	20	18	9	7	3
Silver Creek (6)	8	17	196	88	88	76	71	81	84	32	48	4
White Creek (5)	33	182	322	110	74	120	125	135	107	46	85	83

Appendix 3.1. Decile-flow distribution of samples collected at 10 surface-water sites in the Western Lake Michigan Drainages study unit, water years 1971–90, for determination of dissolved nitrite plus nitrate
[sites locations are shown in figure 24]

Site (site number)	Low flow				Percentiles of flow[1]					High flow
	90+	90–80	80–70	70–60	60–50	50–40	40–30	30–20	20–10	10–0
Escanaba River (1)	5	9	9	5	11	8	10	6	8	7
Ford River (2)	6	7	6	5	7	5	10	6	7	4
Fox River (8)	6	6	4	6	11	8	5	5	4	7
Green Lake Inlet (7)	0	0	0	0	0	0	0	0	0	0
Manitowoc River (9)	6	1	10	4	6	4	7	4	8	7
Menominee River (4)	2	2	3	6	3	4	10	3	7	8
Milwaukee River (10)	4	5	7	6	11	6	6	6	7	7
Popple River (3)	4	11	11	6	8	9	8	8	11	10
Silver Creek (6)	0	0	0	0	0	0	0	0	0	0
White Creek (5)	0	0	0	0	0	0	0	0	0	0

[1]Each decile of flow refers to a flow range that occurred 10 percent of the time.

Appendix 3.2. Decile-flow distribution of samples collected at 10 surface-water sites in the Western Lake Michigan Drainages study unit, water years 1971–90, for determination of dissolved nitrite
[sites locations are shown in figure 24]

Site (site number)	Low flow				Percentiles of flow[1]					High flow
	90+	90–80	80–70	70–60	60–50	50–40	40–30	30–20	20–10	10–0
Escanaba River (1)	2	6	2	2	2	3	3	4	2	2
Ford River (2)	4	2	3	1	1	1	2	4	2	0
Fox River (8)	6	0	0	1	4	0	2	2	1	4
Green Lake Inlet (7)	0	0	0	0	0	0	0	0	0	0
Manitowoc River (9)	3	1	3	1	2	1	1	2	3	3
Menominee River (4)	1	0	0	1	1	0	0	1	1	1
Milwaukee River (10)	2	1	0	2	5	1	3	3	1	3
Popple River (3)	2	2	2	3	2	2	1	2	3	1
Silver Creek (6)	0	0	0	0	0	0	0	0	0	0
White Creek (5)	0	0	0	0	0	0	0	0	0	0

[1]Each decile of flow refers to a flow range that occurred 10 percent of the time.

Appendix 3.3. Decile-flow distribution of samples collected at 10 surface-water sites in the Western Lake Michigan Drainages study unit, water years 1971–90, for determination of total Kjeldahl nitrogen (ammonia plus organics)
[sites locations are shown in figure 24]

Site (site number)	Low flow				Percentiles of flow[1]					High flow
	90+	90–80	80–70	70–60	60–50	50–40	40–30	30–20	20–10	10–0
Escanaba River (1)	14	15	12	8	18	11	13	10	12	15
Ford River (2)	15	7	15	10	10	8	14	12	12	10
Fox River (8)	13	14	9	9	17	15	10	10	6	13
Green Lake Inlet (7)	0	0	0	0	0	0	0	0	0	0
Manitowoc River (9)	5	1	11	5	6	4	9	4	8	11
Menominee River (4)	2	6	8	8	3	7	10	5	7	11
Milwaukee River (10)	14	10	12	13	14	11	12	12	17	15
Popple River (3)	4	6	7	5	5	6	3	4	8	5
Silver Creek (6)	0	0	0	0	0	0	0	0	0	0
White Creek (5)	0	0	0	0	3	0	1	0	2	0

[1]Each decile of flow refers to a flow range that occurred 10 percent of the time.

Appendix 3.4. Decile-flow distribution of samples collected at 10 surface-water sites in the Western Lake Michigan Drainages study unit, water years 1971–90, for determination of total ammonia
[sites locations are shown in figure 24]

Site (site number)	Low flow				Percentiles of flow[1]					High flow
	90+	90–80	80–70	70–50	60–50	50–40	40–30	30–20	20–10	10–0
Escanaba River (1)	3	10	9	5	10	5	8	5	10	9
Ford River (2)	6	6	6	6	7	4	8	7	9	7
Fox River (8)	7	5	6	7	13	12	5	4	3	7
Green Lake Inlet (7)	0	0	0	0	0	0	0	0	0	0
Manitowoc River (9)	6	1	8	4	5	2	7	2	5	7
Menominee River (4)	2	5	5	4	2	5	3	5	6	6
Milwaukee River (10)	3	4	6	7	11	8	6	7	11	6
Popple River (3)	4	6	5	4	3	5	2	3	6	3
Silver Creek (6)	0	0	0	0	0	0	0	0	0	0
White Creek (5)	8	4	14	5	15	15	36	54	81	473

[1]Each decile of flow refers to a flow range that occurred 10 percent of the time.

Appendix 3.5. Decile-flow distribution of samples collected at 10 surface-water sites in the Western Lake Michigan Drainages study unit, water years 1971–90, for determination of dissolved ammonia
[sites locations are shown in figure 24]

Site (site number)	Low flow				Percentiles of flow[1]					High flow
	90+	90–80	80–70	70–50	60–50	50–40	40–30	30–20	20–10	10–0
Escanaba River (1)	4	9	8	5	11	6	10	6	6	7
Ford River (2)	6	6	6	4	7	5	9	5	7	4
Fox River (8)	6	6	4	6	11	7	5	5	4	7
Green Lake Inlet (7)	0	0	0	0	0	0	0	0	0	0
Manitowoc River (9)	5	7	4	4	6	4	7	4	8	7
Menominee River (4)	2	2	3	5	3	4	10	3	7	8
Milwaukee River (10)	3	5	7	6	10	5	6	6	7	7
Popple River (3)	4	7	7	5	5	6	3	4	8	5
Silver Creek (6)	0	0	0	0	0	0	0	0	0	0
White Creek (5)	0	0	0	0	0	0	0	0	0	0

[1]Each decile of flow refers to a flow range that occurred 10 percent of the time.

Appendix 3.6. Decile-flow distribution of samples collected at 10 surface-water sites in the Western Lake Michigan Drainages study unit, water years 1971–90, for determination of total phosphorus
[sites locations are shown in figure 24]

Site (site number)	Low flow				Percentiles of flow[1]					High flow
	90+	90–80	80–70	70–60	60–50	50–40	40–30	30–20	20–10	10–0
Escanaba River (1)	14	15	12	8	19	11	13	10	12	16
Ford River (2)	15	7	15	10	11	7	15	12	13	10
Fox River (8)	14	14	10	11	21	15	10	10	7	7
Green Lake Inlet (7)	3	8	11	14	14	15	19	17	27	60
Manitowoc River (9)	6	1	18	10	15	11	15	10	9	11
Menominee River (4)	2	6	8	9	5	7	11	5	7	11
Milwaukee River (10)	14	12	12	16	21	15	15	18	25	24
Popple River (3)	8	21	21	14	19	16	15	12	17	18
Silver Creek (6)	5	11	10	15	9	24	56	72	99	246
White Creek (5)	8	4	14	5	15	15	35	52	79	458

[1]Each decile of flow refers to a flow range that occurred 10 percent of the time.

Appendix 3.7. Decile-flow distribution of samples collected at 10 surface-water sites in the Western Lake Michigan Drainages study unit, water years 1971–90, for determination of dissolved phosphorus
[sites locations are shown in figure 24]

Site (site number)	Low flow				Percentiles of flow[1]					High flow
	90+	90–80	80–70	70–60	60–50	50–40	40–30	30–20	20–10	10–0
Escanaba River (1)	4	10	10	6	15	7	12	7	11	13
Ford River (2)	6	7	9	8	9	6	9	7	12	9
Fox River (8)	7	7	6	8	15	13	7	7	6	10
Green Lake Inlet (7)	0	0	0	0	0	0	0	0	0	0
Manitowoc River (9)	6	1	11	5	6	4	9	4	8	11
Menominee River (4)	2	6	8	9	3	7	11	5	7	11
Milwaukee River (10)	3	6	9	9	14	8	7	8	12	10
Popple River (3)	4	6	7	5	5	6	3	4	8	5
Silver Creek (6)	0	0	0	0	0	0	0	0	0	0
White Creek (5)	0	0	0	0	0	0	0	0	0	0

[1]Each decile of flow refers to a flow range that occurred 10 percent of the time.

Appendix 3.8. Decile-flow distribution of samples collected at 10 surface-water sites in the Western Lake Michigan Drainages study unit, water years 1971–90, for determination of dissolved orthophosphate
[sites locations are shown in figure 24]

Site (site number)	Low flow				Percentiles of flow[1]					High flow
	90+	90–80	80–70	70–60	60–50	50–40	40–30	30–20	20–10	10–0
Escanaba River (1)	3	8	4	3	7	4	7	6	3	6
Ford River (2)	4	4	4	3	3	3	4	5	5	1
Fox River (8)	6	2	0	4	7	1	4	5	4	7
Green Lake Inlet (7)	0	0	0	0	0	0	0	0	0	0
Manitowoc River (9)	3	1	13	7	13	10	9	9	7	7
Menominee River (4)	1	1	3	3	2	2	8	1	2	6
Milwaukee River (10)	2	4	3	7	13	5	7	10	10	14
Popple River (3)	2	4	4	5	4	4	4	5	7	4
Silver Creek (6)	0	0	0	0	0	0	0	0	0	0
White Creek (5)	0	0	0	0	0	0	0	0	0	0

[1]Each decile of flow refers to a flow range that occurred 10 percent of the time.

Appendix 3.9. Decile-flow distribution of samples collected at 10 surface-water sites in the Western Lake Michigan Drainages study unit, water years 1971–90, for determination of suspended sediment
[sites locations are shown in figure 24]

Site (site number)	Low flow				Percentiles of flow[1]					High flow
	90+	90–80	80–70	70–60	60–50	50–40	40–30	30–20	20–10	10–0
Escanaba River (1)	14	15	12	7	17	10	14	10	10	16
Ford River (2)	14	7	15	9	10	8	15	12	13	58
Fox River (8)	26	13	10	9	19	14	9	10	13	13
Green Lake Inlet (7)	1	10	14	12	17	12	19	17	36	68
Manitowoc River (9)	6	4	12	14	8	7	10	5	10	16
Menominee River (4)	2	4	8	9	3	7	11	5	7	11
Milwaukee River (10)	15	15	14	19	27	14	16	16	17	19
Popple River (3)	45	42	39	34	48	39	47	42	64	137
Silver Creek (6)	4	12	27	16	13	37	84	94	145	361
White Creek (5)	25	17	34	30	39	39	97	117	161	864

[1]Each decile of flow refers to a flow range that occurred 10 percent of the time.

