Water-Quality Assessment of Part of the Upper Mississippi River Basin, Minnesota and Wisconsin—Nitrogen and Phosphorus in Streams, Streambed Sediment, and Ground Water, 1971-94

By Sharon E. Kroening and William J. Andrews

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http: / / wwwmn.cr.usgs.gov / umis / index.html

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 policy makers 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 a specific contamination problem; 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 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 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
Chief Hydrologist

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Conversion Factors, Abbreviations, and Acronyms

Multiply	By	To obtain
cubic foot per second (ft^3/s)	28.32	liter per second
foot (ft)	0.3048	meter
gallon per day (gal/day)	3.785	liter per day
pound per acre (lb/ac)	1.121	kilograms per hectare
square miles (mi^2)	2.590	square kilometers
ton (short)	907.2	kilogram
tons/mi^2/year	3.503	kilograms/hectare/year
pounds/acre/year (lb/ac/year)	1.121	kilograms/hectare/year
million gallons/day (Mgal/day)	43.81	liters per second
degree Fahrenheit (°F)	(°F–32)/1.8	degree Celsius

Chemical concentrations: Chemical concentrations of substances in water are given in metric units of milligrams per liter (mg/L.). Milligrams per liter is a unit expressing the concentration of chemical constituents in solution as mass (milligrams) of solute per unit volume (liter) of water. Milligrams per kilogram (mg/kg) is unit expressing the concentration of chemical constituents as mass (milligrams) per unit mass (kilogram).

Acronyms used in this report:

MCES—Metropolitan Council Environmental Services
MDA—Minnesota Department of Agriculture
MDH—Minnesota Department of Health
MPCA—Minnesota Pollution Control Agency
NASQAN—National Stream Quality Accounting Network
NAWQA—National Water Quality Assessment
USACOE—U.S. Army Corps of Engineers
USEPA—U.S. Environmental Protection Agency
USGS—U.S. Geological Survey
WDNR—Wisconsin Department of Natural Resources

Water-Quality Assessment of Part of the Upper Mississippi River Basin, Minnesota and Wisconsin—Nitrogen and Phosphorus in Streams, Streambed Sediment, and Ground Water, 1971–94

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ABSTRACT

Nitrogen and phosphorus in streams, streambed sediment, and ground water were summarized using data from Federal, state, and local agencies as part of an analysis of historical water-quality data for the Upper Mississippi River Basin study unit of the U.S. Geological Survey's National Water-Quality Assessment Program. The Upper Mississippi River Basin study unit encompasses the drainage of the Mississippi River from the source to the outlet of Lake Pepin. This report focuses on a 19,500-square-mile study area in the eastern part of the study unit. The study area included the part of the Upper Mississippi River Basin from Royalton, Minnesota, to the outlet of Lake Pepin, located near Red Wing, Minnesota; the Minnesota River Basin from Jordan, Minnesota, to the confluence with the Mississippi River; and the entire drainage basins of the St. Croix, Cannon, and Vermillion Rivers. The Twin Cities metropolitan area, with a population of approximately 2.3 million people, is located in the south-central part of the study area.

Fertilizers and livestock manure were the greatest sources of nitrogen and phosphorus applied to the land surface of the study unit. Approximately 60 percent of the fertilizer was applied to the Minnesota River Basin, which drains agricultural areas in the southern and western parts of the study unit.

Concentrations of total nitrite plus nitrate nitrogen, total nitrogen, and total phosphorus in streams, generally were greatest in the tributaries to the Mississippi River draining agricultural areas in the western and southern part of the study area. Concentrations of these constituents generally were least in tributaries draining forested land. The greatest total nitrite plus nitrate nitrogen concentrations generally occurred during the spring and summer in streams draining agricultural areas and in the winter in streams draining forested areas. Total phosphorus concentrations generally were greatest in the spring and summer for all streams.

Total nitrite plus nitrate nitrogen, total nitrogen, and total phosphorus concentrations in the Mississippi River increased substantially downstream from the Minnesota River and downstream from wastewater discharges in the Twin Cities metropolitan area. Total ammonia and dissolved orthophosphate concentrations generally were greatest at sites on the Mississippi and Minnesota Rivers downstream from wastewater discharges from the Twin Cities metropolitan area.

Total nitrite plus nitrate nitrogen concentrations in streams generally were less than the Maximum Contaminant Level of 10 mg/L (as nitrogen) established by the U.S. Environmental Protection Agency. Total phosphorus concentrations in streams generally were greater than the 0.1 mg/L concentration recommended by the U.S. Environmental Protection Agency at sites located in agricultural areas and on the Mississippi River downstream from its confluence with the Minnesota River.

Phosphorus and nitrogen yields were greatest in watersheds primarily draining agricultural land. The majority of the nitrogen and phosphorus loading to the Mississippi River was from the Minnesota River. In the Minnesota River, the nitrogen load primarily was total nitrite plus nitrate nitrogen.

Despite increases in fertilizer usage during 1982–91, most stream sites outside of the Twin Cities metropolitan area had no temporal trends in total nitrite plus nitrate nitrogen, total phosphorus, or dissolved orthophosphate concentrations for water years 1984–93. Most sites had a decrease in total ammonia nitrogen concentrations, possibly a result of improvements in wastewater treatment. In the Twin Cities metropolitan area, decreases in total ammonia concentrations in the Mississippi and Minnesota Rivers coincided with increases in total nitrite plus nitrate nitrogen concentrations, probably a result of wastewater treatment plants initiating nitrification processes.

Nitrite plus nitrate nitrogen concentrations in ground water reflect land uses and hydrogeologic settings of major aquifers in the study area. Unconfined sand and gravel, buried sand and gravel, and the Prairie du Chien-Jordan were the aquifers most frequently sampled for nitrite plus nitrate nitrogen because they are the principal sources of ground water in the study area. The greatest nitrite plus nitrate nitrogen concentrations reported by Federal and state agencies, some exceeding the U.S. Environmental Protection Agency's Maximum Contaminant level of 10 mg/L by a factor of four, were in water from shallow wells in agricultural and mixed forested and agricultural areas. Water sampled from buried sand and gravel aquifers, which are more shielded from substances leaching from the land surface by layers of clay or till, generally had lower nitrite plus nitrate nitrogen concentrations than water from unconfined sand and gravel aquifers. Nitrite plus nitrate nitrogen concentrations in water samples from the Prairie du Chien-Jordan aquifer were greatest in the Wisconsin part of the study area and in the vicinity of the Cannon River, where the aquifer is commonly unconfined, exposed at land surface, and overlain by agricultural or by mixed forested and agricultural land covers.

Dissolved phosphorus concentrations in ground water in the study area generally were near detection limits of 0.01 mg/L or lower, indicating that surface-water eutrophication from phosphorus may be more likely to occur from overland runoff of phosphorus compounds and from direct discharges of treated wastewater than from ground-water base flow. The greatest concentrations of dissolved phosphorus in ground water generally were detected in water samples from wells in urban portions of the study area.

INTRODUCTION

In 1991, the USGS began full implementation of the NAWQA Program. Long-term goals of the NAWQA Program are to describe the status of, and trends in, the quality of large representative parts of the Nation's surface- and ground-water resources and to identify the major natural and anthropogenic factors that affect the quality of these resources. To meet these goals, nationally consistent data useful to policy makers, scientists, and managers are being collected and analyzed. Because assessment of the water quality in the entire Nation is impractical, major activities of the NAWQA Program take place within a set of hydrologic systems called study units. Study units comprise diverse hydrologic systems of river basins, aquifer systems, or both, and are assessed on a decadal cycle.

The Upper Mississippi River Basin study unit, which encompasses an area of about 47,000 mi^2, includes the drainage area of the Mississippi River from the source at Lake Itasca to the outlet of Lake Pepin, a natural lake on the river located near Red Wing, Minnesota (figs. 1, 2). Within the study unit, the land cover is very diverse and includes areas of rich agricultural lands, forests, wetlands, lakes, prairies, and the seven-county Twin Cities (Minneapolis and St. Paul) metropolitan area (TCMA). Enrichment of nitrogen and phosphorus in the Mississippi River is of concern nationally because major municipalities rely on the Mississippi River as a source of public water supply, and a zone of hypoxia (oxygen concentrations less than 2 mg/L) that occurs seasonally in the bottom waters of the Gulf of Mexico has been linked to nitrogen and phosphorus loadings from the Mississippi River (Justic and others, 1993; Rabalais and others, 1994; Turner and Rabalais, 1994). Locally, enrichment of phosphorus in the Mississippi River and its tributaries has received recent attention due to concerns about severe algal blooms and fish kills in Lake Pepin during a 1988 drought (Minnesota Pollution Control Agency, 1989; Metropolitan Waste Control Commission, 1993a). Within the study unit, elevated nitrate concentrations in ground water are of concern due to the adverse health effects on infants. Ground water in unconfined, highly permeable sand and gravel aquifers of glacial and alluvial origins is particularly susceptible to degradation from anthropogenic activities at the land surface.

Nitrogen and phosphorus are essential nutrients for human, plant, and animal growth. These elements are integral components of enzymes, chlorophyll, amino

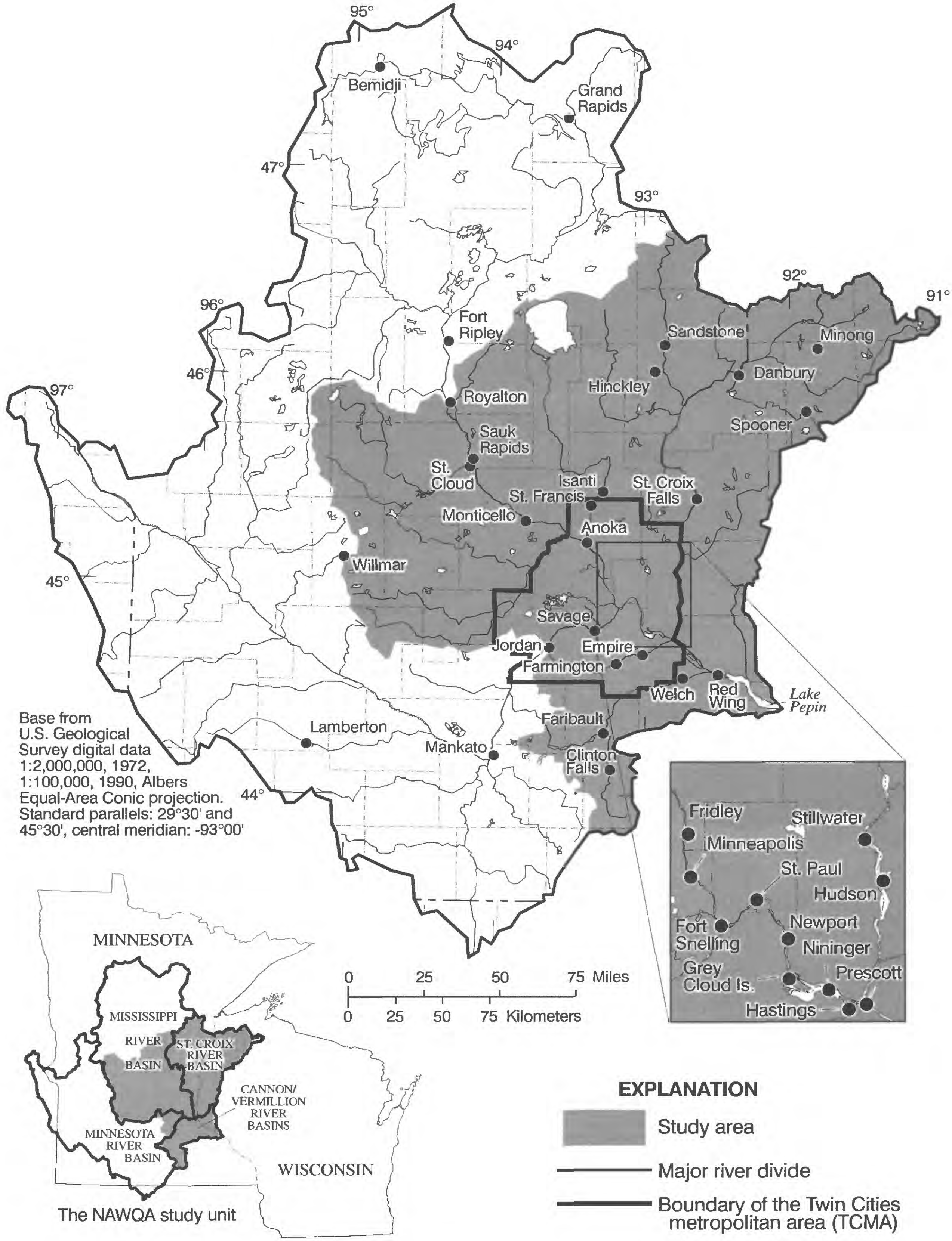


Figure 1.--Location of the study area, selected towns and major cities in the Upper Mississippi River Basin (NAWQA) study unit.

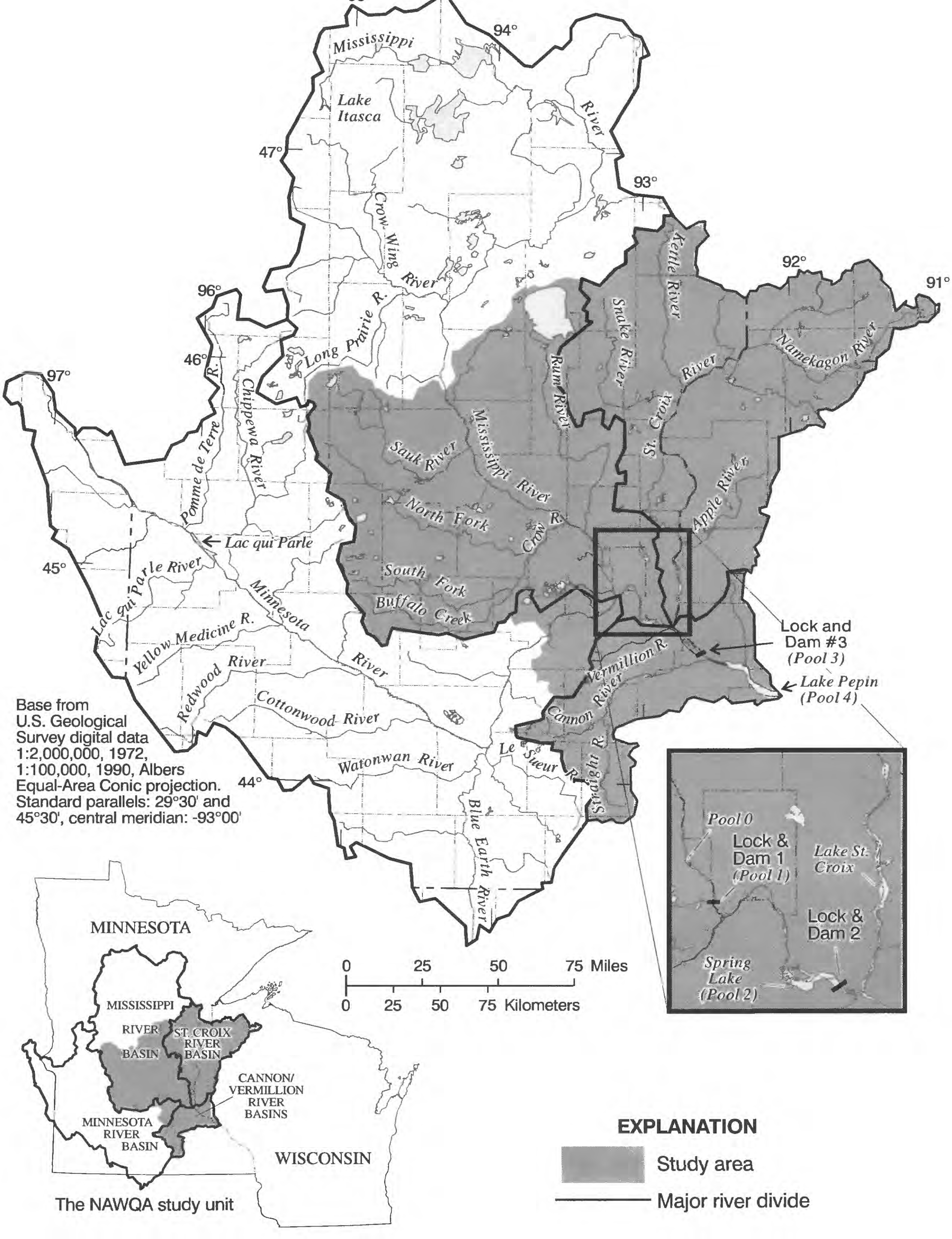


Figure 2.--Hydrography in the Upper Mississippi River Basin study unit.

acids, cell membranes, DNA, RNA, and other proteins. Elevated concentrations of nutrient compounds in water, however, are potentially toxic to humans, livestock, and aquatic life and can cause eutrophication in streams and lakes. Eutrophication is the increased growth of algae and other aquatic plants, which reduces the quality of streams and lakes for recreational uses, such as swimming and boating, and as a potable water supply. The subsequent decay of these plants can lead to the depletion of dissolved oxygen in water. Depletion of oxygen below approximately 5 mg/L in water can impair or kill fish (Thomann and Mueller, 1987).

Natural and anthropogenic activities both produce nitrogen and phosphorus compounds in the environment. These elements occur naturally in the atmosphere and as part of soils, rocks, vegetation, and biota. The largest natural reservoir of nitrogen is the atmosphere, which consists of 78 percent nitrogen gas. Phosphorus occurs naturally in minerals such as apatite (Hem, 1985), although these are not found in large quantities in the study unit. One of the primary uses of nitrogen and phosphorus compounds is in the manufacture of fertilizers. Historically, phosphorus compounds have been used to increase the cleaning power of detergents, but state legislation has restricted their use within the study unit. A 1976 Minnesota law restricts the amount of phosphorus to 0.5 percent (by weight) in laundry detergents and 11 percent (by weight) in dishwashing detergents (Mary Hayes, Minnesota Pollution Control Agency, written commun., 1993).

Nitrogen and phosphorus generally enter streams through runoff of fertilizers, livestock wastes, and soil erosion; direct discharges from municipal and industrial wastewater treatment facilities and livestock feedlots; precipitation; and from ground-water inflow. The principal forms generally found in streams are nitrate nitrogen (NO_3^-), nitrite nitrogen (NO_2^-), organic nitrogen, ammonium nitrogen (NH_4^+), and orthophosphate (PO_4^{3-}).

Nutrients enter ground water through leaching of fertilizers and livestock wastes applied to the land surface. The most common nitrogen and phosphorus species in ground water generally are very water soluble and include nitrate, ammonium, and orthophosphate. Nitrate concentrations greater than 3 mg/L in ground water generally are considered to be associated with anthropogenic activities (Madison and Brunett, 1985).

National water-quality criteria for un-ionized ammonia (NH_3) have been set by the USEPA (1986). These criteria are dependent upon stream pH and temperature. Un-ionized ammonia, which exists in equilibrium with ammonium, is toxic to fish and other aquatic life. National water-quality criteria have not been established for phosphorus compounds in surface water, but the USEPA recommends total phosphates not to exceed 0.05 mg/L as phosphorus in a stream at a point where it enters a lake or reservoir (U.S. Environmental Protection Agency, 1986). In streams that do not directly discharge into lakes or reservoirs, it is recommended by the USEPA (1986) that total phosphate concentrations should not exceed 0.1 mg/L as phosphorus.

Minnesota statutes require municipal point source dischargers of sewage to reduce phosphorus to an effluent concentration of 1 mg/L where the discharge is directly to or affects a lake or reservoir (Minnesota State Statutes, 1996). Water-quality standards for un-ionized ammonia are dependent upon the water use classification of the stream. The standard is 0.016 mg/L for streams classified as cold-water fisheries (class 2A) and 0.040 mg/L for streams classified as warm-water fisheries (class 2B). Un-ionized ammonia concentrations are calculated based on the stream total ammonia concentration, pH, and temperature. As a result, higher total ammonia concentrations in the streams are permissible during the winter.

In drinking water supplies, the USEPA has established a Maximum Contaminant Level (MCL) for nitrate of 10 mg/L (as nitrogen). Nitrate concentrations exceeding 10 mg/L in drinking water can cause a potentiallyfatal condition known as methemo-globinemia, which primarily affects infants. Elevated concentrations of nitrate in drinking water also have been tentatively linked to increased incidences of stomach cancer, leukemia, and birth defects (World Health Organization, 1977; National Research Council, 1978; Scragg and others, 1982; Strange and Krupicka, 1984; Stewart, 1990).

Purpose and Scope

This report describes the major sources and sinks of nitrogen and phosphorus to the study unit, concentrations in part of the Upper Mississippi River and its tributaries, concentrations in the major aquifers within the study unit, stream loads and yields, and seasonal and temporal trends in stream concentrations using historical data collected by Federal, state, and local agencies. Relations between nutrient concentrations and land use and land cover, surficial geology, and well depth also were examined. For streams, water-column total nitrite plus nitrate nitrogen, total organic plus ammonia nitrogen, total nitrogen, total ammonia, total phosphorus, and dissolved orthophosphorus concentrations were summarized for the most common period of record, water years 1984–93 (October 1, 1983 through September 30, 1993). Because less streambed-sediment and ground-water-quality data were available, streambed-sediment total organic plus ammonia nitrogen, total ammonia nitrogen, and total phosphorus concentration data, and ground-water nitrate nitrogen and dissolved phosphorus concentration data were summarized for the entire period of records available, 1974–89 and 1971–94, respectively. Sources of data were the MCES, MDA, MDH, MPCA, USACOE, WDNR, and the USGS.

Analyses of historical water-quality data focused on a smaller study area, encompassing 19,500 mi^2 in the eastern portion of the study unit (fig. 1), in this report. This assessment was done principally to examine the effects of the TCMA on water quality. The study area includes the part of the Upper Mississippi River Basin from Royalton, Minnesota, to the outlet of Lake Pepin; the Minnesota River Basin from Jordan, Minnesota, to the confluence with the Mississippi River; and the entire drainage basins of the St. Croix, Cannon; and Vermillion Rivers (figs. 1, 2). Most of the TCMA, with a population in 1990 of approximately 2.3 million people (Stark and others, 1996), is included in the south-central part of the study area.

Environmental Setting of the Study Unit

The concentrations of nitrogen and phosphorus in streams, streambed sediment, and ground water are affected by natural and anthropogenic factors. The major factors that affect concentrations of nitrogen and phosphorus compounds include climate, land use and land cover, population, soils, surface-water hydrology, and the hydrogeologic characteristics and settings of sand and gravel aquifers and bedrock aquifers.

The climate of the study unit affects the presence and distribution of nitrogen and phosphorus compounds in streams and ground water and influences the effect these compounds have on stream and lake eutrophication. At higher temperatures, these compounds generally have the greatest effect on the growth rate of algae and other biota in streams (Thomann and Mueller, 1987). In the study unit, the monthly temperature is the highest, on average, during July, and average monthly temperatures range from 11 degrees Fahrenheit in January to 74 degrees Fahrenheit in July (Stark and others, 1996).

Higher precipitation affects stream- and ground-water quality by enhancing runoff and leaching from the land surface, increasing dilution of these constituents in water, or both. Average annual precipitation increases from less than 22 inches in the western part of the study unit to greater than 32 inches in the eastern part (Stark and others, 1996). About three-fourths of the annual precipitation falls from May through September (Baker and others, 1979). Runoff in the study unit varies spatially and temporally, but most occurs from April through May from snowmelt and from rains falling on nearly saturated soils (Stark and others, 1996).

Within the study unit, the Mississippi River derives most of its discharge from its drainage upstream of Anoka, Minnesota, and its two major tributaries, the Minnesota and St. Croix Rivers (figs. 1, 2). These two tributaries respectively contribute on average 22 and 26 percent of the mean annual flow (18,600 ft^3/s) of the Mississippi River at Prescott, Wisconsin (Stark and others, 1996). The natural hydraulic characteristics of the Mississippi, Minnesota, and St. Croix Rivers have been altered by construction of dams or stream channelization. In the headwaters of the Mississippi River, stream discharge is regulated by dams on six large lakes. Farther downstream, construction of a series of locks and dams has transformed the Mississippi River from a free-flowing stream to a series of slack-water pools. Within the TCMA, the Minnesota River has been channelized for navigation which, combined with backwater effects from Lock and Dam 2 on the Mississippi River, has transformed part of the Minnesota River into a deeper, slower-flowing stream (Minnesota Pollution Control Agency, 1985).

National assessments of stream- and ground-water quality (Omernik, 1976; Mueller and others, 1995) have shown concentrations of nitrogen and phosphorus compounds generally are greater in agricultural and urban areas than in forested and undisturbed areas. Based on the land-cover classification system of Anderson and others (1976), agriculture is the dominant land use in the western and southern parts of the study unit, overlying about 68 percent of the study unit (fig. 3). Principal crops raised in this part of the study unit include corn, soybeans and hay (Stark and others, 1996). Mixed deciduous and coniferous forests and wetlands comprise 30 percent of the study unit, primarily in the northeastern part (fig. 3). The central part of the study unit, between the agricultural lands to the south and west and the forests to the north, is transitional between forest and agriculture (fig. 3). Cropland in the central part of the study unit is limited due to rocky, marginally fertile soils. Hay and oats are the principal crops grown in this area and are primarily grown to feed livestock, mainly dairy cows (Stark and others, 1996).