APPENDIX 4

Appendix 4.1. Summary statistics for constituents in surface water, by category, for the Western Lake Michigan Drainages (WMIC) study unit, water years 1971–90: dissolved nitrite plus nitrate

[--, no data available or, if less than 10 values, only median and mean calculated; percentiles and mean are expressed in milligrams per liter (mg/L) and are based on midmonth samples, except for category WMIC, which was based on all data; highest reported minimum detection limit = <0.1 mg/L; NAC, National Average Concentration for that land-use category from Alexander and Smith (1990)]

Category	Number of samples	Percentile 10th	25th	50th (median)	75th	90th	Mean
WMIC	12,458	0.04	0.15	0.50	1.17	2.10	0.93
General land use:							
NAC agriculture	--	.09	.26	.72	1.40	3.90	--
WMIC agriculture	1,180	.04	.22	.92	1.96	3.70	1.47
WMIC agriculture/forest	12	.03	.79	1.09	1.60	1.90	1.10
NAC forest	--	.04	.10	.21	.30	.69	--
WMIC forest	434	.01	.05	.09	.17	.27	.14
NAC urban	--	.04	.23	.47	1.50	2.90	--
WMIC urban	702	.05	.19	.44	.92	1.62	.70
Land use, by source[1]:							
USGS agriculture	89	.05	.19	.64	1.40	2.20	1.27
Other agriculture	1,091	.03	.22	.95	2.00	3.70	1.49
USGS agriculture/forest	6	--	--	1.60	--	--	1.63
Other agriculture/forest	6	--	--	.78	--	--	.57
USGS forest	169	.00	.05	.10	.18	.25	.13
Other forest	265	.02	.05	.09	.17	.28	.15
USGS urban	1	--	--	.05	--	--	.05
Other urban	701	.05	.19	.44	.92	1.62	.70
Relatively Homogeneous Unit:							
Ag1	488	.08	.69	1.66	3.00	4.60	2.17
Ag2	4	--	--	2.35	--	--	2.11
Ag3	202	.12	.60	1.33	2.20	4.70	1.92
Ag4	10	.04	.62	.85	1.35	1.56	.85
Ag15	0	--	--	--	--	--	--
Ag23	0	--	--	--	--	--	--
Ag24	2	--	--	.61	--	--	.61
Ag25	0	--	--	--	--	--	--
Ag27	0	--	--	--	--	--	--
Ag28	0	--	--	--	--	--	--
AF5	0	--	--	--	--	--	--
AF12	0	--	--	--	--	--	--
AF20	0	--	--	--	--	--	--
AF26	12	.03	.79	1.09	1.60	1.90	1.10
F6	0	--	--	--	--	--	--
F7	13	.00	.00	.00	.00	.09	.02
F8	0	--	--	--	--	--	--
F13	0	--	--	--	--	--	--
F14	0	--	--	--	--	--	--
F16	1	--	--	.00	--	--	.00
F17	0	--	--	--	--	--	--
F18	1	--	--	.00	--	--	.00
F19	13	.04	.05	.11	.13	.70	.25
F21	0	--	--	--	--	--	--
F22	206	.01	.03	.09	.18	.24	.12
U9	702	.05	.19	.44	.92	1.62	.70
U10	0	--	--	--	--	--	--
U11	0	--	--	--	--	--	--

[1]USGS, U.S. Geological Survey National Water Inventory System (NWIS) data; Other, STORET, Milwaukee Metropolitan Sewerage District, and/or Green Bay Metropolitan Sewerage District data.

Appendix 4.2. Summary statistics for constituents in surface water, by category, for the Western Lake Michigan Drainages (WMIC) study unit, water years 1971–90: dissolved nitrite

[--, no data available or, if less than 10 values, only median and mean calculated; percentiles and mean are expressed in milligrams per liter (mg/L) and are based on midmonth samples, except for category WMIC, which was based on all data; highest reported minimum detection limit = <0.2 mg/L; NAC, National Average Concentration for that land-use category from Alexander and Smith (1990)]

Category	Number of samples	Percentile					Mean
		10th	25th	50th (median)	75th	90th	
WMIC	1,031	0.01	0.01	0.02	0.04	0.09	0.05
General land use:							
NAC agriculture	--	--	--	--	--	--	--
WMIC agriculture	102	.01	.01	.02	.05	.09	.04
WMIC agriculture/forest	0	--	--	--	--	--	--
NAC forest	--	--	--	--	--	--	--
WMIC forest	63	.01	.01	.01	.01	.01	.01
NAC urban	--	--	--	--	--	--	--
WMIC urban	140	.01	.02	.03	.06	.10	.05
Land use, by source[1]:							
USGS agriculture	43	.01	.01	.02	.02	.06	.03
Other agriculture	59	.01	.01	.03	.06	.09	.04
USGS agriculture/forest	0	--	--	--	--	--	--
Other agriculture/forest	0	--	--	--	--	--	--
USGS forest	59	.01	.01	.01	.01	.01	.01
Other forest	4	--	--	.01	--	--	.01
USGS urban	1	--	--	.01	--	--	.01
Other urban	139	.01	.02	.03	.06	.10	.05
Relatively Homogeneous Unit:							
Ag1	45	.01	.01	.02	.05	.09	.04
Ag2	0	--	--	--	--	--	--
Ag3	21	.01	.02	.05	.08	.09	.05
Ag4	0	--	--	--	--	--	--
Ag15	0	--	--	--	--	--	--
Ag23	0	--	--	--	--	--	--
Ag24	0	--	--	--	--	--	--
Ag25	0	--	--	--	--	--	--
Ag27	0	--	--	--	--	--	--
Ag28	0	--	--	--	--	--	--
AF5	0	--	--	--	--	--	--
AF12	0	--	--	--	--	--	--
AF20	0	--	--	--	--	--	--
AF26	0	--	--	--	--	--	--
F6	0	--	--	--	--	--	--
F7	0	--	--	--	--	--	--
F8	0	--	--	--	--	--	--
F13	0	--	--	--	--	--	--
F14	0	--	--	--	--	--	--
F16	0	--	--	--	--	--	--
F17	0	--	--	--	--	--	--
F18	0	--	--	--	--	--	--
F19	7	--	--	.01	--	--	.01
F21	0	--	--	--	--	--	--
F22	51	.01	.01	.01	.01	.01	.01
U9	140	.01	.02	.03	.06	.10	.05
U10	0	--	--	--	--	--	--
U11	0	--	--	--	--	--	--

[1]USGS, U.S. Geological Survey National Water Inventory System (NWIS) data; Other, STORET, Milwaukee Metropolitan Sewerage District, and/or Green Bay Metropolitan Sewerage District data.

Appendix 4.3. Summary statistics for constituents in surface water, by category, for the Western Lake Michigan Drainages (WMIC) study unit, water years 1971–90: total Kjeldahl nitrogen (ammonia plus organics)

[--, no data available or, if less than 10 values, only median and mean calculated; percentiles and mean are expressed in milligrams per liter (mg/L) and are based on midmonth samples, except for category WMIC, which was based on all data; highest reported minimum detection limit = <0.1 mg/L; NAC, National Average Concentration for that land-use category from Alexander and Smith (1990)]

Category	Number of samples	Percentile					Mean
		10th	25th	50th (median)	75th	90th	
WMIC	6,551	0.40	0.60	1.00	1.50	2.10	1.34
General land use:							
NAC agriculture	--	--	--	--	--	--	--
WMIC agriculture	753	.60	.90	1.20	1.60	2.40	1.94
WMIC agriculture/forest	34	.27	.42	.55	.75	1.18	.68
NAC forest	--	--	--	--	--	--	--
WMIC forest	521	.28	.40	.54	.80	1.30	1.41
NAC urban	--	--	--	--	--	--	--
WMIC urban	219	.40	.50	.80	1.31	1.90	1.05
Land use, by source[1]:							
USGS agriculture	103	.80	1.10	1.60	1.90	2.40	1.59
Other agriculture	650	.60	.83	1.18	1.60	2.40	2.00
USGS agriculture/forest	0	--	--	--	--	--	--
Other agriculture/forest	34	.27	.42	.55	.75	1.18	.68
USGS forest	92	.29	.37	.50	.70	1.00	.58
Other forest	429	.27	.40	.57	.80	1.40	1.59
USGS urban	1	--	--	.53	--	--	.53
Other urban	218	.40	.50	.81	1.31	1.90	1.05
Relatively Homogeneous Unit:							
Ag1	253	.80	1.0	1.20	1.60	2.60	2.16
Ag2	4	--	--	2.85	--	--	2.70
Ag3	36	.20	.83	1.75	4.25	11.50	7.51
Ag4	0	--	--	--	--	--	--
Ag15	0	--	--	--	--	--	--
Ag23	6	--	--	1.63	--	--	1.59
Ag24	2	--	--	.90	--	--	.90
Ag25	42	.83	1.10	1.40	1.76	2.40	1.50
Ag27	0	--	--	--	--	--	--
Ag28	0	--	--	--	--	--	--
AF5	0	--	--	--	--	--	--
AF12	0	--	--	--	--	--	--
AF20	8	--	--	.41	--	--	.37
AF26	26	.40	.50	.62	.86	1.32	.78
F6	0	--	--	--	--	--	--
F7	0	--	--	--	--	--	--
F8	0	--	--	--	--	--	--
F13	0	--	--	--	--	--	--
F14	0	--	--	--	--	--	--
F16	0	--	--	--	--	--	--
F17	0	--	--	--	--	--	--
F18	26	.05	.15	.35	.68	1.08	.46
F19	14	.36	.40	.50	.70	1.00	.57
F21	0	--	--	--	--	--	--
F22	167	.30	.43	.60	.80	1.10	.67
U9	219	.40	.50	.80	1.31	1.90	1.05
U10	0	--	--	--	--	--	--
U11	0	--	--	--	--	--	--

[1]USGS, U.S. Geological Survey National Water Inventory System (NWIS) data; Other, STORET, Milwaukee Metropolitan Sewerage District, and/or Green Bay Metropolitan Sewerage District data.

Appendix 4.4. Summary statistics for constituents in surface water, by category, for the Western Lake Michigan Drainages (WMIC) study unit, water years 1971–90: total ammonia

[--, no data available or, if less than 10 values, only median and mean calculated; percentiles and mean are expressed in milligrams per liter (mg/L) and are based on midmonth samples, except for category WMIC, which was based on all data; highest reported minimum detection limit = <0.05 mg/L; NAC, National Average Concentration for that land-use category from Alexander and Smith (1990)]

Category	Number of samples	Percentile					Mean
		10th	25th	50th (median)	75th	90th	
WMIC	5,091	0.01	0.04	0.10	0.28	0.61	0.29
General land use:							
NAC agriculture	--	--	--	--	--	--	--
WMIC agriculture	390	.03	.05	.10	.21	.53	.33
WMIC agriculture/forest	32	.03	.04	.09	.13	.19	.10
NAC forest	--	--	--	--	--	--	--
WMIC forest	721	.01	.01	.03	.08	.20	.29
NAC urban	--	--	--	--	--	--	--
WMIC urban	102	.23	.35	.54	.73	1.08	.60
Land use, by source[1]:							
USGS agriculture	86	.02	.04	.06	.15	.39	.16
Other agriculture	304	.03	.05	.12	.22	.64	.38
USGS agriculture/forest	1	--	--	.03	--	--	.03
Other agriculture/forest	31	.03	.05	.09	.14	.19	.10
USGS forest	122	.01	.01	.02	.05	.08	.03
Other forest	599	.01	.01	.03	.09	.23	.34
USGS urban	1	--	--	.10	--	--	.10
Other urban	101	.25	.36	.54	.73	1.08	.61
Relatively Homogeneous Unit:							
Ag1	74	.04	.06	.11	.23	2.10	.86
Ag2	0	--	--	--	--	--	--
Ag3	23	.05	.06	.12	.40	.78	.35
Ag4	0	--	--	--	--	--	--
Ag15	0	--	--	--	--	--	--
Ag23	0	--	--	--	--	--	--
Ag24	0	--	--	--	--	--	--
Ag25	42	.02	.03	.06	.17	.42	.15
Ag27	0	--	--	--	--	--	--
Ag28	0	--	--	--	--	--	--
AF5	0	--	--	--	--	--	--
AF12	0	--	--	--	--	--	--
AF20	10	.03	.05	.07	.09	.13	.07
AF26	22	.03	.03	.10	.15	.21	.11
F6	0	--	--	--	--	--	--
F7	0	--	--	--	--	--	--
F8	0	--	--	--	--	--	--
F13	41	.05	.11	.25	.70	1.70	.74
F14	0	--	--	--	--	--	--
F16	2	--	--	.01	--	--	.01
F17	0	--	--	--	--	--	--
F18	15	.02	.03	.05	.08	.18	.07
F19	18	.01	.01	.02	.02	.09	.03
F21	0	--	--	--	--	--	--
F22	69	.01	.02	.04	.07	.12	.05
U9	102	.23	.35	.54	.73	1.08	.60
U10	0	--	--	--	--	--	--
U11	0	--	--	--	--	--	--

[1]USGS, U.S. Geological Survey National Water Inventory System (NWIS) data; Other, STORET, Milwaukee Metropolitan Sewerage District, and/or Green Bay Metropolitan Sewerage District data.