Urban and suburban land uses contribute nitrogen and phosphorus to surface and ground water through permitted effluent discharges from municipal wastewater treatment plants, industrial facilities, and urban runoff. Urban land use (including suburban land) comprises approximately 2 percent of the study unit and

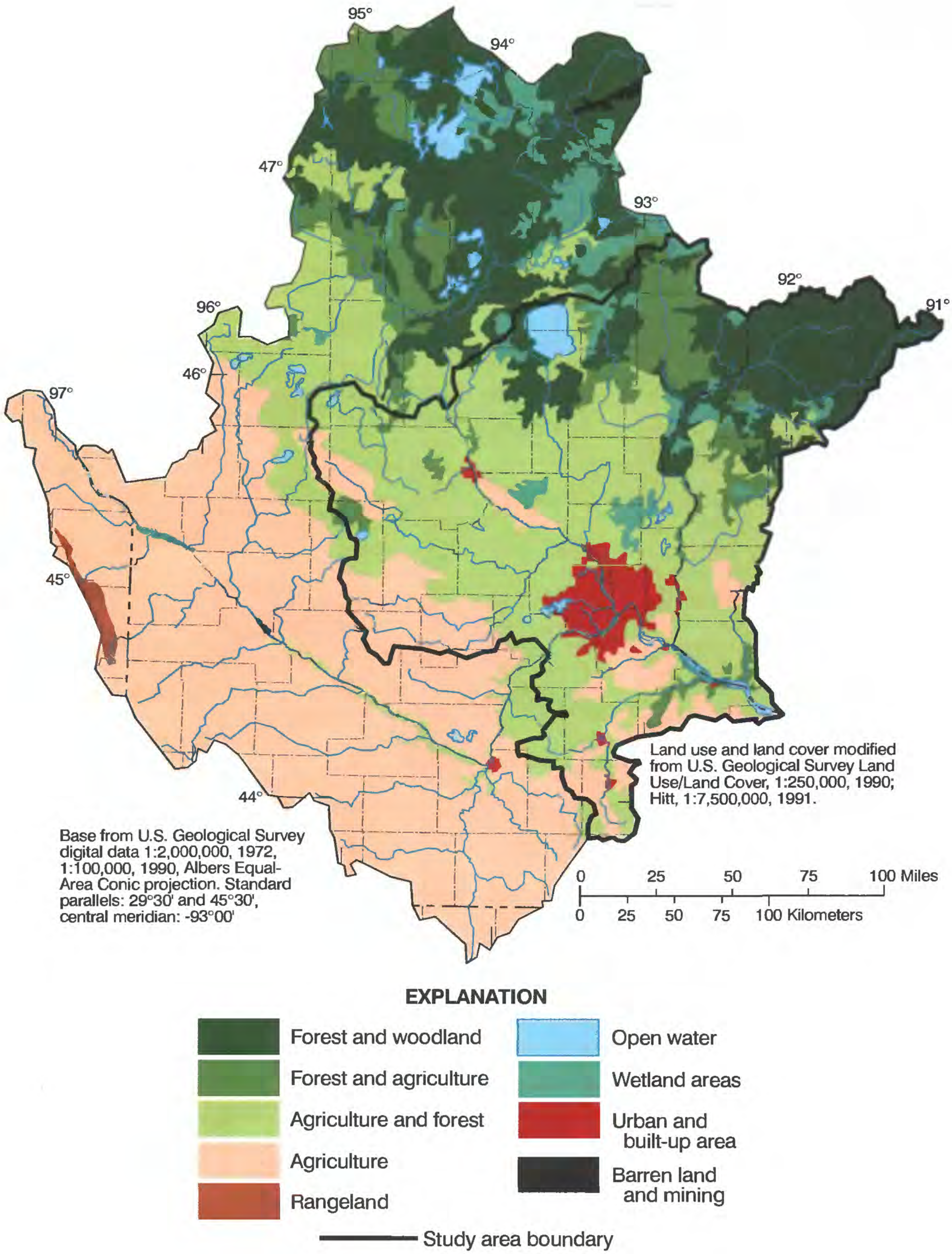


Figure 3.--Land use and land cover in the Upper Mississippi River Basin study unit.

is concentrated primarily within the TCMA (fig. 1 and 3). Data obtained from the USEPA's Permit Compliance System (PCS) (Theresa Flom, Minnesota Pollution Control Agency, written commun., 1994; Arnie Leder, U.S. Environmental Protection Agency, written commun., 1995; Charles Furrey, Iowa Department of Natural Resources, electronic commun., 1997) indicated that 294 municipal wastewater treatment facilities discharged into the study unit in 1993 (fig. 4). The majority of these facilities (269 of 294) discharged into streams. The remaining facilities discharged into lakes (19 of 294) or on land (6 of 294). Most of the municipal wastewater treatment facilities (260 of 294) have design flows less than 1 Mgal/day. The largest facilities that had design flows of 10 Mgal/day or greater in 1993 discharge into the Mississippi and Minnesota Rivers and are located within the TCMA and in the communities of Grand Rapids, St. Cloud, and Mankato.

The thickness, hydraulic properties, and mineralogy of materials overlying an aquifer affect the transport of nitrogen and phosphorus compounds to ground water. Soils with relatively high permeabilities formed on sands are highly conducive to leaching of nutrients, such as nitrate, from the land surface to ground water. Clayey soils formed on glacial tills are much less permeable and more likely to produce runoff of nutrients to streams. The study unit is covered by up to 100 ft of unconsolidated deposits on bedrock uplands and up to 600 ft of deposits in bedrock valleys and terminal moraines (figs. 5 and 6). The unconsolidated deposits progressively thin toward the northeast and southeast in the study unit (Trotta and Cotter, 1973; Woodward, 1986). Along the courses of streams and rivers, unconsolidated sediments were reworked, forming terrace and alluvial deposits. The uppermost aquifers underlying much of the study unit are composed of sand and gravel deposited as glacial outwash, alluvium, or glacial lake sediments and are either unconfined or buried by tills or clays. The most extensive unconfined sand and gravel aquifers in the study unit are located in east-central Minnesota (the Anoka Sand Plain) and in northwestern Wisconsin (fig. 6). Buried sand and gravel aquifers are formed where clay or till overlie sand and gravel deposits. Buried sand and gravel aquifers primarily are located in northwestern Wisconsin and the western part of the study unit.

Bedrock aquifers of varying compositions and thicknesses underlie the sand and gravel deposits throughout the study unit. The principal bedrock aquifers in the eastern part of the study unit are composed of sandstones and dolomites of Precambrian to Ordovician age deposited in a trough in igneous and metamorphic rocks known as the Hollandale Embayment (Delin and Woodward, 1984). The bedrock hydrogeologic units of the eastern part of study unit consist of four principal aquifers separated by confining units. The principal aquifers are, in descending order: St. Peter; Prairie du Chien-Jordan in Minnesota, and Prairie du Chien-Trempeleau in Wisconsin (both of which are referred to as "Prairie du Chien-Jordan" for this report); Franconia-Ironton-Galesville (Tunnel City-Wonewoc-Eau Claire in Wisconsin); and Mt. Simon-Hinckley-Fond du Lac (Adolphson and others, 1981; Mudrey and others, 1987; Brown, 1988) (figs. 5, 7). Confining units for these aquifers are, in descending order: Glenwood; basal part of the St. Peter Sandstone; St. Lawrence-Franconia (the Franconia Formation is a fine-grained silty sandstone that also is utilized locally as an aquifer); and Eau Claire (fig. 5). In the western part of the study unit, sand and gravel deposits are underlain by aquifers in sandstones of Cretaceous age and in fractured igneous and metamorphic rocks of Precambrian age (Anderson, 1986; Woodward and Anderson, 1986). Fractured igneous and metamorphic rocks of Precambrian age also are sources of water where sand and gravel deposits are thin or of low permeability in the northeastern part of the study unit (fig. 7). The bedrock aquifers are susceptible to contamination by nutrients, by seepage from hydraulically-connected unconsolidated sand and gravel aquifers, or where the bedrock aquifers subcrop beneath thin, permeable unconsolidated deposits, as occurs with the Prairie du Chien-Jordan aquifer in the southern half of the Wisconsin part of the study unit and in the vicinity of the Cannon River in Minnesota (Trotta and Cotter, 1973; Wisconsin Department of Natural Resources and Wisconsin Geological and Natural History Survey, 1987).

Elevated nitrate and phosphorus concentrations in streams and ground water may affect the usefulness of those sources as water supplies for municipalities, power plants, and industries. In 1990, 2,710 Mgal/day of surface and ground water was withdrawn from the study unit (Stark and others, 1996). Most of the water withdrawn was from surface water (75 percent), primarily as cooling water for power generation plants. Ground water accounted for 25 percent of the withdrawals. For public water supplies, an average of 413 Mgal/day was withdrawn; 59 percent was from ground water, and 41 percent was from surface water. The Mississippi River is the primary source of public water supply for Minneapolis, St. Paul, and St. Cloud. In Minneapolis and St. Paul, the water supply intakes are located upstream of Minneapolis, near Fridley, Minnesota. Ground water is the primary source of water supply for most other communities in the study unit, including most of the suburban communities in the TCMA. Bedrock aquifers, where present, are the most commonly used sources of ground water in the study unit owing to the large yields obtainable from wells completed in those aquifers. The Prairie du Chien-Jordan aquifer is

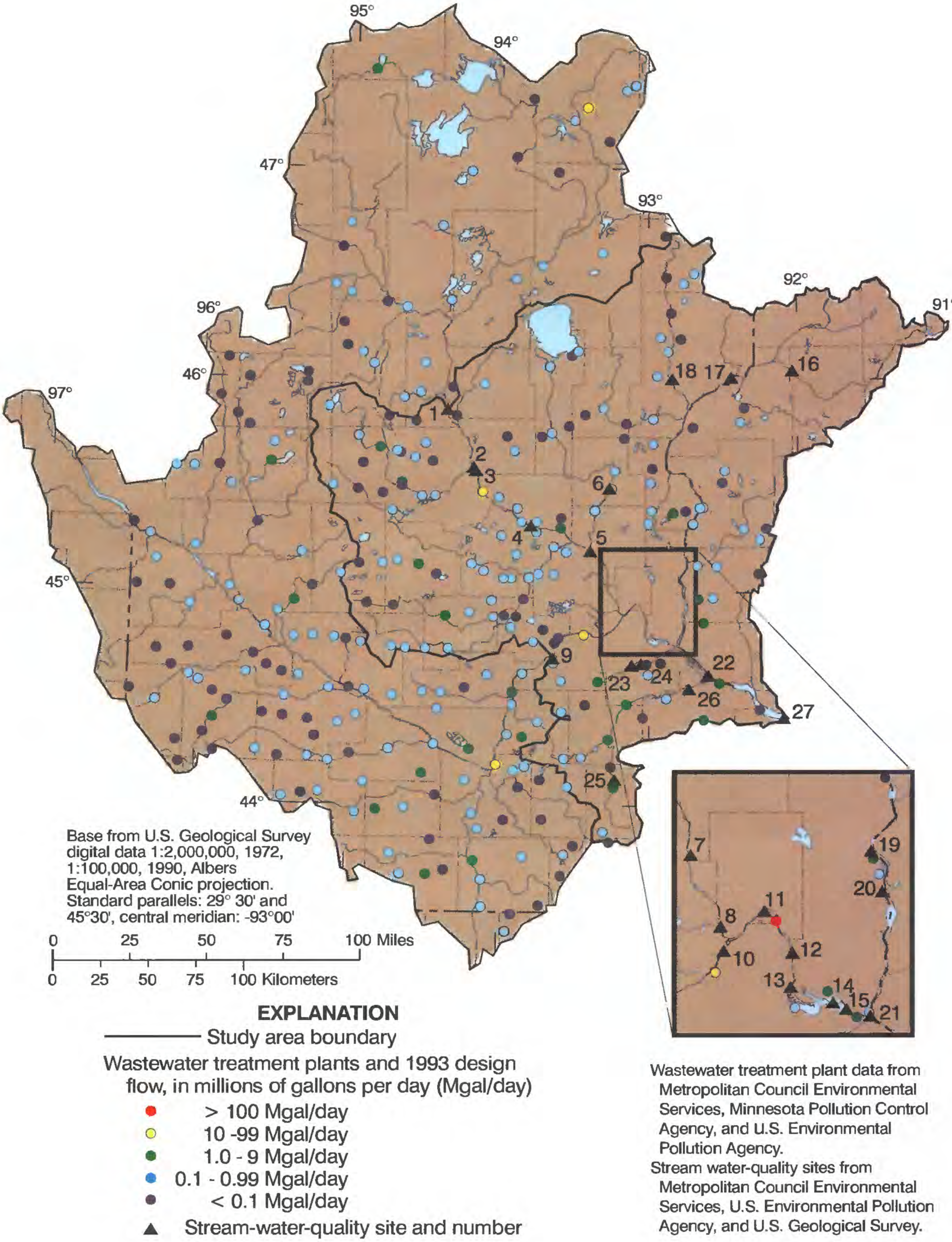
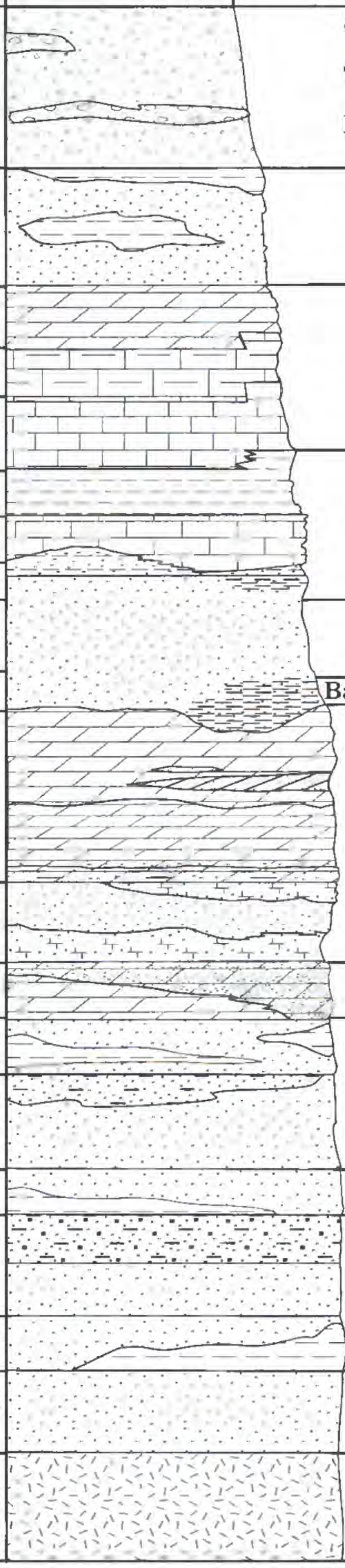


Figure 4.--Location of wastewater treatment plants and stream-water-quality sites in the Upper Mississippi River Basin study unit.