Appendix 4.5. Summary statistics for constituents in surface water, by category, for the Western Lake Michigan Drainages (WMIC) study unit, water years 1971–90: dissolved ammonia

[--, no data available or, if less than 10 values, only median and mean calculated; percentiles and mean are expressed in milligrams per liter (mg/L) and are based on midmonth samples, except for category WMIC, which was based on all data; highest reported minimum detection limit = <0.02 mg/L; NAC, National Average Concentration for that land-use category from Alexander and Smith (1990)]

Category	Number of samples	Percentile					Mean
		10th	25th	50th (median)	75th	90th	
WMIC	12,489	0.02	0.04	0.11	0.28	0.69	0.35
General land use:							
NAC agriculture	--	--	--	--	--	--	--
WMIC agriculture	1,155	.02	.04	.09	.21	.53	.42
WMIC agriculture/forest	14	.04	.05	.08	.20	.84	.37
NAC forest	--	--	--	--	--	--	--
WMIC forest	408	.01	.02	.03	.07	.13	.07
NAC urban	--	--	--	--	--	--	--
WMIC urban	699	.02	.05	.13	.27	.57	.30
Land use, by source[1]:							
USGS agriculture	79	.02	.03	.05	.13	.40	.14
Other agriculture	1,076	.02	.04	.10	.22	.57	.44
USGS agriculture/forest	0	--	--	--	--	--	--
Other agriculture/forest	14	.04	.05	.08	.20	.84	.37
USGS forest	99	.01	.02	.04	.07	.11	.05
Other forest	309	.01	.02	.03	.07	.15	.08
USGS urban	0	--	--	--	--	--	--
Other urban	699	.02	.05	.13	.27	.57	.30
Relatively Homogeneous Unit:							
Ag1	411	.03	.06	.11	.21	.61	.60
Ag2	4	--	--	1.66	--	--	1.56
Ag3	208	.03	.05	.18	.48	1.70	.77
Ag4	10	.03	.04	.07	.08	.18	.08
Ag15	0	--	--	--	--	--	--
Ag23	0	--	--	--	--	--	--
Ag24	2	--	--	.06	--	--	.06
Ag25	0	--	--	--	--	--	--
Ag27	65	.00	.04	.09	.28	.69	.22
Ag28	0	--	--	--	--	--	--
AF5	0	--	--	--	--	--	--
AF12	0	--	--	--	--	--	--
AF20	0	--	--	--	--	--	--
AF26	14	.04	.05	.08	.20	.84	.37
F6	0	--	--	--	--	--	--
F7	0	--	--	--	--	--	--
F8	0	--	--	--	--	--	--
F13	0	--	--	--	--	--	--
F14	0	--	--	--	--	--	--
F16	0	--	--	--	--	--	--
F17	0	--	--	--	--	--	--
F18	0	--	--	--	--	--	--
F19	13	.02	.02	.03	.03	.04	.03
F21	0	--	--	--	--	--	--
F22	214	.01	.02	.05	.10	.22	.10
U9	699	.02	.05	.13	.27	.57	.30
U10	0	--	--	--	--	--	--
U11	0	--	--	--	--	--	--

[1]USGS, U.S. Geological Survey National Water Inventory System (NWIS) data; Other, STORET, Milwaukee Metropolitan Sewerage District, and/or Green Bay Metropolitan Sewerage District data.

Appendix 4.6. Summary statistics for constituents in surface water, by category, for the Western Lake Michigan Drainages (WMIC) study unit, water years 1971–90: total phosphorus

[--, no data available or, if less than 10 values, only median and mean calculated; percentiles and mean are expressed in milligrams per liter (mg/L) and are based on midmonth samples, except for category WMIC, which was based on all data; highest reported minimum detection limit = <0.02 mg/L; NAC, National Average Concentration for that land-use category from Alexander and Smith (1990)]

Category	Number of samples	Percentile					Mean
		10th	25th	50th (median)	75th	90th	
WMIC	21,413	0.03	0.07	0.16	0.35	0.77	0.64
General land use:							
NAC agriculture	--	.06	.12	.23	.34	.55	--
WMIC agriculture	2,298	.04	.08	.13	.26	.51	.46
WMIC agriculture/forest	50	.01	.02	.03	.10	79.50	14.5
NAC forest	--	.02	.03	.05	.09	.18	--
WMIC forest	1,106	.01	.02	.02	.04	.08	.15
NAC urban	--	.02	.08	.20	.46	1.30	--
WMIC urban	847	.03	.06	.11	.21	.46	.27
Land use, by source[1]:							
USGS agriculture	143	.08	.12	.21	.33	.53	.30
Other agriculture	2,155	.04	.07	.13	.25	.50	.47
USGS agriculture/forest	0	--	--	--	--	--	--
Other agriculture/forest	50	.01	.02	.03	.10	79.50	14.52
USGS forest	208	.01	.02	.02	.03	.05	.03
Other forest	898	.01	.02	.02	.04	.10	.18
USGS urban	1	--	--	.07	--	--	.07
Other urban	846	.03	.06	.11	.21	.46	.27
Relatively Homogeneous Unit:							
Ag1	831	.06	.10	.16	.30	.60	.51
Ag2	4	--	--	1.24	--	--	1.05
Ag3	263	.08	.14	.26	.57	3.45	1.53
Ag4	15	.08	.08	.10	.12	.14	.11
Ag15	0	--	--	--	--	--	--
Ag23	8	--	--	.32	--	--	.33
Ag24	2	--	--	.06	--	--	.06
Ag25	42	.03	.04	.07	.15	.23	.11
Ag27	87	.03	.06	.10	.20	.39	.17
Ag28	0	--	--	--	--	--	--
AF5	0	--	--	--	--	--	--
AF12	0	--	--	--	--	--	--
AF20	9	--	--	80.00	--	--	80.44
AF26	41	.01	.02	.02	.04	.10	.04
F6	0	--	--	--	--	--	--
F7	0	--	--	--	--	--	--
F8	0	--	--	--	--	--	--
F13	41	.01	.01	.04	.64	2.40	.63
F14	0	--	--	--	--	--	--
F16	8	--	--	.01	--	--	.02
F17	0	--	--	--	--	--	--
F18	2	--	--	.05	--	--	.05
F19	12	.01	.01	.04	.08	.17	.11
F21	0	--	--	--	--	--	--
F22	336	.01	.02	.03	.04	.07	.04
U9	847	.03	.06	.11	.21	.46	.27
U10	0	--	--	--	--	--	--
U11	0	--	--	--	--	--	--

[1]USGS, U.S. Geological Survey National Water Inventory System (NWIS) data; Other, STORET, Milwaukee Metropolitan Sewerage District, and/or Green Bay Metropolitan Sewerage District data.

Appendix 4.7. Summary statistics for constituents in surface water, by category, for the Western Lake Michigan Drainages (WMIC) study unit, water years 1971–90: dissolved phosphorus

[--, no data available or, if less than 10 values, only median and mean calculated; percentiles and mean are expressed in milligrams per liter (mg/L) and are based on midmonth samples, except for category WMIC, which was based on all data; highest reported minimum detection limit = <0.01 mg/L; NAC, National Average Concentration for that land-use category from Alexander and Smith (1990)]

Category	Number of samples	Percentile					Mean
		10th	25th	50th (median)	75th	90th	
WMIC	2,168	0.009	0.02	0.03	0.07	0.13	0.06
General land use:							
NAC agriculture	--	--	--	--	--	--	--
WMIC agriculture	183	.03	.05	.10	.14	.23	.13
WMIC agriculture/forest	0	--	--	--	--	--	--
NAC forest	--	--	--	--	--	--	--
WMIC forest	85	.005	.01	.01	.02	.03	.02
NAC urban	--	--	--	--	--	--	--
WMIC urban	94	.01	.02	.03	.05	.07	.04
Land use, by source[1]:							
USGS agriculture	86	.03	.06	.12	.18	.37	.19
Other agriculture	97	.03	.04	.08	.11	.16	.09
USGS agriculture/forest	0	--	--	--	--	--	--
Other agriculture/forest	0	--	--	--	--	--	--
USGS forest	85	.005	.01	.01	.02	.03	.02
Other forest	0	--	--	--	--	--	--
USGS urban	0	--	--	--	--	--	--
Other urban	94	.01	.02	.03	.05	.07	.04
Relatively Homogeneous Unit:							
Ag1	19	.005	.07	.11	.42	2.00	.37
Ag2	0	--	--	--	--	--	--
Ag3	0	--	--	--	--	--	--
Ag4	0	--	--	--	--	--	--
Ag15	0	--	--	--	--	--	--
Ag23	0	--	--	--	--	--	--
Ag24	0	--	--	--	--	--	--
Ag25	0	--	--	--	--	--	--
Ag27	0	--	--	--	--	--	--
Ag28	0	--	--	--	--	--	--
AF5	0	--	--	--	--	--	--
AF12	0	--	--	--	--	--	--
AF20	0	--	--	--	--	--	--
AF26	0	--	--	--	--	--	--
F6	0	--	--	--	--	--	--
F7	0	--	--	--	--	--	--
F8	0	--	--	--	--	--	--
F13	0	--	--	--	--	--	--
F14	0	--	--	--	--	--	--
F16	0	--	--	--	--	--	--
F17	0	--	--	--	--	--	--
F18	0	--	--	--	--	--	--
F19	6	--	--	.005	--	--	.006
F21	0	--	--	--	--	--	--
F22	79	.005	.01	.01	.02	.03	.02
U9	94	.01	.02	.03	.05	.07	.04
U10	0	--	--	--	--	--	--
U11	0	--	--	--	--	--	--

[1]USGS, U.S. Geological Survey National Water Inventory System (NWIS) data; Other, STORET, Milwaukee Metropolitan Sewerage District, and/or Green Bay Metropolitan Sewerage District data.

Appendix 4.8. Summary statistics for constituents in surface water, by category, for the Western Lake Michigan Drainages (WMIC) study unit, water years 1971–90: total orthophosphate

[--, no data available or, if less than 10 values, only median and mean calculated; percentiles and mean are expressed in milligrams per liter (mg/L) and are based on midmonth samples, except for category WMIC, which was based on all data; highest reported minimum detection limit = <0.02 mg/L; NAC, National Average Concentration for that land-use category from Alexander and Smith (1990)]

Category	Number of samples	Percentile					Mean
		10th	25th	50th (median)	75th	90th	
WMIC	1,438	0.00	0.01	0.01	0.04	0.15	0.06
General land use:							
NAC agriculture	--	--	--	--	--	--	--
WMIC agriculture	132	.02	.04	.09	.16	.29	.12
WMIC agriculture/forest	14	.02	.02	.03	.04	.07	.03
NAC forest	--	--	--	--	--	--	--
WMIC forest	524	.00	.00	.01	.01	.03	.04
NAC urban	--	--	--	--	--	--	--
WMIC urban	0	--	--	--	--	--	--
Land use, by source[1]:							
USGS agriculture	17	.04	.11	.16	.19	.36	.18
Other agriculture	115	.02	.05	.08	.16	.26	.11
USGS agriculture/forest	0	--	--	--	--	--	--
Other agriculture/forest	14	.02	.02	.03	.04	.07	.03
USGS forest	21	.01	.01	.01	.01	.01	.01
Other forest	503	.00	.00	.01	.01	.03	.05
USGS urban	0	--	--	--	--	--	--
Other urban	0	--	--	--	--	--	--
Relatively Homogeneous Unit:							
Ag1	23	.01	.04	.12	.18	.34	.14
Ag2	0	--	--	--	--	--	--
Ag3	7	--	--	.09	--	--	.09
Ag4	0	--	--	--	--	--	--
Ag15	0	--	--	--	--	--	--
Ag23	0	--	--	--	--	--	--
Ag24	0	--	--	--	--	--	--
Ag25	0	--	--	--	--	--	--
Ag27	86	.02	.04	.08	.16	.29	.12
Ag28	0	--	--	--	--	--	--
AF5	0	--	--	--	--	--	--
AF12	0	--	--	--	--	--	--
AF20	0	--	--	--	--	--	--
AF26	14	.02	.02	.03	.04	.07	.03
F6	0	--	--	--	--	--	--
F7	0	--	--	--	--	--	--
F8	0	--	--	--	--	--	--
F13	40	.01	.01	.01	.56	1.65	.45
F14	0	--	--	--	--	--	--
F16	2	--	--	.00	--	--	.00
F17	0	--	--	--	--	--	--
F18	2	--	--	.02	--	--	.02
F19	2	--	--	.01	--	--	.01
F21	0	--	--	--	--	--	--
F22	67	.01	.01	.01	.03	.05	.02
U9	0	--	--	--	--	--	--
U10	0	--	--	--	--	--	--
U11	0	--	--	--	--	--	--

[1]USGS, U.S. Geological Survey National Water Inventory System (NWIS) data; Other, STORET, Milwaukee Metropolitan Sewerage District, and/or Green Bay Metropolitan Sewerage District data.

Appendix 4.9. Summary statistics for constituents in surface water, by category, for the Western Lake Michigan Drainages (WMIC) study unit, water years 1971–90: dissolved orthophosphate

[--, no data available or, if less than 10 values, only median and mean calculated; percentiles and mean are expressed in milligrams per liter (mg/L) and are based on midmonth samples, except for category WMIC, which was based on all data; highest reported minimum detection limit = <0.01 mg/L; NAC, National Average Concentration for that land-use category from Alexander and Smith (1990)]

Category	Number of samples	Percentile 10th	25th	50th (median)	75th	90th	Mean
WMIC	13,928	0.004	0.01	0.05	0.11	0.22	0.20
General land use:							
NAC agriculture	--	--	--	--	--	--	--
WMIC agriculture	1,748	.005	.02	.05	.13	.26	.42
WMIC agriculture/forest	30	.003	.003	.003	.006	.01	.005
NAC forest	--	--	--	--	--	--	--
WMIC forest	330	.002	.003	.006	.01	.17	.29
NAC urban	--	--	--	--	--	--	--
WMIC urban	576	.005	.01	.03	.10	.21	.10
Land use, by source[1]:							
USGS agriculture	79	.01	.04	.09	.15	.31	.15
Other agriculture	1,669	.005	.02	.05	.13	.26	.43
USGS agriculture/forest	1	--	--	.01	--	--	.01
Other agriculture/forest	29	.003	.003	.003	.005	.009	.005
USGS forest	54	.000	.005	.005	.01	.02	.007
Other forest	276	.002	.003	.006	.01	.30	.35
USGS urban	1	--	--	.000	--	--	.000
Other urban	575	.005	.01	.03	.10	.21	.10
Relatively Homogeneous Unit:							
Ag1	733	.01	.04	.07	.13	.27	.76
Ag2	4	--	--	1.18	--	--	1.00
Ag3	250	.02	.04	.10	.24	.71	.32
Ag4	15	.01	.04	.05	.08	.10	.06
Ag15	0	--	--	--	--	--	--
Ag23	0	--	--	--	--	--	--
Ag24	2	--	--	.02	--	--	.02
Ag25	43	.008	.01	.02	.08	.16	.06
Ag27	0	--	--	--	--	--	--
Ag28	0	--	--	--	--	--	--
AF5	0	--	--	--	--	--	--
AF12	0	--	--	--	--	--	--
AF20	0	--	--	--	--	--	--
AF26	30	.003	.003	.003	.006	.01	.005
F6	0	--	--	--	--	--	--
F7	0	--	--	--	--	--	--
F8	0	--	--	--	--	--	--
F13	0	--	--	--	--	--	--
F14	0	--	--	--	--	--	--
F16	0	--	--	--	--	--	--
F17	0	--	--	--	--	--	--
F18	0	--	--	--	--	--	--
F19	9	--	--	.01	--	--	.12
F21	0	--	--	--	--	--	--
F22	103	.005	.005	.005	.010	.03	.02
U9	576	.005	.01	.03	.10	.21	.10
U10	0	--	--	--	--	--	--
U11	0	--	--	--	--	--	--

[1]USGS, U.S. Geological Survey National Water Inventory System (NWIS) data; Other, STORET, Milwaukee Metropolitan Sewerage District, and/or Green Bay Metropolitan Sewerage District data.

Appendix 4.10. Summary statistics for constituents in surface water, by category, for the Western Lake Michigan Drainages (WMIC) study unit, water years 1971–90: suspended sediment

[--, no data available or, if less than 10 values, only median and mean calculated; percentiles and mean are expressed in milligrams per liter (mg/L) and are based on midmonth samples, except for category WMIC, which was based on all data; highest reported minimum detection limit = <1 mg/L; NAC, National Average Concentration for that land-use category from Alexander and Smith (1990)]

Category	Number of samples	Percentile					Mean
		10th	25th	50th (median)	75th	90th	
WMIC	11,022	3.6	9.0	23.0	53.5	270.0	285.1
General land use:							
NAC agriculture	--	21.0	52.0	131.0	291.0	654.0	--
WMIC agriculture	477	4.0	10.0	25.0	57.0	152.0	65.2
WMIC agriculture/forest	5	0.0	5.0	18.0	24.0	24.0	14.2
NAC forest	--	5.0	9.0	19.0	43.0	99.0	--
WMIC forest	215	1.0	2.0	4.0	7.0	14.0	6.9
NAC urban	--	4.0	12.0	25.0	115.0	229.0	--
WMIC urban	76	13.0	51.5	148.0	394.5	817.0	283.4
Land use, by source[1]:							
USGS agriculture	477	4.0	10.0	25.0	57.0	152.0	65.2
Other agriculture	0	--	--	--	--	--	--
USGS agriculture/forest	5	.0	5.0	18.0	24.0	24.0	14.2
Other agriculture/forest	0	--	--	--	--	--	--
USGS forest	215	1.0	2.0	4.0	7.0	14.0	6.9
Other forest	0	--	--	--	--	--	--
USGS urban	76	13.0	51.5	148.0	394.5	817.0	283.4
Other urban	0	--	--	--	--	--	--
Relatively Homogeneous Unit:							
Ag1	139	9.0	22.0	50.0	138.0	254.0	133.1
Ag2	0	--	--	--	--	--	--
Ag3	156	3.0	6.0	12.3	37.8	84.0	32.1
Ag4	0	--	--	--	--	--	--
Ag15	0	--	--	--	--	--	--
Ag23	8	--	--	103.0	--	--	136.3
Ag24	0	--	--	--	--	--	--
Ag25	0	--	--	--	--	--	--
Ag27	0	--	--	--	--	--	--
Ag28	0	--	--	--	--	--	--
AF5	0	--	--	--	--	--	--
AF12	0	--	--	--	--	--	--
AF20	4	--	--	14.5	--	--	13.3
AF26	1	--	--	18.0	--	--	18.0
F6	0	--	--	--	--	--	--
F7	0	--	--	--	--	--	--
F8	0	--	--	--	--	--	--
F13	0	--	--	--	--	--	--
F14	0	--	--	--	--	--	--
F16	0	--	--	--	--	--	--
F17	0	--	--	--	--	--	--
F18	0	--	--	--	--	--	--
F19	0	--	--	--	--	--	--
F21	0	--	--	--	--	--	--
F22	187	1.0	2.0	4.0	6.0	13.0	6.4
U9	76	13.0	51.5	148.0	394.5	817.0	283.4
U10	0	--	--	--	--	--	--
U11	0	--	--	--	--	--	--

[1]USGS, U.S. Geological Survey National Water Inventory System (NWIS) data; Other, STORET, Milwaukee Metropolitan Sewerage District, and/or Green Bay Metropolitan Sewerage District data.

Appendix 4.11. Summary statistics for constituents in ground water, by category, for the Western Lake Michigan Drainages (WMIC) study unit, water years 1971–90: dissolved nitrite plus nitrate

[--, no data available or, if less than 10 values, only median and mean calculated; percentiles and mean are expressed in milligrams per liter (mg/L) and are based on one sample (the most recent one collected) from each well; highest reported minimum detection limit = <0.1 mg/L]

Category	Number of samples/wells	Percentile					Mean
		10th	25th	50th (median)	75th	90th	
WMIC	949/789	0.03	0.05	0.40	3.90	9.40	3.08
Source[1]							
NWIS	404	.01	.04	.05	.535	3.60	1.14
GIN	385	.10	.30	2.90	7.00	13.20	5.10
STORET	0	--	--	--	--	--	--
Well type:							
Commercial	13	.01	.02	.05	.16	.23	.11
Domestic	636	.03	.10	.60	4.40	9.60	3.26
Irrigation	8	--	--	.12	--	--	2.81
Industrial	13	.01	.02	.03	.09	.60	4.64
Public supply	72	.02	.03	.48	2.75	9.90	2.59
Recreation	5	--	--	.05	--	--	.66
Stock	13	.04	.05	2.30	4.60	10.00	3.57
Institution	9	--	--	.07	--	--	1.12
Other	3	--	--	.05	--	--	.15
Aquifer:							
Basement complex	27	.05	.05	.10	.30	.52	.27
Sandstone	104	.01	.02	.05	2.00	6.80	1.84
Silurian dolomite	188	.01	.05	.24	1.65	5.40	1.59
Sand and gravel	159	.03	.05	.06	1.50	5.40	2.01
Well depth (meters):							
0–15.2	74	.10	.35	3.10	6.60	12.30	5.18
15.3–30.5	124	.03	.05	.60	4.75	9.10	3.61
30.6–45.7	96	.03	.05	.46	3.60	9.20	2.58
45.8–61.0	75	.01	.02	.15	1.90	5.80	1.80
>61.0	197	.01	.03	.07	.70	4.60	1.25
General land use:							
Agriculture	521	.02	.06	.32	3.70	8.60	2.74
Agriculture/forest	98	.60	2.20	5.45	12.00	20.80	8.31
Forest	97	.05	.05	.23	.84	3.60	1.14
Urban	44	.01	.02	.05	.08	.29	.35
Wetland	0	--	--	--	--	--	--
Texture of surficial deposits:							
Clay	334	.01	.05	.20	1.90	5.80	1.88
Clay/sand	10	.03	.05	.27	2.50	3.90	1.26
Loam	36	.05	.10	.10	1.15	4.40	1.23
Loam/sand and gravel	11	.05	.05	.70	2.50	3.70	1.68
Sand/sand and gravel	369	.05	.09	1.60	6.50	13.00	4.50