ERATHEM	SYSTEM OR SERIES	FORMATION OR GROUP: MINNESOTA	FORMATION OR GROUP: WISCONSIN	THICKNESS (IN FEET)	HYDROGEOLOGIC UNIT: MINNESOTA	HYDROGEOLOGIC UNIT: WISCONSIN
CENOZOIC	QUATERNARY	Drift and alluvium	Drift and alluvium	0-600	Surficial sand and gravel aquifer Till and clay confining units Buried sand and gravel aquifer	Surficial sand and gravel aquifer Till and clay confining units Buried sand and gravel aquifer
MESO-ZOIC	CRETA-CEOUS	Carlisle Shale Greenhorn Fm. Graneros Shale Dakota Fm.	--	0-500	Cretaceous aquifers	--
PALEOZOIC	DEVON-IAN	Cedar Valley Limestone	--	0-50?	Upper carbonate aquifer	Devonian aquifer
	ORDOVICIAN	Maquoketa Shale	--	0-50?		Maquoketa shale confining unit
		Galena Dolomite	Galena Dolomite	0-110?		Galena-Platteville aquifer
		Decorah Shale	--	0-90	Decorah-Platteville-Glenwood confining unit	
		Platteville Formation	Platteville Formation	0-30		
		Glenwood Shale	Glenwood Shale	0-16		Glenwood confining unit
		St. Peter Sandstone	St. Peter Sandstone	0-130	St. Peter aquifer	St. Peter aquifer
				0-65	Basal St. Peter confining unit	
		Prairie du Chien Group	Prairie du Chien Group	0-335	Prairie du Chien-Jordan aquifer	Prairie du Chien-Trempealeau aquifer
	CAMBRIAN	Jordan Sandstone	Trempealeau Formation	0-130		
		St. Lawrence Formation	St. Lawrence Formation	0-70	St. Lawrence confining unit	St. Lawrence confining unit
		Franconia Formation	Tunnel City Formation	0-200	Franconia-Ironton-Galesville aquifer	Tunnel City-Wonewoc-Eau Claire aquifer
		Ironton Sandstone	Wonewoc Formation	0-100		
		Galesville Sandstone				
		Eau Claire Formation	Eau Claire Formation	0-200	Eau Claire confining unit	
		Mt. Simon Sandstone	Mt. Simon Sandstone	0-200	Mt. Simon-Hinckley-Fond du Lac aquifer	Mt. Simon-Hinckley-Fond du Lac aquifer
PROTEROZOIC	PRECAMBRIAN	Hinckley Sandstone	Bayfield Group			
		Fond du Lac Sandstone		0-650		
		Solor Church Formation	Oronto Group	0-1,100	Undifferentiated Precambrian sandstone	Undifferentiated Precambrian sandstone
		Igneous and metamorphic rocks	Igneous and metamorphic rocks	UP TO 20,000	Precambrian igneous and metamorphic aquifers	Precambrian igneous and metamorphic aquifers

GENERAL LITHOLOGY



EXPLANATION OF GENERAL LITHOLOGY

Figure 5.--Generalized hydrogeologic column showing aquifers and confining units in the Upper Mississippi River Basin study unit (modified from Green, 1977; Delin and Woodward, 1984; and Olcott, 1992).

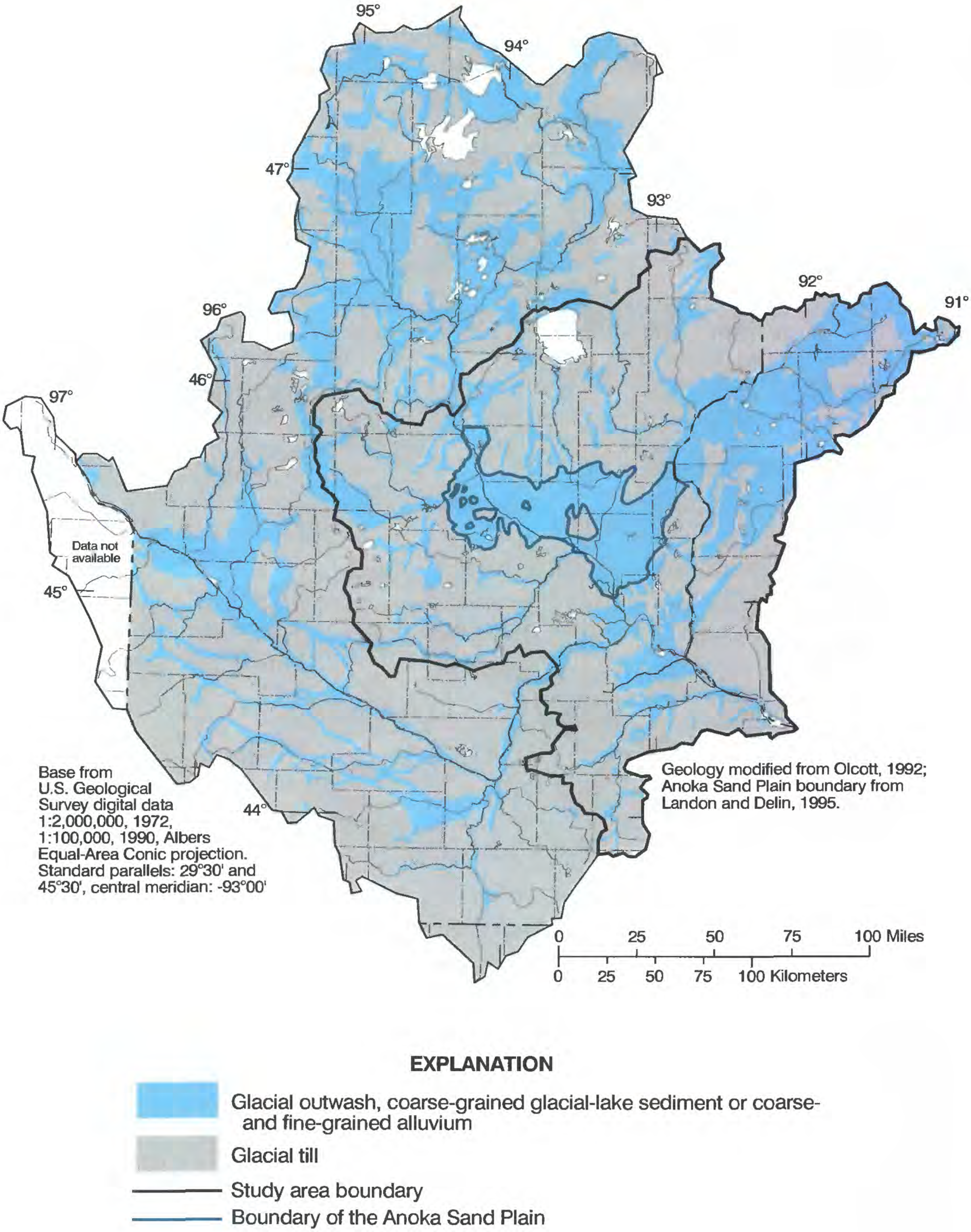


Figure 6.--Surficial geology in the Upper Mississippi River Basin study unit.

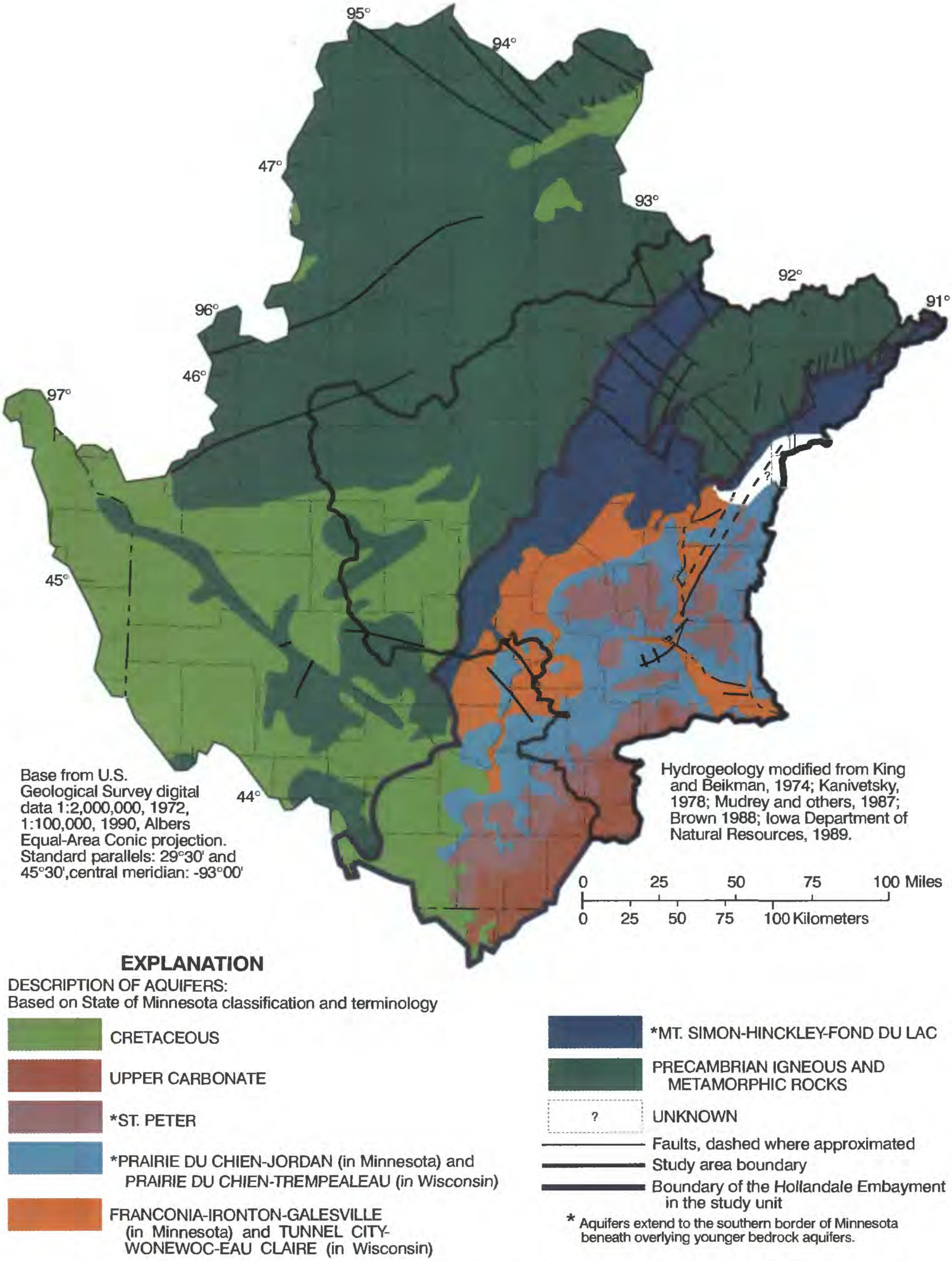


Figure 7.--Bedrock hydrogeology of the Upper Mississippi River Basin study unit.

the primary bedrock aquifer used for water supply in Minnesota (Andrews and others, 1995). In the southern one-half of the Wisconsin part of the study unit, the Prairie du Chien-Jordan aquifer is the principal source of ground water.

Sources of Water-Quality Data

Water-quality data analyzed in this report were obtained from monitoring programs and studies conducted by the MCES, MDA, MDH, USACOE, WDNR, and the USGS. Data from these programs were obtained from the WAter Data STOrage and REtrieval system (WATSTORE) data base of the USGS, the STOrage and RETrieval (STORET) data base of the USEPA, electronic data bases maintained by the MCES, MDA, MPCA, USACOE, and the WDNR, and the files of the MDH.

The stream-water-quality data analyzed in this report were collected as part of long-term ambient monitoring networks operated by the MCES, MPCA, WDNR, and the USGS (fig. 4, table 1). These and other Federal, state, and local agencies, including the U.S. Forest Service, USEPA, and Minnesota Department of Natural Resources, have sampled stream water in the study unit to determine nutrient concentrations for many other studies. Data from those studies were not included because they usually collected fewer samples per site, and data from those studies were not collected during a common period of record. Because nutrient concentrations in stream water usually vary seasonally and with streamflow conditions, data collected in every season and during a common period of record are preferred to more accurately estimate loads and yields and describe the average spatial distribution and long-term temporal or seasonal trends.

The largest stream-water-quality data set, in terms of spatial coverage, was collected by the MPCA (fig. 4; table 2), which conducted monitoring as required by section 305b of the Water Pollution Control Act Amendments of 1972. The MPCA routinely collected grab samples for analyses of nutrient concentrations. Fifteen sites in the study area were included in this report. Sampling sites generally were located on the Mississippi River and near the mouths of its major tributaries. Water-quality samples usually were collected nine times per year, and the majority of samples were obtained monthly during the ice-free season from March through October. The second largest data set was collected by the MCES. The MCES routinely collected grab samples to determine nutrient concentrations. Thirteen sites, included in this report, were located in the TCMA on the Mississippi, Minnesota, St. Croix, and Vermillion Rivers (table 2), primarily upstream and downstream of municipal wastewater treatment plant outfalls. The WDNR collected samples for nutrient analyses as part of an ambient water-quality monitoring program at three sites on the Mississippi and

Table 1.--Sources of historical stream water and streambed-sediment data for the study area

Source	General purpose for collecting data	Number of sites sampled	Sampling frequency	Period of record
Metropolitan Council Environmental Services—Conventional River Pollutant Sampling Network	Determine the effectiveness of wastewater treatment programs and compliance with Federal and State regulations.	13	weekly to monthly	ca. 1930–93
Minnesota Pollution Control Agency-Ambient Stream Monitoring Network	Assess regional water quality and determine compliance with Federal and State regulations.	15	9 times per year	1958–93
U.S. Army Corps of Engineers	Determine the quality of dredge material in the Mississippi, Minnesota, and St. Croix River navigation channels.	170	annually to every five years	1974–89
Wisconsin Department of Natural Resources—Ambient Stream Water-Quality Monitoring Network	Assess regional water quality and determine compliance with Federal and State regulations.	3	monthly	1977–93
U.S. Geological Survey—National Stream Quality Accounting Network	Obtain information of the quantity and quality of water moving within and from the United States	3	quarterly	1972–93

Table 2.--Description of stream water-quality sites for the study area
[stream sites are listed in downstream order. MCES, Metropolitan Council Environmental Services; MPCA, Minnesota Pollution Control Agency; N/A, information was not available; WDNR, Wisconsin Department of Natural Resources; and USGS, U.S. Geological Survey]

Site number (fig. 4)	Location	Agency	Approximate drainage area, square miles	Period of record analyzed
1	Mississippi River near Royalton, Minnesota	USGS	11,600	1984–93
2	Sauk River downstream of bridge on County State Aid Highway 1 at Sauk Rapids, Minnesota	MPCA	1,030	1984–93
3	Mississippi River upstream of bridge on Minnesota State Highway 15 at Sauk Rapids, Minnesota	MPCA	N/A	1984–93
4	Mississippi River at bridge on Minnesota State Highway 25 at Monticello, Minnesota	MPCA	N/A	1984–93
5	Mississippi River downstream of bridge on U.S. Highway 169 at Anoka, Minnesota	MCES	17,100	1984–93
6	Rum River at bridge on County State Aid Highway 5 near Isanti, Minnesota	MPCA	1,190	1984–93
7	Mississippi River at the city of Minneapolis waterworks intake at Fridley, Minnesota	MPCA	19,110	1984–93
8	Mississippi River above Lock and Dam 1, Minnesota	MCES	19,700	1984–93
9	Minnesota River downstream of bridge on County Road 9 near Jordan, Minnesota	MCES, USGS	16,200	1984–93
10	Minnesota River near mouth in Fort Snelling State Park, Minnesota	MCES, MPCA	16,900	1984–93
11	Mississippi River at St. Paul, Minnesota	MCES, MPCA	36,800	1984–93
12	Mississippi River at automonitor site in Newport, Minnesota	MCES	36,900	1984–93
13	Mississippi River at automonitor site near J.L. Shiely Company, Grey Cloud Island, Minnesota	MCES, MPCA	37,000	1984–93
14	Mississippi River at Nininger, Minnesota	USGS	37,050	1984–93
15	Mississippi River at Lock and Dam 2, Hastings, Minnesota	MCES, MPCA	37,080	1984–93
16	Namekagon River near Minong, Wisconsin	WDNR	N/A	1984–91
17	St. Croix River at bridge on Minnesota State Highway 48 near Danbury, Wisconsin	MPCA	1,580	1984–93
18	Kettle River at bridge on Minnesota State Highway 48 near Hinckley, Minnesota	MPCA	863	1984–93
19	St. Croix River downstream from Chestnut Street bridge at Stillwater, Minnesota	MCES	7,040	1984–93
20	St. Croix River at Hudson, Wisconsin	MPCA	7,370	1984–93
21	St. Croix River downstream from U.S. Highway 10 bridge at Prescott, Wisconsin.	MCES	7,760	1984–93
22	Mississippi River at Lock and Dam 3, Red Wing, Minnesota	MCES, WDNR	46,600	1984–93
23	Vermillion River at Biscayne Avenue bridge, Farmington, Minnesota	MCES	110	1985–93
24	Vermillion River at bridge on County Road 79 near Empire, Minnesota	MPCA, MCES	138	1984–93
25	Straight River at bridge on County Road 1 near Clinton Falls, Minnesota	MPCA	250	1984–93
26	Cannon River at bridge on County State Aid Highway 7 near Welch, Minnesota	MPCA	1,320	1984–93
27	Mississippi River near the outlet of Lake Pepin	WDNR	47,000	1984–91

Namekagon Rivers (fig. 4; table 2). The USGS routinely collected samples for nutrient analyses at three sites on the Mississippi and Minnesota Rivers as part of the NASQAN (fig. 4; table 2).

Streambed-sediment data were collected by the USACOE (table 1). During 1974–89, the USACOE sampled the Mississippi River navigation channel from the TCMA to the outlet of the study area in Lake Pepin, the 14-mile-long reach of the Minnesota River from Savage, Minnesota, to the mouth, and a 12-mile-long reach of the St. Croix River from Hudson, Wisconsin, to 6 miles upstream from the mouth.

Ground-water-quality data analyzed in this report were collected for the Ground Water Monitoring Program of the MDA, the Safe Drinking Water Program of the MDH, the Ambient Ground-Water Quality Network and Ground Water Monitoring and Assessment Programs (GWMAP) of the MPCA, the Ground-Water Quality Monitoring Network of the WDNR, and local and regional projects of the USGS (table 3). Water-quality data were available from wells completed in unconfined sand and gravel, buried sand and gravel, and bedrock aquifers in the study area.

Methods of Data Review and Analysis

Water-quality data were analyzed to determine median concentrations at stream sites and in aquifers; variations in concentrations among stream sites, among aquifers, and within aquifers; stream loads and yields; and seasonal as well as temporal trends in concentrations in streams. No trends in ground water were analyzed.

An analysis period of water years 1984–93 was selected for summarizing the stream-water-quality data set because this was the most common period of record for the majority of sites. Sites with less than 5 years of data were not included in this analysis. Because fewer data were available, the entire period of record was analyzed for the streambed-sediment (1974–89) data set.

Concentrations of nitrogen and phosphorus constituents in stream water were summarized graphically as truncated boxplots (Helsel and Hirsch, 1992). Differences in constituent concentrations between sites were quantified with a one-way analysis of variance (ANOVA) and Tukey multiple comparison (Helsel and Hirsch, 1992). Prior to these statistical tests, data were log-transformed to make them more normally distributed and consistent in variance. For all statistical tests used in this report, the criterion for statistical

Table 3.--Sources of historical ground-water nitrate and dissolved phosphorus data analyzed for the study area.

Source	General purpose for collecting data	Number of wells sampled for nitrate (phosphorus)	Sampling frequency	Period of record
Minnesota Department of Agriculture—Water-Quality Monitoring Network	Determination of the occurrence of nitrate and pesticides in ground water, generally from shallow wells in agricultural areas	103 (0)	variable	1987–93
Minnesota Department of Health—Safe Drinking Water Program	Determination of compliance of treated surface- and ground-water supplies with Federal and State drinking water standards.	43 (0)	quarterly to every 3 years	1989–94
Minnesota Pollution Control Agency—Ambient Ground Water Monitoring Program	Investigations of ambient ground-water quality in major aquifers in a geographically distributed network of wells	51 (0)	multi-year	1978–91
Minnesota Pollution Control Agency—Ground Water Monitoring and Assessment Program	Determination of ambient ground-water quality conditions in major aquifers sampled in a statewide grid.	138 (0)	multi-year	1992--94
Wisconsin Department of Natural Resources—Ground-Water-Quality Monitoring Network	Monitoring of the quality of untreated ground water used for public water supplies and private wells.	256 (0)	quarterly to annually	1980–94
U.S. Geological Survey	Obtained in the course of regional ground-water-quality investigations conducted in cooperation with state and local agencies	492 (181)	variable	1971–93

significance was the 0.05 significance level. To eliminate any biases in median concentration values due to the MPCA's sampling frequency, which focused on the ice-free season, only data collected by the MPCA during the months of January, April, July, and October were used in these analyses.

The MCES data set did not contain total nitrogen and total nitrite plus nitrate nitrogen concentrations. For this data set, total nitrogen concentration values were calculated by summing total nitrate nitrogen, total organic plus ammonia nitrogen, and total nitrite nitrogen concentrations from samples collected on the same day. Total nitrite plus nitrate nitrogen concentrations were similarly calculated by summing total nitrate nitrogen and total nitrite nitrogen concentrations from samples collected on the same day.

Stream-water-quality data sets were analyzed to determine whether there were significant differences between values obtained from the MCES, MPCA, WDNR, and USGS. Sites selected for this analysis were located on the Mississippi, Minnesota, St. Croix, and Vermillion Rivers within the TCMA (sites 9–11, 13, 15, 22, 24; table 2).

Signed-rank tests (Helsel and Hirsch, 1992) were used to determine if there were differences in the nutrient concentrations measured between agencies. To eliminate differences due to seasonal or hydrologic conditions, only data collected on the same day were compared. Data compared between the MCES, MPCA, and WDNR were obtained from water years 1984–93. No comparisons were made between the USGS and MCES total ammonia nitrogen data sets because only one pair of samples were collected on the same day. For the remaining constituents, the data compared between the USGS and MCES were obtained during 1980.

There were no significant differences among data from the MCES and USGS, MCES and WDNR, and the total nitrite plus nitrate nitrogen concentration data obtained from the MCES and MPCA. P-values (attained significance values) for comparisons between these data sets ranged from 0.56 to 1.00. However, differences were significant between the total nitrogen ($p=0.02$), total ammonia nitrogen ($p=0.00$), and total phosphorus ($p=0.03$) data from the MCES and MPCA.

Data were further compared by site with a Wilcoxon-rank sum test (Helsel and Hirsch, 1992) to determine whether there were differences in median constituent concentrations (water years 1984–93) by agency at each site. Of the 37 comparisons made, there were significant differences ($p=0.0241$) between total organic plus ammonia nitrogen concentrations at site 15, total ammonia nitrogen concentrations at site 24 ($p=0.0027$), and total phosphorus concentrations at site 9 ($p=0.0010$). Because there were few significant differences in concentrations reported between agencies and sites, stream-nutrient data were grouped together in this report.

Censored values are those listed below the method reporting limit. In the stream-water-quality data sets, censored values were handled by substituting one-half the reporting limit for each censored value. Several studies (Gleit, 1985;Helsel and Cohn, 1988; and Helsel, 1990) have shown that distributional methods and robust methods perform better than substitution methods to estimate summary statistics for censored data sets. The substitution of one-half the reporting limit for each censored value introduced little error in the calculation of summary statistics for stream sites in this study because the amount of censored data per site generally was small. The average amount of censored data per site ranged from approximately 3 percent for total phosphorus to approximately 13 percent for total ammonia nitrogen concentration data. Sites generally contained less than 25 percent censored data. Six sites with total ammonia nitrogen (sites 5, 8, 9, 19, 23, 24), five sites with total nitrite plus nitrate nitrogen (sites 5, 8, 19, 21, 23), and one site with dissolved orthophosphate data (site 1, table 2) had greater than 25 percent censored values.