Appendix 4.11. Summary statistics for constituents in ground water, by category, for the Western Lake Michigan Drainages (WMIC) study unit, water years 1971–90: dissolved nitrite plus nitrate—Continued

Category	Number of samples/wells	Percentile					Mean
		10th	25th	50th (median)	75th	90th	
Bedrock type:							
Carbonate	463	.02	.05	.20	3.00	8.00	2.47
Igneous/metamorphic	155	.05	.05	.71	5.40	13.20	4.18
Shale	22	.01	.03	.10	.10	.30	.26
Sandstone	120	.05	.33	2.75	6.50	12.90	4.73
Relatively Homogenous Unit:							
Ag1	241	.02	.09	.30	2.20	6.40	2.24
Ag2	25	.10	.10	.10	.80	3.70	.82
Ag3	152	.03	.05	.68	6.40	12.00	3.74
Ag4	1	--	--	.10	--	--	.10
Ag15	4	--	--	1.30	--	--	3.03
Ag23	22	.01	.03	.10	.10	.30	.26
Ag24	11	.05	.06	.30	3.30	5.60	2.15
Ag25	24	.73	2.60	5.50	10.00	15.70	7.29
Ag27	10	.03	.05	.27	2.50	3.90	1.26
Ag28	31	.02	.10	1.00	3.80	5.90	2.19
AF5	0	--	--	--	--	--	--
AF12	0	--	--	--	--	--	--
AF20	54	.60	3.20	6.00	14.60	21.10	9.74
AF26	44	.60	1.80	3.25	9.90	17.60	6.55
F6	0	--	--	--	--	--	--
F7	0	--	--	--	--	--	--
F8	0	--	--	--	--	--	--
F13	0	--	--	--	--	--	--
F14	0	--	--	--	--	--	--
F16	0	--	--	--	--	--	--
F17	7	--	--	.70	--	--	.91
F18	0	--	--	--	--	--	--
F19	56	.05	.05	.16	1.35	3.60	1.10
F21	0	--	--	--	--	--	--
F22	34	.05	.05	.28	.80	3.00	1.25
U9	40	.01	.02	.05	.09	.32	.38
U10	4	--	--	.05	--	--	.38
U11	0	--	--	--	--	--	--

[1]NWIS, U.S. Geological Survey National Water Inventory System; GIN, Wisconsin Department of Natural Resources Groundwater Inventory Network; STORET, U.S. Environmental Protection Agency Storage and Retrieval System.

Appendix 4.12. Summary statistics for constituents in ground water, by category, for the Western Lake Michigan Drainages (WMIC) study unit, water years 1971–90: dissolved nitrite

[--, no data available or, if less than 10 values, only median and mean calculated; percentiles and mean are expressed in milligrams per liter (mg/L) and are based on one sample (the most recent one collected) from each well; highest reported minimum detection limit = <0.01 mg/L]

Category	Number of samples/wells	Percentile					Mean
		10th	25th	50th (median)	75th	90th	
WMIC	350/337	0.005	0.005	0.005	0.01	0.01	0.009
Source[1]							
NWIS	337	.005	.005	.005	.01	.01	.009
GIN	0	--	--	--	--	--	--
STORET	0	--	--	--	--	--	--
Well type:							
Commercial	9	--	--	.005	--	--	.008
Domestic	239	.005	.005	.005	.005	.01	.009
Irrigation	4	--	--	.005	--	--	.006
Industrial	10	.005	.005	.008	.01	.03	.01
Public supply	46	.005	.005	.005	.01	.02	.01
Recreation	4	--	--	.005	--	--	.006
Stock	12	.005	.005	.005	.005	.005	.005
Institution	7	--	--	.005	--	--	.02
Other	3	--	--	.005	--	--	.01
Aquifer:							
Basement complex	21	.005	.005	.005	.005	.01	.007
Sandstone	85	.005	.005	.005	.005	.01	.007
Silurian dolomite	117	.005	.005	.005	.01	.01	.01
Sand and gravel	113	.005	.005	.005	.005	.02	.008
Well depth (meters):							
0–15.2	23	.005	.005	.005	.01	.01	.008
15.3–30.5	66	.005	.005	.005	.005	.01	.006
30.6–45.7	62	.005	.005	.005	.005	.01	.009
45.8–61.0	47	.005	.005	.005	.01	.03	.01
>61.0	139	.005	.005	.005	.01	.01	.01
General land use:							
Agriculture	217	.005	.005	.005	.009	.01	.009
Agriculture/forest	11	.005	.005	.005	.01	.01	.009
Forest	58	.005	.005	.005	.005	.005	.006
Urban	35	.005	.005	.005	.01	.01	.01
Texture of surficial deposits:							
Clay	137	.005	.005	.005	.01	.02	.01
Clay/sand	8	--	--	.005	--	--	.005
Loam	7	--	--	.005	--	--	.01
Loam/sand and gravel	7	.005	.005	.005	.01	.01	.006
Sand/sand and gravel	162	.005	.005	.005	.005	.01	.006

Appendix 4.12. Summary statistics for constituents in ground water, by category, for the Western Lake Michigan Drainages (WMIC) study unit, water years 1971–90: dissolved nitrite—Continued

Category	Number of samples/wells	Percentile					Mean
		10th	25th	50th (median)	75th	90th	
Bedrock type:							
Carbonate	203	.005	.005	.005	.01	.01	.01
Igneous/metamorphic	65	.005	.005	.005	.005	.005	.007
Shale	11	.005	.005	.005	.005	.01	.006
Sandstone	42	.005	.005	.005	.01	.01	.009
Relatively Homogenous Unit:							
Ag1	87	.005	.005	.005	.01	.02	.01
Ag2	2	--	--	.005	--	--	.005
Ag3	79	.005	.005	.005	.005	.01	.007
Ag4	0	--	--	--	--	--	--
Ag15	1	--	--	.005	--	--	.005
Ag23	11	.005	.005	.005	.005	.01	.006
Ag24	5	--	--	.01	--	--	.01
Ag25	16	.005	.005	.005	.005	.005	.005
Ag27	8	--	--	.005	--	--	.005
Ag28	8	--	--	.008	--	--	.02
AF5	0	--	--	--	--	--	--
AF12	0	--	--	--	--	--	--
AF20	6	--	--	.005	--	--	.009
AF26	5	--	--	.01	--	--	.008
F6	0	--	--	--	--	--	--
F7	0	--	--	--	--	--	--
F8	0	--	--	--	--	--	--
F13	0	--	--	--	--	--	--
F14	0	--	--	--	--	--	--
F16	0	--	--	--	--	--	--
F17	6	--	--	.005	--	--	.007
F18	0	--	--	--	--	--	--
F19	35	.005	.005	.005	.005	.005	.007
F21	0	--	--	--	--	--	--
F22	17	.005	.005	.005	.005	.005	.005
U9	31	.005	.005	.005	.005	.01	.02
U10	4	--	--	.005	--	--	.005
U11	0	--	--	--	--	--	--

[1]NWIS, U.S. Geological Survey National Water Inventory System; GIN, Wisconsin Department of Natural Resources Groundwater Inventory Network; STORET, U.S. Environmental Protection Agency Storage and Retrieval System.

Appendix 4.13. Summary statistics for constituents in ground water, by category, for the Western Lake Michigan Drainages (WMIC) study unit, water years 1971–90: total Kjeldahl nitrogen (ammonia plus organics)

[--, no data available or, if less than 10 values, only median and mean calculated; percentiles and mean are expressed in milligrams per liter (mg/L) and are based on one sample (the most recent one collected) from each well; highest reported minimum detection limit = <0.2 mg/L]

Category	Number of samples/wells	Percentile					Mean
		10th	25th	50th (median)	75th	90th	
WMIC	93/80	0.05	0.05	0.10	0.32	0.54	0.31
Source[1]							
NWIS	47	.05	.06	.10	.33	.70	.24
GIN	8	--	--	.30	--	--	1.04
STORET	25	.05	.05	.05	.26	.42	.19
Well type:							
Commercial	0	--	--	--	--	--	--
Domestic	44	.05	.05	.10	.29	.57	.35
Irrigation	0	--	--	--	--	--	--
Industrial	0	--	--	--	--	--	--
Public supply	2	--	--	.17	--	--	.17
Recreation	1	--	--	.20	--	--	.20
Stock	3	--	--	.11	--	--	.49
Institution	1	--	--	.05	--	--	.05
Other	0	--	--	--	--	--	--
Aquifer:							
Basement complex	6	--	--	.10	--	--	.17
Sandstone	18	.05	.10	.10	.40	.70	.26
Silurian dolomite	7	--	--	.25	--	--	.28
Sand and gravel	20	.05	.06	.10	.39	1.10	.55
Well depth (meters):							
0–15.2	33	.05	.05	.12	.27	.57	.38
15.3–30.5	20	.05	.05	.08	.40	.70	.26
30.6–45.7	7	--	--	.10	--	--	.36
45.8–61.0	4	--	--	.20	--	--	.23
>61.0	16	.05	.10	.10	.37	.50	.21
General land use:							
Agriculture	8	--	--	.20	--	--	1.13
Agriculture/forest	7	--	--	.10	--	--	.18
Forest	43	.05	.05	.10	.30	.50	.22
Urban	3	--	--	.40	--	--	.38
Texture of surficial deposits:							
Clay	7	--	--	.40	--	--	1.18
Clay/sand	0	--	--	--	--	--	--
Loam	7	--	--	.10	--	--	.25
Loam/sand and gravel	1	--	--	.07	--	--	.07
Sand/sand and gravel	46	.05	.05	.10	.28	.57	.23

Appendix 4.13. Summary statistics for constituents in ground water, by category, for the Western Lake Michigan Drainages (WMIC) study unit, water years 1971–90: total Kjeldahl nitrogen (ammonia plus organics)—Continued

Category	Number of samples/wells	Percentile					Mean
		10th	25th	50th (median)	75th	90th	
Bedrock type:							
Carbonate	26	.05	.10	.24	.29	.50	.30
Igneous/metamorphic	29	.05	.05	.07	.16	.70	.20
Shale	0	--	--	--	--	--	--
Sandstone	6	--	--	.20	--	--	1.21
Relatively Homogenous Unit:							
Ag1	0	--	--	--	--	--	--
Ag2	0	--	--	--	--	--	--
Ag3	3	--	--	.20	--	--	.48
Ag4	0	--	--	--	--	--	--
Ag15	0	--	--	--	--	--	--
Ag23	0	--	--	--	--	--	--
Ag24	0	--	--	--	--	--	--
Ag25	0	--	--	--	--	--	--
Ag27	0	--	--	--	--	--	--
Ag28	4	--	--	.35	--	--	1.78
AF5	0	--	--	--	--	--	--
AF12	4	--	--	.10	--	--	.10
AF20	1	--	--	.70	--	--	.70
AF26	2	--	--	.08	--	--	.08
F6	0	--	--	--	--	--	--
F7	3	--	--	.40	--	--	.46
F8	0	--	--	--	--	--	--
F13	2	--	--	.25	--	--	.25
F14	10	.05	.05	.17	.42	.50	.23
F16	0	--	--	--	--	--	--
F17	1	--	--	.07	--	--	.07
F18	4	--	--	.13	--	--	.14
F19	8	--	--	.06	--	--	.11
F21	0	--	--	--	--	--	--
F22	15	.05	.05	.06	.16	.89	.25
U9	3	--	--	.40	--	--	.38
U10	0	--	--	--	--	--	--
U11	0	--	--	--	--	--	--

[1]NWIS, U.S. Geological Survey National Water Inventory System; GIN, Wisconsin Department of Natural Resources Groundwater Inventory Network; STORET, U.S. Environmental Protection Agency Storage and Retrieval System.

Appendix 4.14. Summary statistics for constituents in ground water, by category, for the Western Lake Michigan Drainages (WMIC) study unit, water years 1971–90: total ammonia

[--, no data available or, if less than 10 values, only median and mean calculated; percentiles and mean are expressed in milligrams per liter (mg/L) and are based on one sample (the most recent one collected) from each well; highest reported minimum detection limit = <0.05 mg/L]

Category	Number of samples/wells	Percentile					Mean
		10th	25th	50th (median)	75th	90th	
WMIC	62/53	0.01	0.03	0.05	0.09	0.15	0.08
Source[1]							
NWIS	34	.01	.02	.06	.09	.14	.08
GIN	0	--	--	--	--	--	--
STORET	19	.03	.03	.03	.08	.23	.09
Well type:							
Commercial	0	--	--	--	--	--	--
Domestic	22	.01	.03	.03	.08	.23	.10
Irrigation	0	--	--	--	--	--	--
Industrial	0	--	--	--	--	--	--
Public supply	1	--	--	.01	--	--	.01
Recreation	1	--	--	.08	--	--	.08
Stock	1	--	--	.01	--	--	.01
Institution	2	--	--	.03	--	--	.03
Other	0	--	--	--	--	--	--
Aquifer:							
Basement complex	2	--	--	.04	--	--	.04
Sandstone	17	.03	.04	.08	.12	.15	.08
Silurian dolomite	4	--	--	.05	--	--	.05
Sand and gravel	11	.005	.005	.01	.07	.09	.08
Well depth (meters):							
0–15.2	17	.005	.03	.05	.08	.14	.06
15.3–30.5	15	.005	.02	.03	.11	.58	.11
30.6–45.7	4	--	--	.06	--	--	.07
45.8–61.0	3	--	--	.01	--	--	.05
>61.0	14	.04	.05	.08	.09	.12	.08
General land use:							
Agriculture	1	--	--	.08	--	--	.08
Agriculture/forest	6	.01	.01	.06	.12	.15	.07
Forest	32	.01	.03	.05	.08	.18	.09
Urban	0	--	--	--	--	--	--
Texture of surficial deposits:							
Clay	0	--	--	--	--	--	--
Clay/sand	0	--	--	--	--	--	--
Loam	7	--	--	.08	--	--	.08
Loam/sand and gravel	0	--	--	--	--	--	--
Sand/sand and gravel	32	.01	.03	.05	.08	.18	.09

Appendix 4.14. Summary statistics for constituents in ground water, by category, for the Western Lake Michigan Drainages (WMIC) study unit, water years 1971–90: total ammonia—Continued

Category	Number of samples/wells	Percentile 10th	25th	50th (median)	75th	90th	Mean
Bedrock type:							
Carbonate	17	.02	.03	.07	.11	.15	.07
Igneous/metamorphic	21	.01	.03	.03	.07	.23	.10
Shale	0	--	--	--	--	--	--
Sandstone	1	--	--	.01	--	--	.01
Relatively Homogenous Unit:							
Ag1	0	--	--	--	--	--	--
Ag2	0	--	--	--	--	--	--
Ag3	1	--	--	.08	--	--	.08
Ag4	0	--	--	--	--	--	--
Ag15	0	--	--	--	--	--	--
Ag23	0	--	--	--	--	--	--
Ag24	0	--	--	--	--	--	--
Ag25	0	--	--	--	--	--	--
Ag27	0	--	--	--	--	--	--
Ag28	0	--	--	--	--	--	--
AF5	0	--	--	--	--	--	--
AF12	4	--	--	.10	--	--	.10
AF20	1	--	--	.01	--	--	.01
AF26	1	--	--	.01	--	--	.01
F6	0	--	--	--	--	--	--
F7	3	--	--	.03	--	--	.06
F8	0	--	--	--	--	--	--
F13	2	--	--	.08	--	--	.08
F14	7	--	--	.06	--	--	.06
F16	0	--	--	--	--	--	--
F17	0	--	--	--	--	--	--
F18	5	--	--	.06	--	--	.09
F19	2	--	--	.05	--	--	.05
F21	0	--	--	--	--	--	--
F22	13	.01	.03	.03	.05	.58	.11
U9	0	--	--	--	--	--	--
U10	0	--	--	--	--	--	--
U11	0	--	--	--	--	--	--

[1]NWIS, U.S. Geological Survey National Water Inventory System; GIN, Wisconsin Department of Natural Resources Groundwater Inventory Network; STORET, U.S. Environmental Protection Agency Storage and Retrieval System.

Appendix 4.15. Summary statistics for constituents in ground water, by category, for the Western Lake Michigan Drainages (WMIC) study unit, water years 1971–90: dissolved ammonia

[--, no data available or, if less than 10 values, only median and mean calculated; percentiles and mean are expressed in milligrams per liter (mg/L) and are based on one sample (the most recent one collected) from each well; highest reported minimum detection limit = <0.01 mg/L]

Category	Number of samples/wells	Percentile					Mean
		10th	25th	50th (median)	75th	90th	
WMIC	200/184	0.005	0.01	0.06	0.16	0.32	0.22
Source[1]							
NWIS	164	.005	.01	.05	.150	.29	.16
GIN	20	.10	.10	.10	.24	3.30	.72
STORET	0	--	--	--	--	--	--
Well type:							
Commercial	5	--	--	.18	--	--	.18
Domestic	113	.005	.005	.10	.18	.36	.27
Irrigation	3	--	--	.04	--	--	.03
Industrial	7	--	--	.18	--	--	.57
Public supply	29	.02	.04	.06	.11	.15	.08
Recreation	3	--	--	.15	--	--	.41
Stock	7	--	--	.005	--	--	.01
Institution	4	--	--	.02	--	--	.07
Other	3	--	--	.28	--	--	.40
Aquifer:							
Basement complex	12	.005	.005	.015	.03	.03	.02
Sandstone	74	.005	.005	.05	.15	.23	.18
Silurian dolomite	26	.40	.10	.11	.21	.34	.16
Sand and gravel	61	.005	.005	.04	.18	.39	.26
Well depth (meters):							
0–15.2	23	.005	.04	.10	.10	.90	.61
15.3–30.5	39	.005	.005	.04	.15	.36	.14
30.6–45.7	33	.005	.005	.03	.13	.21	.09
45.8–61.0	21	.005	.02	.10	.17	.27	.12
>61.0	68	.005	.03	.09	.18	.34	.23
General land use:							
Agriculture	115	.005	.02	.10	.18	.34	.27
Agriculture/forest	10	.005	.005	.008	.01	.04	.01
Forest	32	.005	.005	.01	.04	.09	.08
Urban	21	.05	.09	.12	.20	.30	.28
Texture of surficial deposits:							
Clay	84	.02	.06	.12	.21	.36	.32
Clay/sand	8	--	--	.05	--	--	.51
Loam	7	--	--	.03	--	--	.06
Loam/sand and gravel	1	--	--	.27	--	--	.27
Sand/sand and gravel	78	.005	.005	.01	.09	.18	.10

Appendix 4.15. Summary statistics for constituents in ground water, by category, for the Western Lake Michigan Drainages (WMIC) study unit, water years 1971–90: dissolved ammonia—Continued

Category	Number of samples/wells	Percentile					Mean
		10th	25th	50th (median)	75th	90th	
Bedrock type:							
Carbonate	84	.03	.09	.12	.19	.30	.21
Igneous/metamorphic	40	.005	.005	.008	.04	.14	.07
Shale	11	.05	.07	.20	.34	.55	.27
Sandstone	43	.005	.005	.01	.05	.10	.38
Relatively Homogenous Unit:							
Ag1	46	.02	.08	.13	.21	.34	.16
Ag2	2	--	--	.15	--	--	.15
Ag3	15	.03	.07	.10	.15	.29	.24
Ag4	0	--	--	--	--	--	--
Ag15	1	--	--	.27	--	--	.27
Ag23	11	.05	.07	.20	.34	.55	.27
Ag24	5	--	--	.02	--	--	.03
Ag25	16	.005	.005	.005	.005	.02	.009
Ag27	8	--	--	.05	--	--	.51
Ag28	11	.01	.02	.08	.10	5.70	1.08
AF5	0	--	--	--	--	--	--
AF12	0	--	--	--	--	--	--
AF20	7	--	--	.005	--	--	.01
AF26	3	--	--	.01	--	--	.02
F6	0	--	--	--	--	--	--
F7	0	--	--	--	--	--	--
F8	0	--	--	--	--	--	--
F13	0	--	--	--	--	--	--
F14	0	--	--	--	--	--	--
F16	0	--	--	--	--	--	--
F17	0	--	--	--	--	--	--
F18	0	--	--	--	--	--	--
F19	17	.005	.005	.02	.04	.06	.08
F21	0	--	--	--	--	--	--
F22	15	.005	.005	.005	.03	.18	.08
U9	16	.04	.06	.12	.19	.30	.27
U10	4	--	--	.21	--	--	.37
U11	1	--	--	.10	--	--	.10

[1]NWIS, U.S. Geological Survey National Water Inventory System; GIN, Wisconsin Department of Natural Resources Groundwater Inventory Network; STORET, U.S. Environmental Protection Agency Storage and Retrieval System.

Appendix 4.16. Summary statistics for constituents in ground water, by category, for the Western Lake Michigan Drainages (WMIC) study unit, water years 1971–90: total phosphorus

[--, no data available or, if less than 10 values, only median and mean calculated; percentiles and mean are expressed in milligrams per liter (mg/L) and are based on one sample (the most recent one collected) from each well; highest reported minimum detection limit = <0.03 mg/L]

Category	Number of samples/wells	Percentile					Mean
		10th	25th	50th (median)	75th	90th	
WMIC	138/128	0.01	0.01	0.01	0.03	0.06	0.03
Source[1]							
NWIS	125	.01	.01	.01	.03	.06	.03
GIN	3	--	--	.02	--	--	.03
STORET	0	--	--	--	--	--	--
Well type:		--	--	--	--	--	--
Commercial	0	--	--	--	--	--	--
Domestic	82	.01	.01	.01	.03	.06	.03
Irrigation	0	--	--	--	--	--	--
Industrial	1	--	--	.06	--	--	.06
Public supply	6	--	--	.01	--	--	.01
Recreation	1	--	--	.01	--	--	.01
Stock	8	--	--	.01	--	--	.00
Institution	1	--	--	.02	--	--	.02
Other	0	--	--	--	--	--	--
Aquifer:							
Basement complex	21	.01	.01	.01	.02	.05	.02
Sandstone	40	.01	.01	.01	.02	.06	.03
Silurian dolomite	9	--	--	.01	--	--	.02
Sand and gravel	56	.01	.01	.01	.03	.07	.03
Well depth (meters):							
0–15.2	21	.01	.01	.01	.03	.03	.02
15.3–30.5	37	.01	.01	.01	.02	.09	.03
30.6–45.7	28	.01	.01	.02	.03	.14	.04
45.8–61.0	9	--	--	.02	--	--	.03
>61.0	33	.01	.01	.01	.02	.05	.02
General land use:							
Agriculture	30	.01	.01	.01	.01	.05	.02
Agriculture/forest	8	.01	.01	.01	.02	.28	.04
Forest	75	.01	.01	.01	.03	.07	.03
Urban	3	--	--	.06	--	--	.04
Texture of surficial deposits:							
Clay	5	--	--	.01	--	--	.03
Clay/sand	4	--	--	.04	--	--	.07
Loam	7	--	--	.01	--	--	.01
Loam/sand and gravel	2	--	--	.01	--	--	.01
Sand/sand and gravel	98	.01	.01	.01	.03	.07	.03