Stream nitrogen and phosphorus loads were calculated at 21 stream sites (table 4) using the version 94.06 of the ESTIMATOR program (G. Baier, T. Cohn, and E. Gilroy, U.S. Geological Survey, written commun., 1993). Total nitrogen loads were calculated by summing total nitrite plus nitrate nitrogen and total organic plus ammonia nitrogen loads. The ESTIMATOR program uses a multivariate log-linear regression model to estimate daily constituent loads and implements a minimum variance unbiased estimator to compensate for the retransformation bias incurred by transforming the logarithmic predicted loads back to the original, untransformed units. The regression model used to estimate daily stream constituent loads used the following terms: a constant; a quadratic and square-root fit to discharge to account for variations in loads due to streamflow; a time term used to account for monotonic long-term temporal trends; and two sinusoidal terms to account for seasonal fluctuations in loads. At sites sampled by the MCES, MPCA, and WDNR, daily-streamflow data from the closest USGS stream-gaging station that most closely approximated the flow at the water-quality site (table 4) was used in the calculations because streamflow was not measured in these monitoring programs. Load calculations for site 5 (table 4) were made using the discharge from the Mississippi River near Anoka, Minnesota minus discharge from the

Table 4.--Stream-water-quality sites and corresponding U.S. Geological Survey streamflow-gaging sites used for load calculations from water years 1984–93 for the study area
[listed in downstream order]

Site number (fig. 4)	Water-quality site	U.S. Geological Survey stream-gaging site	
	Location	Station name	Station identification number
1	Mississippi River near Royalton, Minnesota	Mississippi River near Royalton, Minnesota	05267000
5	Mississippi River downstream of bridge on U.S. Highway 169 at Anoka, Minnesota	Mississippi River near Anoka, Minnesota, Rum River near St. Francis, Minnesota	05288500 05286000
6	Rum River at bridge on County State Aid Highway 5 near Isanti, Minnesota	Rum River near St. Francis, Minnesota	05286000
7	Mississippi River at the city of Minneapolis waterworks intake at Fridley, Minnesota	Mississippi River near Anoka, Minnesota	05288500
8	Mississippi River above Lock and Dam 1, Minnesota	Mississippi River near Anoka, Minnesota	05288500
9	Minnesota River downstream of bridge on County Road 9 near Jordan, Minnesota	Minnesota River near Jordan, Minnesota	05330000
10	Minnesota River near mouth in Fort Snelling State Park, Minnesota	Minnesota River near Jordan, Minnesota	05330000
11	Mississippi River at St. Paul, Minnesota	Mississippi River near St. Paul, Minnesota	05331000
12	Mississippi River at automonitor site in Newport, Minnesota	Mississippi River near St. Paul, Minnesota	05331000
13	Mississippi River at automonitor site near J.L. Shiely Company, Grey Cloud Island, Minnesota	Mississippi River near St. Paul, Minnesota	05331000
14	Mississippi River at Nininger, Minnesota	Mississippi River near St. Paul, Minnesota	05331000
15	Mississippi River at Lock and Dam 2, Hastings, Minnesota	Mississippi River near St. Paul, Minnesota	05331000
17	St. Croix River at bridge on Minnesota State Highway 48 near Danbury, Wisconsin	St. Croix River near Danbury, Wisconsin	05333500
18	Kettle River at bridge on Minnesota State Highway 48 near Hinckley, Minnesota	Kettle River below Sandstone, Minnesota	05336700
19	St. Croix River downstream from Chestnut Street bridge at Stillwater, Minnesota	St. Croix River at St. Croix Falls, Wisconsin	05340500
21	St. Croix River downstream from U.S. Highway 10 bridge at Prescott, Wisconsin	St. Croix River at St. Croix Falls, Wisconsin	05340500
22	Mississippi River at Lock and Dam 3, Red Wing, Minnesota	Mississippi River at Prescott, Wisconsin	05344500
23	Vermillion River at Biscayne Avenue bridge, Farmington, Minnesota	Vermillion River near Empire, Minnesota	05345000
24	Vermillion River at bridge on County Road 79 near Empire, Minnesota	Vermillion River near Empire, Minnesota	05345000
25	Straight River at bridge on County Road 1 near Clinton Falls, Minnesota	Straight River near Faribault, Minnesota	05353800
27	Mississippi River near the outlet of Lake Pepin	Mississippi River at Prescott, Wisconsin	05344500

Rum River near St. Francis, Minnesota (site 6). Concentration data sets were reduced to monthly time series by systematically keeping the observation closest to the 15th day of the month when the regression model indicated serial correlation of the residuals.

Seasonal trends in stream-water nitrogen and phosphorus concentrations were analyzed by LOcally WEighted Scatterplot Smoothing (LOWESS) (Helsel and Hirsch, 1992). As a result of this procedure, the sum of smoothed total nitrite plus nitrate nitrogen and total organic plus ammonia nitrogen concentrations may not equal the smoothed total nitrogen concentration.

Temporal trends in concentrations at stream sites were quantified by the Seasonal Kendall test (Helsel and Hirsch, 1992) and LOWESS smoothing. The Seasonal Kendall test is a nonparametric test for monotonic trends that accounts for seasonality in constituent concentrations by performing a separate Mann-Kendall test (Helsel and Hirsch, 1992) on data collected in each season of the year. Four seasons were used to test for trends. Trend test results were adjusted for serial correlation. At sites where streamflow data were available (table 4), concentration data were flow-adjusted by the method of Crawford and others (1983) to remove the effects of discharge.

Nitrate ($NO_2 + NO_3$ as N) and dissolved phosphorus were the two nutrients summarized for ground water in this report. Nitrate is summarized because it is the most prevalent form of dissolved nitrogen in ground water and because of its implications for human health and eutrophication. Dissolved phosphorus is the form of phosphorus most likely to be transported to surface water by ground-water flow.

Determinations of the aquifers providing water to wells sampled by the MDA, MDH, and USGS were made by comparing unique numbers to the Minnesota Geological Survey County Well Index data base for wells in Minnesota. Aquifer designations for the wells sampled by WDNR were determined by examining microfiche and paper copies of well logs at regional WDNR offices. Only water-quality data from wells with known depths and aquifers were summarized for this report.

Only the water-quality data from the last sample collected from each well were included in data sets to avoid overweighting data from the more frequently analyzed wells. In addition to evenly weighting analyses from all sites, this method also provides data more representative of recent ground-water quality.

Ground-water-quality data were grouped by the sampling agency and aquifer sampled because agencies sampled in different areas, sampled different types of wells, and used differing sample collection methods and laboratories. Ground-water-quality data reviewed for this report included water samples from the following aquifers: unconfined sand and gravel, buried sand and gravel, Cretaceous, upper carbonate/Galena-Platteville, St. Peter, Prairie du Chien-Jordan, Franconia-Ironton-Galesville (Tunnel City-Wonewoc-Eau Claire in Wisconsin), Mt. Simon-Hinckley-Fond du Lac, and Precambrian igneous and metamorphic rocks. Most of the water samples were from unconfined sand and gravel, buried sand and gravel, and the Prairie du Chien-Jordan aquifers, so data from those aquifers are emphasized in this report.

Because these data sets at times were heavily censored (many values were below reporting limits), distributional methods (Helsel and Hirsch, 1992) were used to compute summary statistics. For statistical summaries of data, listed on tables and shown on boxplots in this report, log-probability regression (Helsel and Cohn, 1988) was used to estimate distributions of data below reporting limits. Because of the heavily censored nature of many of the data sets, nutrient concentrations between agency data sets from each aquifer were compared through the use of chi-square testing of contingency tables of detection frequencies to see if data from various agencies was similar for each aquifer sampled (Helsel and Hirsch, 1992; Ott, 1993). The criterion for statistical significance of the chi-square tests was a significance level of 0.05. Testing of nitrate data from the agencies indicated that 6 of 9 of the aquifers had significant differences between agency data sets. The aquifers with similar frequencies of detection of nitrate in samples collected by the agencies included undifferentiated Precambrian aquifers, the Galena-Platteville aquifer, and Cretaceous aquifers, which also were the least-sampled aquifers in the study area. Frequencies of detection of dissolved phosphorus were similar for agency data sets from the sampled aquifers because only one sampling agency, the USGS (in Minnesota and Wisconsin) analyzed water samples for dissolved phosphorus concentrations; and sample collection and analytical methods would have been quite similar for those samples. Frequencies of detection of dissolved phosphorus were significantly different for 2 of the 7 aquifer data sets (Mt. Simon-Hinckley and unconfined sand and gravel aquifers).

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SOURCES AND SINKS OF NITROGEN AND PHOSPHORUS

Sources of nitrogen and phosphorus to a watershed include fertilizers; human and animal wastes; atmospheric deposition; and fixation by biota in streams, lakes, and soils. Once in the watershed, nitrogen and phosphorus can remain on the land surface, be deposited as lake and stream sediments, utilized as nutrients by the biota, exported through streamflow from the watershed, leached to ground water, exported as part of crops and livestock, or lost from the watershed via nutrient cycling reactions such as volatilization or denitrification.

The major sources, sinks, and exports of nitrogen and phosphorus to the study unit were quantified on an annual basis using a mass-balance approach from historical data obtained from Federal, state, and local agencies. The mass balance included sources from fertilizer applications, livestock manure generation, municipal wastewater treatment plant discharges, nitrogen fixation, and atmospheric deposition. Sinks of nitrogen and phosphorus included the uptake by agricultural crops, export from the study unit by streamflow, and a residual term that includes nutrients remaining on the land surface, sedimentation in lakes and slower-moving stream reaches, uptake by biota in streams and lakes, ammonia volatilization, and denitrification. Estimates of these sources and sinks were made on a yearly basis using literature values and the most recently available data.

The amount of nitrogen and phosphorus applied in the form of fertilizer was calculated using county fertilizer-sales data from fertilizer year 1991 (July 1, 1990, to June 30, 1991) (Battaglin and Goolsby, 1995). These data were compiled from annual state fertilizer-sales data reported as tonnages of nitrogen and phosphate to the National Fertilizer and Environmental Research Center of the Tennessee Valley Authority and were expressed as total county sales using the method of Battaglin and Goolsby (1995). For counties not completely within the study unit, the amount of fertilizer sold was estimated by multiplying the total county-fertilizer sales of nitrogen or phosphorus by the percentage of county area within the study unit.

The amount of nitrogen and phosphorus in livestock manure produced within the study unit was estimated using data from 1992 (L.J. Puckett, U.S. Geological Survey, written commun., 1995). The livestock manure data set was constructed by multiplying county animal population data obtained from the 1992 Census of Agriculture by their respective average weights, manure production rates, and manure nutrient content. These data also were expressed as total county tonnages. For counties not completely within the study unit, the amount of nitrogen and phosphorus in livestock manure was estimated by multiplying the total amount of livestock manure generated in each county by the percentage of county area within the study unit.

Wet deposition of ammonium and nitrate nitrogen was calculated using 1993 data collected from the National Atmospheric Deposition/National Trends Network (Cathy Copeland, National Atmospheric Deposition/National Trends Network coordination office, written commun., 1995). Wet deposition of phosphate was not included because no data were available. Wet-deposition data were obtained from eight discrete sites located within or bordering the study unit. Precipitation-monitoring sites used in these calculations were located at Fort Ripley, Minnesota; Lamberton, Minnesota; Spooner, Wisconsin; Grand Rapids, Minnesota (fig. 1); Wildcat Mountain, Wisconsin (outside of the study unit); Big Springs Fish Hatchery in Clayton County, Iowa (outside of the study unit); Woodworth in Stutsman County, North Dakota (outside of the study unit); and Huron County, South Dakota (outside of the study unit). Wet-deposition data from these stations were spatially extrapolated to the entire study unit using an inverse-distance-squared weighted average to the centroid of the study unit (Wei and McGuinness, 1973). The effect of urban land use on increasing wet nitrate deposition was taken into account using the method of Sisterson (1990).

The amount of nitrate from dry deposition was estimated using the method developed by Sisterson (1990). Dry deposition of ammonium was not included to minimize double accounting of ammonium that is recirculated by the volatization from livestock manure.

Symbiotic nitrogen fixation by legumes was estimated using average first-year values obtained from the Wisconsin Agricultural Extension office (Bundy and others, 1992). Legume crop areas and crop yields were obtained from the Iowa, North Dakota, South Dakota, Wisconsin, and Minnesota 1993 state agricultural statistics (Iowa State University, 1994; North Dakota Agricultural Statistics Service, 1994; South Dakota Agricultural Statistics Service, 1994; Wisconsin Agricultural Statistics Service, 1994; and Minnesota Agricultural Statistics Service, 1995).