Appendix 4.16. Summary statistics for constituents in ground water, by category, for the Western Lake Michigan Drainages (WMIC) study unit, water years 1971–90: total phosphorus—Continued

Category	Number of samples/wells	Percentile					Mean
		10th	25th	50th (median)	75th	90th	
Bedrock type:							
Carbonate	23	.01	.01	.01	.02	.06	.02
Igneous/metamorphic	69	.01	.01	.01	.03	.07	.03
Shale	0	--	--	--	--	--	--
Sandstone	24	.01	.01	.01	.02	.17	.04
Relatively Homogenous Unit:							
Ag1	0	--	--	--	--	--	--
Ag2	0	--	--	--	--	--	--
Ag3	8	--	--	.01	--	--	.01
Ag4	0	--	--	--	--	--	--
Ag15	1	--	--	.01	--	--	.01
Ag23	0	--	--	--	--	--	--
Ag24	0	--	--	--	--	--	--
Ag25	15	.01	.01	.01	.01	.04	.03
Ag27	4	--	--	.04	--	--	.07
Ag28	2	--	--	.01	--	--	.01
AF5	0	--	--	--	--	--	--
AF12	4	--	--	.01	--	--	.01
AF20	1	--	--	.01	--	--	.01
AF26	3	--	--	.01	--	--	.10
F6	0	--	--	--	--	--	--
F7	3	--	--	.01	--	--	.01
F8	0	--	--	--	--	--	--
F13	2	--	--	.05	--	--	.05
F14	3	--	--	.01	--	--	.01
F16	0	--	--	--	--	--	--
F17	1	--	--	.01	--	--	.01
F18	4	--	--	.01	--	--	.03
F19	9	--	--	.01	--	--	.02
F21	0	--	--	--	--	--	--
F22	53	.01	.01	.01	.03	.07	.03
U9	3	--	--	.06	--	--	.04
U10	0	--	--	--	--	--	--
U11	0	--	--	--	--	--	--

[1]NWIS, U.S. Geological Survey National Water Inventory System; GIN, Wisconsin Department of Natural Resources Groundwater Inventory Network; STORET, U.S. Environmental Protection Agency Storage and Retrieval System.

Appendix 4.17. Summary statistics for constituents in ground water, by category, for the Western Lake Michigan Drainages (WMIC) study unit, water years 1971–90: dissolved phosphorus

[--, no data available or, if less than 10 values, only median and mean calculated; percentiles and mean are expressed in milligrams per liter (mg/L) and are based on one sample (the most recent one collected) from each well; highest reported minimum detection limit = <0.01 mg/L]

Category	Number of samples/wells	Percentile					Mean
		10th	25th	50th (median)	75th	90th	
WMIC	118/108	0.005	0.005	0.01	0.03	0.05	0.02
Source[1]							
NWIS	108	.005	.005	.01	.03	.05	.02
GIN	0	--	--	--	--	--	--
STORET	0	--	--	--	--	--	--
Well type:		--	--				
Commercial	4	--	--	.04	--	--	.04
Domestic	66	.005	.005	.01	.02	.04	.02
Irrigation	1	--	--	.09	--	--	.09
Industrial	6	--	--	.01	--	--	.03
Public supply	20	.005	.005	.008	.03	.04	.02
Recreation	2	--	--	.01	--	--	.01
Stock	1	--	--	.01	--	--	.01
Institution	0	--	--	--	--	--	--
Other	2	--	--	.05	--	--	.05
Aquifer:							
Basement complex	9	--	--	.02	--	--	.02
Sandstone	36	.005	.005	.008	.02	.04	.02
Silurian dolomite	18	.005	.005	.005	.005	.01	.006
Sand and gravel	45	.005	.01	.01	.03	.06	.03
Well depth (meters):							
0–15.2	15	.005	.01	.01	.03	.04	.02
15.3–30.5	28	.005	.005	.01	.03	.07	.02
30.6–45.7	16	.005	.005	.005	.03	.04	.02
45.8–61.0	9	--	--	.005	--	--	.01
>61.0	40	.005	.005	.01	.02	.05	.02
General land use:							
Agriculture	49	.005	.005	.005	.01	.03	.01
Agriculture/forest	8	--	--	.04	--	--	.03
Forest	34	.005	.01	.02	.03	.06	.03
Urban	13	.005	.005	.005	.01	.05	.02
Texture of surficial deposits:							
Clay	49	.005	.005	.005	.01	.02	.01
Clay/sand	0	--	--	--	--	--	--
Loam	5	--	--	.01	--	--	.02
Loam/sand and gravel	0	--	--	--	--	--	--
Sand/sand and gravel	50	.005	.01	.02	.03	.07	.03

Appendix 4.17. Summary statistics for constituents in ground water, by category, for the Western Lake Michigan Drainages (WMIC) study unit, water years 1971–90: dissolved phosphorus—Continued

Category	Number of samples/wells	Percentile					Mean
		10th	25th	50th (median)	75th	90th	
Bedrock type:							
Carbonate	49	.005	.005	.005	.01	.03	.01
Igneous/metamorphic	40	.005	.01	.02	.03	.06	.03
Shale	8	--	--	.005	--	--	.01
Sandstone	7	.01	.01	.02	.03	.05	.02
Relatively Homogenous Unit:							
Ag1	30	.005	.005	.005	.01	.02	.01
Ag2	2	--	--	.005	--	--	.005
Ag3	4	--	--	.015	--	--	.03
Ag4	0	--	--	--	--	--	--
Ag15	0	--	--	--	--	--	--
Ag23	0	--	--	--	--	--	--
Ag24	8	--	--	.005	--	--	.01
Ag25	3	--	--	.02	--	--	.03
Ag27	0	--	--	--	--	--	--
Ag28	0	--	--	--	--	--	--
AF5	2	--	--	.02	--	--	.02
AF12	0	--	--	--	--	--	--
AF20	6	--	--	.04	--	--	.03
AF26	2	--	--	.02	--	--	.02
F6	0	--	--	--	--	--	--
F7	0	--	--	--	--	--	--
F8	0	--	--	--	--	--	--
F13	0	--	--	--	--	--	--
F14	0	--	--	--	--	--	--
F16	0	--	--	--	--	--	--
F17	0	--	--	--	--	--	--
F18	0	--	--	--	--	--	--
F19	14	.005	.01	.01	.01	.02	.01
F21	0	--	--	--	--	--	--
F22	20	.005	.01	.03	.04	.09	.04
U9	9	--	--	.005	--	--	.01
U10	4	--	--	.005	--	--	.03
U11	0	--	--	--	--	--	--

[1]NWIS, U.S. Geological Survey National Water Inventory System; GIN, Wisconsin Department of Natural Resources Groundwater Inventory Network; STORET, U.S. Environmental Protection Agency Storage and Retrieval System.

Appendix 4.18. Summary statistics for constituents in ground water, by category, for the Western Lake Michigan Drainages (WMIC) study unit, water years 1971–90: total orthophosphate

[--, no data available or, if less than 10 values, only median and mean calculated; percentiles and mean are expressed in milligrams per liter (mg/L) and are based on one sample (the most recent one collected) from each well; highest reported minimum detection limit = <0.01 mg/L]

Category	Number of samples/wells	Percentile					Mean
		10th	25th	50th (median)	75th	90th	
WMIC	34/27	0.005	0.005	0.005	0.005	0.03	0.01
Source[1]							
NWIS	27	.005	.005	.005	.005	.03	.01
GIN	0	--	--	--	--	--	--
STORET	0	--	--	--	--	--	--
Well type:							
Commercial	0	--	--	--	--	--	--
Domestic	0	--	--	--	--	--	--
Irrigation	0	--	--	--	--	--	--
Industrial	0	--	--	--	--	--	--
Public supply	0	--	--	--	--	--	--
Recreation	1	--	--	.005	--	--	.005
Stock	0	--	--	--	--	--	--
Institution	0	--	--	--	--	--	--
Other	26	.005	.005	.005	.005	.03	.01
Aquifer:							
Basement complex	2	--	--	.005	--	--	.005
Sandstone	17	.005	.005	.005	.005	.01	.007
Silurian dolomite	4	--	--	.008	--	--	.005
Sand and gravel	4	--	--	.04	--	--	.04
Well depth (meters):							
0–15.2	3	--	--	.07	--	--	.05
15.3–30.5	5	--	--	.005	--	--	.006
30.6–45.7	2	--	--	.005	--	--	.005
45.8–61.0	3	--	--	.005	--	--	.007
>61.0	14	.005	.005	.005	.005	.01	.007
General land use:							
Agriculture	1	--	--	.005	--	--	.005
Agriculture/forest	4	--	--	.005	--	--	.006
Forest	13	.005	.005	.005	.005	.07	.02
Urban	0	--	--	--	--	--	--
Texture of surficial deposits:							
Clay	0	--	--	--	--	--	--
Clay/sand	0	--	--	--	--	--	--
Loam	7	--	--	.005	--	--	.006
Loam/sand and gravel	0	--	--	--	--	--	--
Sand/sand and gravel	11	.005	.005	.005	.01	.07	.02

Appendix 4.18. Summary statistics for constituents in ground water, by category, for the Western Lake Michigan Drainages (WMIC) study unit, water years 1971–90: total orthophosphate—Continued

Category	Number of samples/wells	Percentile					Mean
		10th	25th	50th (median)	75th	90th	
Bedrock type:							
Carbonate	13	.005	.005	.005	.005	.01	.006
Igneous/metamorphic	5	--	--	.005	--	--	.03
Shale	0	--	--	--	--	--	--
Sandstone	0	--	--	--	--	--	--
Relatively Homogenous Unit:							
Ag1	0	--	--	--	--	--	--
Ag2	0	--	--	--	--	--	--
Ag3	1	--	--	.005	--	--	.005
Ag4	0	--	--	--	--	--	--
Ag15	0	--	--	--	--	--	--
Ag23	0	--	--	--	--	--	--
Ag24	0	--	--	--	--	--	--
Ag25	0	--	--	--	--	--	--
Ag27	0	--	--	--	--	--	--
Ag28	0	--	--	--	--	--	--
AF5	0	--	--	--	--	--	--
AF12	4	--	--	.005	--	--	.006
AF20	0	--	--	--	--	--	--
AF26	0	--	--	--	--	--	--
F6	0	--	--	--	--	--	--
F7	3	--	--	.005	--	--	.005
F8	0	--	--	--	--	--	--
F13	2	--	--	.005	--	--	.005
F14	3	--	--	.005	--	--	.007
F16	0	--	--	--	--	--	--
F17	0	--	--	--	--	--	--
F18	4	--	--	.04	--	--	.04
F19	1	--	--	.005	--	--	.005
F21	0	--	--	--	--	--	--
F22	0	--	--	--	--	--	--
U9	0	--	--	--	--	--	--
U10	0	--	--	--	--	--	--
U11	0	--	--	--	--	--	--

[1]NWIS, U.S. Geological Survey National Water Inventory System; GIN, Wisconsin Department of Natural Resources Groundwater Inventory Network; STORET, U.S. Environmental Protection Agency Storage and Retrieval System.