Nonsymbiotic nitrogen fixation by other crops, forests, and wetlands in the study unit were estimated using nitrogen fixation rates reported by Burns and Hardy (1975) for nonlegume-producing agricultural land (4.5 lb/ac/year), wetlands (17.8 lb/ac/year), and forest and woodland (8.9 lb/ac/year). Areas of agricultural, wetland, and forest and woodland land cover were obtained from the Geographic Information and Retrieval and Analysis System (GIRAS) (U.S. Geological Survey, 1990) and were adjusted to include only nonlegume-producing cropland.

Annual nitrogen and phosphorus loads from municipal wastewater treatment facilities in the study unit were calculated using 1993 data from the PCS, MCES, and the National Oceanic and Atmospheric Administration (1993). For 11 wastewater treatment plants in the TCMA, annual nitrogen and phosphorus loads were calculated by multiplying effluent volumes by reported nitrogen and phosphorus concentrations obtained from the MCES (L.C. Dyste, Metropolitan Council Environmental Services, electronic commun., 1996). Loads were estimated for facilities that did not have adequate nitrogen and phosphorus data in PCS by using literature values for average concentrations of nitrogen (11 mg/L) and phosphorus (7.2 mg/L) in the effluents of treatment plants providing secondary treatment (National Oceanic and Atmospheric Administration, 1993).

Nitrogen and phosphorus contained in harvested crops in 1993 were estimated from the nutrient content of plants (Zublena, 1991). Crop yields and the areas of crops harvested were obtained from state agricultural statistics (Iowa State University, 1994; North Dakota Agricultural Statistics Service, 1994; South Dakota Agricultural Statistics Service, 1994; Wisconsin Agricultural Statistics Service, 1994; and Minnesota Agricultural Statistics Service, 1995).

Nitrogen and phosphorus exported from the study unit by streamflow were determined by estimating loads at the outlet of Lake Pepin using version 94.06 of the ESTIMATOR program (G. Baier, T. Cohn, and E. Gilroy, U.S. Geological Survey, written commun., 1993). Water-quality data collected by the WDNR near the outlet of Lake Pepin and streamflow data collected by the USGS on the Mississippi River at Prescott, Wisconsin, were used as inputs to the program.

A compilation of the sources of nitrogen and phosphorus applied to the study unit (fig. 8) indicated 778,839 tons of nitrogen and 132,067 tons of phosphorus each year. The majority of the nitrogen and phosphorus applied to the study unit was from fertilizers and livestock manure. These two sources accounted for 72 percent of the nitrogen and 98 percent of the phosphorus added each year. Nitrogen fixation and atmospheric deposition also were substantial sources of nitrogen to the study unit, contributing 15 and 11 percent, respectively. Discharges from municipal wastewater treatment facilities accounted for about 2 percent of the total amounts of nitrogen and phosphorus added each year, but may be more substantial sources to streams than indicated because most of these facilities discharge directly to streams.

The Minnesota River Basin accounted for over 60 percent of both the nitrogen and phosphorus from fertilizer usage in the study unit. The Minnesota River Basin contributed 61 percent of the fertilizer nitrogen (234,720 tons) and the fertilizer phosphorus (40,670 tons) applied to the study unit. The part of the Mississippi River Basin above the confluence with the Minnesota River contributed approximately 25 percent of both the fertilizer nitrogen (93,887 tons) and the fertilizer phosphorus (16,290 tons) applied. The remainder of the fertilizer nitrogen and phosphorus primarily was contributed from the Vermillion, Cannon, and St. Croix River Basins, and the TCMA.

Greater than 80 percent of the nitrogen and phosphorus generated as part of livestock manure was produced in the Minnesota River Basin and in the part of the Mississippi River Basin upstream of the confluence with the Minnesota River. The Minnesota River Basin produced 48 percent of the nitrogen (87,940 tons) and 57 percent of the phosphorus (35,782 tons) generated from livestock manure. The part of the Mississippi River Basin upstream of the confluence with the Minnesota River produced 33 percent of the nitrogen (60,297 tons) and 27 percent of the phosphorus (16,944 tons) generated from livestock manure.

Crop uptake and nutrient loads exported from the study unit accounted for only a small portion of the nitrogen and phosphorus sinks and exports (fig. 8). Crop uptake accounted for 17 and 13 percent of the nitrogen and phosphorus sinks and exports, respectively. Mississippi River outflow from Lake Pepin accounted for 11 percent of the nitrogen and 3 percent of the phosphorus. The remainder of the nitrogen and phosphorus sinks was

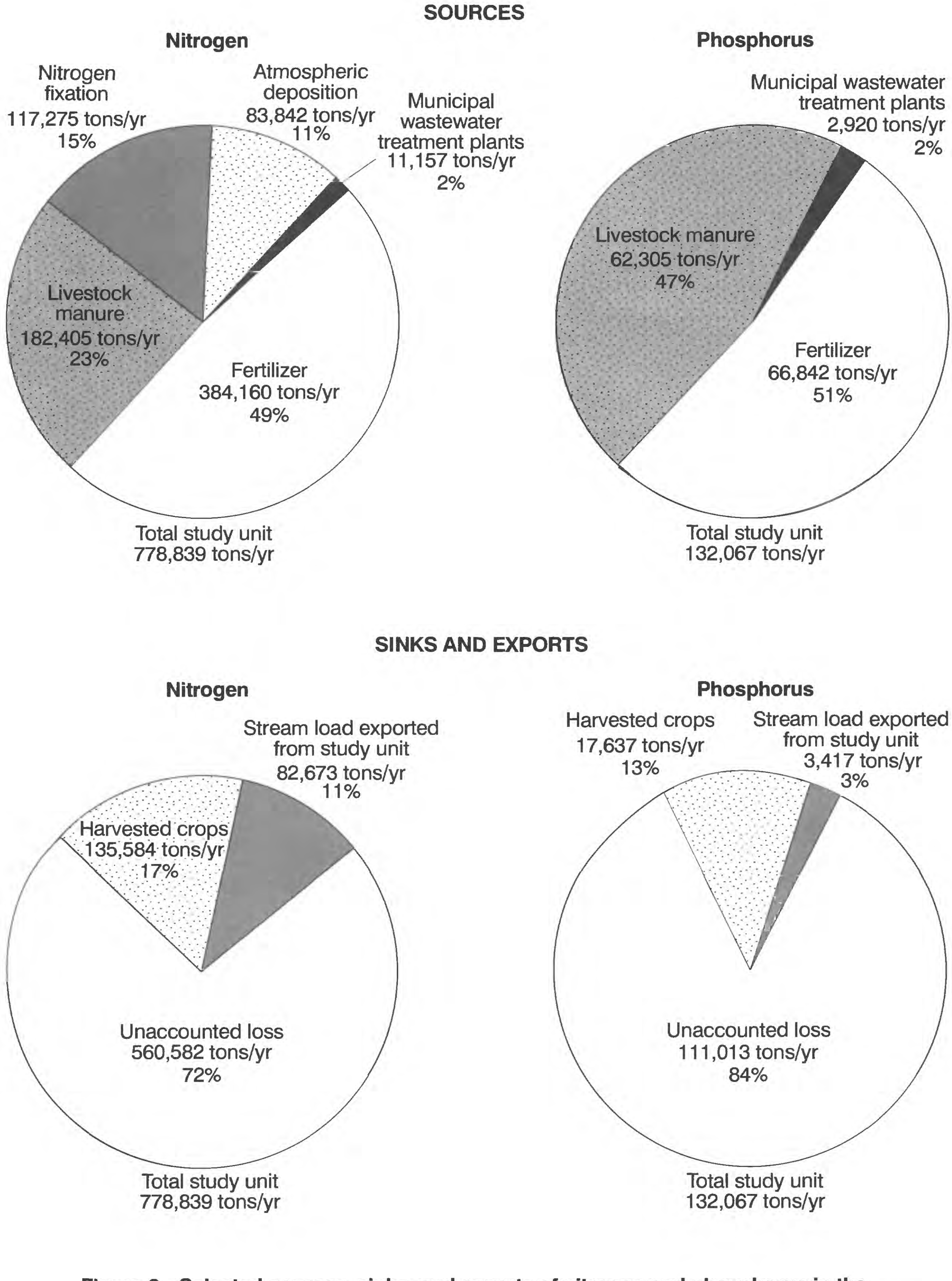

Figure 8.--Selected sources, sinks, and exports of nitrogen and phosphorus in the Upper Mississippi River Basin study unit, 1991-93.

unaccounted for and may be cycled through the watershed by volatilization and denitrification, deposited in the sediments of streams and lakes or on the land surface as crop residues, used as nutrients by biota, or leached to ground water.

NITROGEN DISTRIBUTION AND TRENDS

Nitrogen reaches streams and ground water from municipal and industrial wastewater discharges; combined sanitary and storm sewer overflows; urban areas; logging areas; construction sites; improperly functioning septic systems; and solid waste disposal sites. The combustion of fossil fuels from coal- and oil-burning utilities, industries, automobiles, trucks, and buses also is a source of nitrogen oxides to the environment because these compounds are readily dispersed after they are emitted to the atmosphere. Once in the atmosphere, nitrogen oxides are readily converted by a series of photochemical reactions to nitrite and nitrate (Wayne, 1993).

Agricultural nonpoint sources of nitrogen are recognized nationally as significantly affecting water quality (Myers and others, 1985; Puckett, 1995). Fertilizers and livestock manure are major sources of nitrogen in agricultural runoff. Fertilizers contain nitrogen primarily in the forms of nitrate, urea, and ammonia; and livestock manure typically contains nitrogen in the forms of organic nitrogen and ammonia.

Streams

The predominant forms of nitrogen in streams are nitrate, nitrite, ammonia, and organic nitrogen. Ammonia nitrogen in streams is partitioned between the ammonium ion and un-ionized ammonia, which is dependent upon water pH and temperature. At higher pH and temperature, ammonia is present largely in the un-ionized form, which can be toxic to fish and other biota.

Nitrogen compounds in streams can be transformed through a series of microbially mediated reactions referred to as the nitrogen cycle. The nitrogen cycle consists of five major reactions: assimilation, nitrogen fixation, mineralization, nitrification, and denitrification. Biota in the water and sediments can readily assimilate ammonia and nitrate. Through the process of nitrogen fixation, certain types of blue-green algae and bacteria in water and sediments assimilate dissolved nitrogen gas, which enables these species to survive in environments with smaller amounts of nitrate or ammonia. Under aerobic conditions, ammonia can be oxidized to nitrate through the process of nitrification. Nitrification is a two-step process. First, ammonia is oxidized to nitrite by the bacteria *Nitrosomonas*, and the nitrite produced is subsequently oxidized to nitrate by the bacteria *Nitrobacter*. Because nitrite is rapidly oxidized, it is seldom found in appreciable quantities in streams. Nitrogen can be removed from stream water and sediments under anaerobic conditions through the process of denitrification, which reduces nitrate to nitrogen gases.

Concentrations

Concentrations of the major forms of nitrogen occurring in streams— total nitrogen, total nitrite plus nitrate nitrogen, total organic plus ammonia nitrogen, and total ammonia nitrogen— were analyzed in this report. No total ammonia data were available from the WDNR. Throughout the remainder of this report, total nitrite plus nitrate nitrogen will be referred to as nitrate because nitrite concentrations in streams are generally low compared to nitrate concentrations, and nitrate in water generally occurs in the dissolved form.

Nitrate

Nitrate concentrations (fig. 9) in the tributaries to the Mississippi River were significantly greater in streams draining extensive agricultural lands (sites 9, 10, 23–26; table 2; figs. 3, 4) relative to mixed forest and agriculture (sites 2, 6, 19–21; table 2; figs. 3, 4) and forested areas (sites 16–18; table 2; figs. 3, 4). Median concentrations in agricultural areas ranged from 2.0 to 5.3 mg/L. In areas of mixed forest and agriculture, median concentrations ranged from 0.2 to 0.6 mg/L. Median concentrations were lowest in the forested areas and ranged from 0.05 to 0.1 mg/L.

In the Mississippi River, nitrate concentrations were significantly greater downstream of the Minnesota River relative to the upstream sites. Median concentrations upstream from the Minnesota River (sites 1, 3–5, 7, 8; fig. 9) ranged from 0.1 to 0.8 mg/L. Downstream of the Minnesota River, median concentrations ranged from 1.5 to 2.1 mg/L. Concentrations decreased slightly at Lock and Dam 3 and near the outlet of Lake Pepin (sites 22, 27; fig. 9), but were not significantly different from concentrations at St. Paul, Minnesota, through Lock and Dam 2.

In the St. Croix River, nitrate concentrations at sites within the TCMA (sites 19–21; fig. 9) were significantly greater than near Danbury, Wisconsin (site 17; fig. 9). Median concentrations ranged from 0.2 to 0.5 mg/L at Stillwater, Minnesota, and Hudson and Prescott, Wisconsin. Near Danbury, Wisconsin, the median concentration was lower, 0.05 mg/L.