Appendix 4.19. Summary statistics for constituents in ground water, by category, for the Western Lake Michigan Drainages (WMIC) study unit, water years 1971–90: dissolved orthophosphate

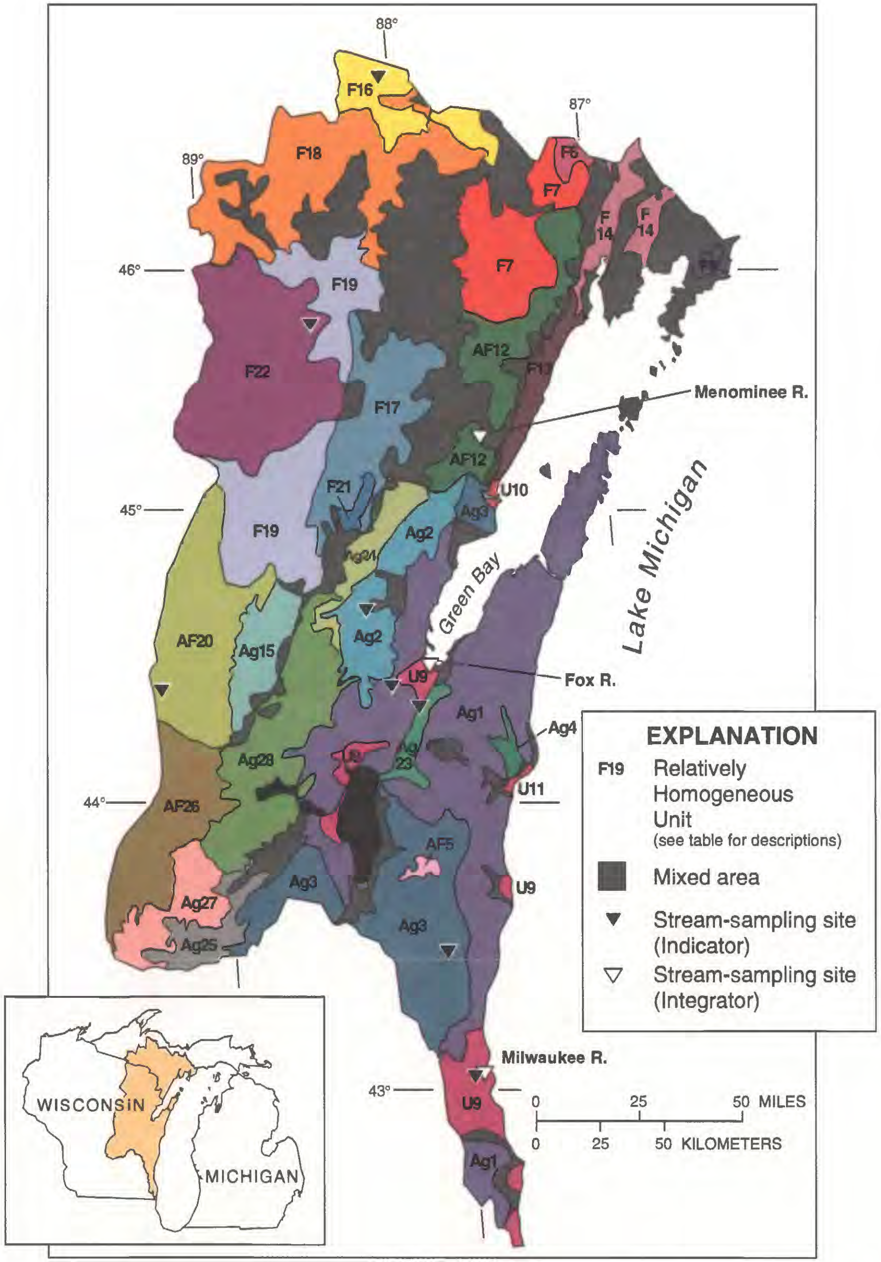
[--, no data available or, if less than 10 values, only median and mean calculated; percentiles and mean are expressed in milligrams per liter (mg/L) and are based on one sample (the most recent one collected) from each well; highest reported minimum detection limit = <0.01 mg/L]

Category	Number of samples/wells	Percentile					Mean
		10th	25th	50th (median)	75th	90th	
WMIC	15/9	--	--	0.02	--	--	0.04
Source[1]							
NWIS	9	--	--	.02	--	--	.04
GIN	0	--	--	--	--	--	--
STORET	0	--	--	--	--	--	--
Well type:							
Commercial	0	--	--	--	--	--	--
Domestic	5	--	--	.02	--	--	.04
Irrigation	1	--	--	.07	--	--	.07
Industrial	0	--	--	--	--	--	--
Public supply	1	--	--	.02	--	--	.02
Recreation	1	--	--	.005	--	--	.005
Stock	1	--	--	.03	--	--	.03
Institution	0	--	--	--	--	--	--
Other	0	--	--	--	--	--	--
Aquifer:							
Basement complex	0	--	--	--	--	--	--
Sandstone	1	--	--	.01	--	--	.01
Silurian dolomite	1	--	--	.005	--	--	.005
Sand and gravel	7	--	--	.03	--	--	.05
Well depth (meters):							
0–15.2	2	--	--	.05	--	--	.05
15.3–30.5	3	--	--	.03	--	--	.05
30.6–45.7	2	--	--	.04	--	--	.04
45.8–61.0	0	--	--	--	--	--	--
>61.0	2	--	--	.008	--	--	.008
General land use:							
Agriculture	3	--	--	.01	--	--	.03
Agriculture/forest	1	--	--	.03	--	--	.03
Forest	5	--	--	.02	--	--	.04
Urban	0	--	--	--	--	--	--
Texture of surficial deposits:							
Clay	1	--	--	.01	--	--	.01
Clay/sand	0	--	--	--	--	--	--
Loam	0	--	--	--	--	--	--
Loam/sand and gravel	0	--	--	--	--	--	--
Sand/sand and gravel	8	--	--	.03	--	--	.04

Appendix 4.19. Summary statistics for constituents in ground water, by category, for the Western Lake Michigan Drainages (WMIC) study unit, water years 1971–90: dissolved orthophosphate—Continued

Category	Number of samples/wells	Percentile					Mean
		10th	25th	50th (median)	75th	90th	
Bedrock type:							
Carbonate	2	--	--	.04	--	--	.04
Igneous/metamorphic	5	--	--	.02	--	--	.04
Shale	0	--	--	--	--	--	--
Sandstone	2	--	--	.02	--	--	.02
Relatively Homogenous Unit:							
Ag1	0	--	--	--	--	--	--
Ag2	0	--	--	--	--	--	--
Ag3	2	--	--	.04	--	--	.04
Ag4	0	--	--	--	--	--	--
Ag15	0	--	--	--	--	--	--
Ag23	0	--	--	--	--	--	--
Ag24	0	--	--	--	--	--	--
Ag25	0	--	--	--	--	--	--
Ag27	0	--	--	--	--	--	--
Ag28	1	--	--	.01	--	--	.01
AF5	0	--	--	--	--	--	--
AF12	0	--	--	--	--	--	--
AF20	0	--	--	--	--	--	--
AF26	1	--	--	.03	--	--	.03
F6	0	--	--	--	--	--	--
F7	0	--	--	--	--	--	--
F8	0	--	--	--	--	--	--
F13	0	--	--	--	--	--	--
F14	0	--	--	--	--	--	--
F16	0	--	--	--	--	--	--
F17	0	--	--	--	--	--	--
F18	0	--	--	--	--	--	--
F19	0	--	--	--	--	--	--
F21	0	--	--	--	--	--	--
F22	5	--	--	.02	--	--	.04
U9	0	--	--	--	--	--	--
U10	0	--	--	--	--	--	--
U11	0	--	--	--	--	--	--

[1]NWIS, U.S. Geological Survey National Water Inventory System; GIN, Wisconsin Department of Natural Resources Groundwater Inventory Network; STORET, U.S. Environmental Protection Agency Storage and Retrieval System.



RHU or sampling site	Area (km^2)	Land use (percent)	Surficial deposit (percent)	Bedrock
Ag1	7,531	Ag (80)	Clay (95)	Carb
Duck Cr. (Ag 1)	247	Ag (89)	Clay (76)	Carb
Ag2	1,356	Ag (79)	Loam (95)	Carb
Pensaukee R. (Ag2)	93	Ag (86)	Loam (99)	Carb
Ag3	3,548	Ag (80)	Sand (85)	Carb
N. Br. Milwaukee R. (Ag3)	133	Ag (88)	Sand (89)	Carb
Ag4	142	Ag (78)	S&G (80)	Carb
Ag15	835	Ag (67)	Loam (65)/S&G (32)	I/M
Ag23	304	Ag (84)	Clay (86)	Shale
East R. (Ag23)	122	Ag (92)	Clay (95)	Shale
Ag24	650	Ag (67)	Loam (95)	SS
Ag25	667	Ag (72)	Sand (78)	SS
Ag27	956	Ag (52)	Clay (77)/Sand (23)	SS
Ag28	2,480	Ag (58)	Clay (97)	SS
AF5	81	Ag (31)/For(58)	Sand (34)/S&G (66)	Carb
AF12	1,642	Ag (31)/For(64)	Loam (95)	Carb
AF20	2,519	Ag (44)/For(53)	Sand (32)/S&G (68)	I/M
Tomorrow R. (AF20)	114	Ag (58)/For(39)	Sand (39)/S&G (61)	I/M
AF26	1,854	Ag (52)/For(43)	Sand (31)/S&G (63)	SS
F6	155	Df (97)	Loam (100)	Carb
F7	1,832	Wf (95)	Loam (93)	Carb
F8	103	Wf (97)	Sand (100)	Carb
F13	543	Wf (90)	Sand (85)	Carb
F14	719	Wf (90)	Sand (35)/S&G (55)	Carb
F16	995	Df (90)	Loam (92)	I/M
Peshekee R. (F16)	127	Df (98)	Loam (100)	I/M
F17	1,900	Df (91)	Loam (40)/S&G (59)	I/M
F18	3,098	Df (93)	Sand (86)	I/M
F19	3,160	Df (91)	Sand (36)/S&G (61)	I/M
F21	140	Wf (83)	Clay (91)	I/M
F22	3,701	Wf (92)	Sand (39)/S&G (61)	I/M
Popple R. (F22)	360	Wf (90)	Sand (24)/S&G (76)	I/M
U9	1,227	Urban (69)	Clay (97)	Carb
Lincoln Cr. (U9)	25	Urban (100)	Clay (100)	Carb
U10	40	Urban (50)	Sand (94)	Carb
U11	35	Urban (63)	S&G (71)	Carb
Mixed	8,808	Mixed	Mixed	Mixed
Menominee R.	10,103	Integrator	Integrator	Integrator
Fox R.	15,630	Integrator	Integrator	Integrator
Milwaukee R.	1,782	Integrator	Integrator	Integrator

The figure on the left shows Relatively Homogeneous Units (RHU's) and stream-sampling sites in the Western Lake Michigan Drainages study unit. The table on the right shows the description of RHU's and stream-sampling sites. Land use and surficial deposit are followed by the percentage of the dominant type or deposit. [Abbreviations: km^2; square kilometers; Ag, agriculture; For, forest; Df, dry forest; Wf, wet forest; S&G, sand and gravel; Carb, carbonate; SS, sandstone; I/M, igneous/metamorphic]