In the Vermillion River, nitrate concentrations were significantly greater near Empire, Minnesota (site 24, table 2, fig. 9) than about 5 miles upstream at Farmington, Minnesota (site 23; table 2; fig. 9). Greater

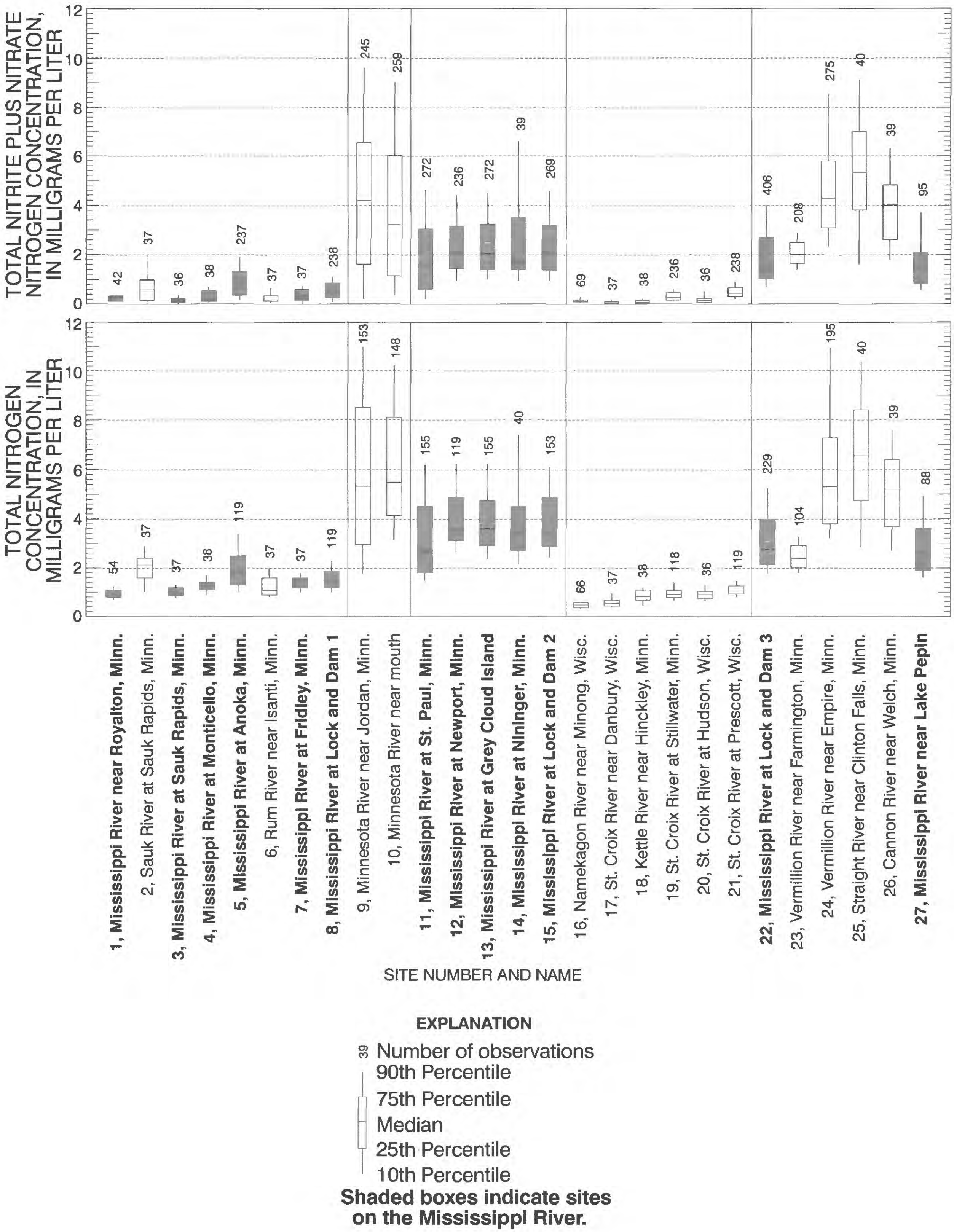

Figure 9.--Total nitrite plus nitrate nitrogen and total nitrogen concentrations at selected stream sites in the study area, water years 1984-93 (shown in downstream order).

concentrations near Empire, Minnesota, were possibly a result of wastewater discharge (fig. 4), because it is a substantial source of nitrate between these two sites (Almendinger and Mitton, 1995).

The variability in nitrate concentrations was greatest in the tributaries to the Mississippi River draining agricultural areas and at sites on the Mississippi River downstream of the Minnesota River. Interquartile ranges at these sites ranged from 0.9 to 4.2 mg/L. At all other sites, interquartile ranges generally were narrower, 0.1 to 1.0 mg/L.

Nitrate concentrations at times exceeded the MCL for drinking water in the Minnesota, Straight, and Vermillion Rivers, and in the Mississippi River at Nininger and at Lock and Dam 2. These stream sites, however, are not immediately upstream of a source of public water supply within the study area. The MCL for nitrate was exceeded in less than 10 percent of the samples collected at each of these sites. Concentrations exceeding the MCL usually corresponded with an increase in stream discharge, except in the Vermillion River near Empire, Minnesota. At this site, exceedances of the MCL typically occurred in years with below-average discharge during base-flow conditions.

In the Minnesota River, exceedances of the nitrate MCL occurred during water years 1984 and 1990–93. Most exceedances of the MCL (9 percent) occurred near Jordan, Minnesota. At this site, 24 of the 265 samples exceeded the MCL. Near the confluence with the Mississippi River, exceedances of the MCL were observed in 18 of the 259 samples. Exceedances usually occurred in the spring and early summer (April through July) during an increase in stream discharge or immediately after stream discharge reached a maximum. Nitrate concentrations exceeding the MCL also occurred during October through December of 1991 and 1992 at both Minnesota River sites when discharge increased from base-flow conditions.

In the Straight River near Clinton Falls, Minnesota, nitrate concentrations exceeded the MCL during water year 1990. At this site, the nitrate MCL was exceeded in three samples. All exceedances of the MCL occurred in the spring and summer when stream discharge was increasing or immediately after stream discharge reached a maximum.

In the Vermillion River near Farmington, Minnesota, nitrate concentrations exceeded the MCL in one sample. The exceedance occurred on April 7, 1993, when stream discharge at the Vermillion River near Empire, Minnesota increased from 50 to 446 ft^3/s (Mitton and others, 1994).

Exceedances of the nitrate MCL in the Vermillion River near Empire, Minnesota, occurred during base-flow conditions, generally during years with below-average discharge. At this site, 18 of the 275 samples (6.5 percent) exceeded the MCL. All exceedances occurred during water years 1988–91. In contrast to the other sites, none of the exceedances of the nitrate MCL occurred in association with an increase in streamflow. All exceedances occurred during base-flow conditions, possibly a result of wastewater discharges from a facility (fig. 4) that nitrifies the effluent year-round (Cathy Larson, Metropolitan Council Environmental Services, electronic commun., 1997).

In the Mississippi River, nitrate concentrations exceeding the MCL occurred at Lock and Dam 2 and Nininger, Minnesota, and occurred immediately following an increase in stream discharge. At Lock and Dam 2, 1 of 269 samples (0.4 percent) exceeded the MCL. The exceedance occurred on May 14, 1991, during flow recession after the stream discharge had increased from 21,500 to 51,700 ft^3/s at St. Paul, Minnesota (Gunard and others, 1992). At Nininger, Minnesota, the nitrate concentration in the Mississippi River exceeded the MCL in 1 of the 39 samples (2.6 percent). The exceedance of the MCL at this site occurred on November 26, 1991. Similar to the results at Lock and Dam 2, this exceedance occurred during flow recession after an increase in stream discharge from 10,200 to 25,900 ft^3/s (Gunard and others, 1993).

Total Organic Plus Ammonia Nitrogen

Total organic plus ammonia nitrogen concentrations (fig. 10) in the tributaries to the Mississippi River were significantly greater at the Sauk, Rum, Minnesota, Straight, and Cannon Rivers relative to the Namekagon, St. Croix, Kettle, and Vermillion Rivers. Median concentrations ranged from 0.9 to 1.8 mg/L in the former set of streams. In the Namekagon, St. Croix, Kettle, and Vermillion Rivers, median concentrations ranged from 0.3 to 0.7 mg/L.

In the Mississippi River, total organic plus ammonia nitrogen concentrations were significantly greater at Newport, Grey Cloud Island, and Lock and Dam 2 than at all sites upstream of the Minnesota River. Median concentrations from Royalton, Minnesota, to Lock and Dam 1 ranged from 0.7 to 1.0 mg/L. Concentrations near Royalton, Minnesota, were significantly lower than at sites from Monticello, Minnesota, to Lock and Dam 1. At the Newport, Grey Cloud Island, and Lock and Dam 2 sites, median concentrations ranged from 1.3 to 1.5 mg/L. However, concentrations at these sites were not significantly different from concentrations at

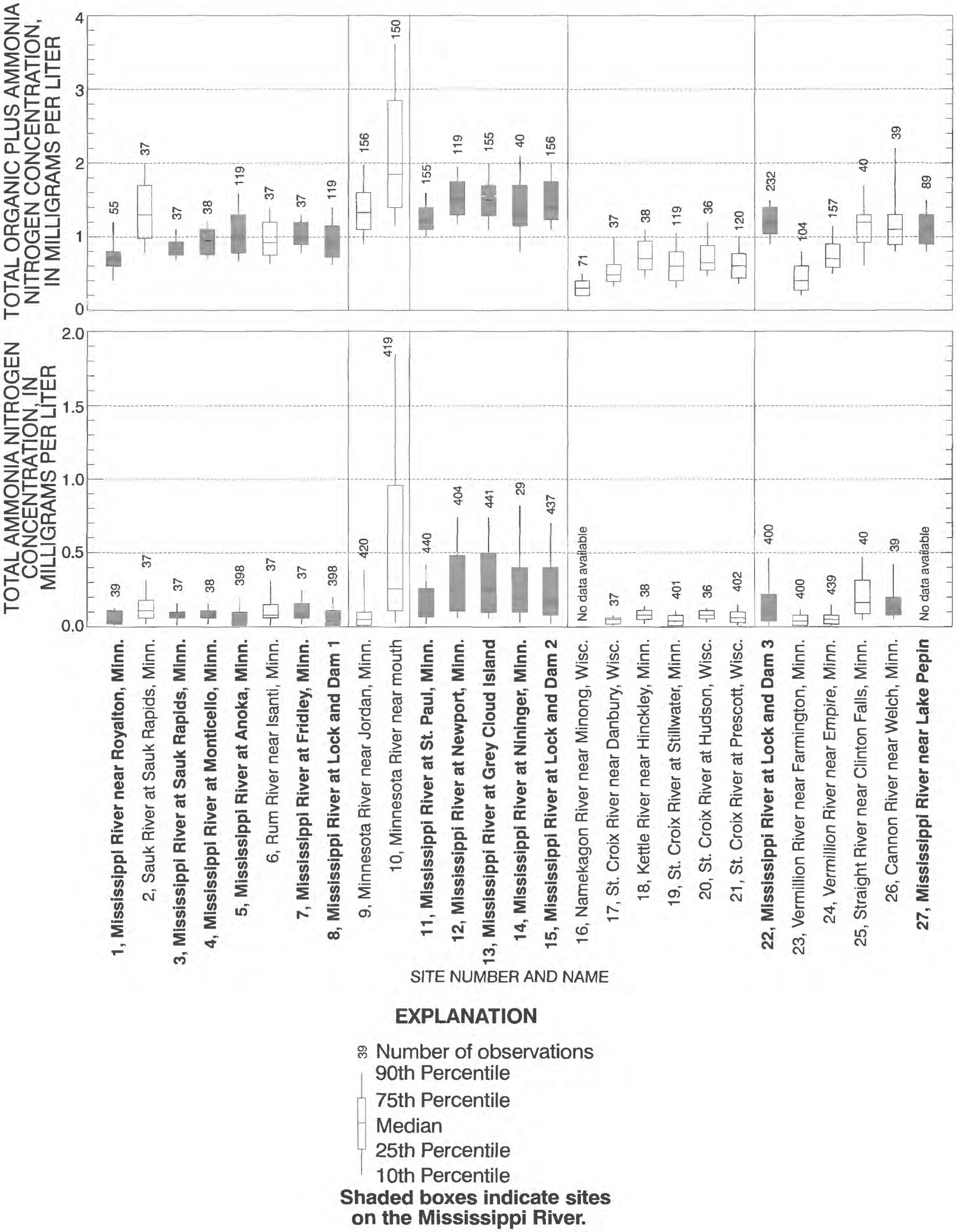

Figure 10.--Total organic plus ammonia nitrogen and total ammonia nitrogen concentrations at selected stream sites in the study area, water years 1984-93 (shown in downstream order).

St. Paul, Nininger, Lock and Dam 3, and the near outlet of Lake Pepin.

In the Vermillion and Minnesota Rivers, total organic plus ammonia nitrogen concentrations were significantly greater at the downstream sites. In the Vermillion River, concentrations were significantly greater near Empire than near Farmington, Minnesota. Similarly in the Minnesota River, concentrations were significantly greater near the mouth than near Jordan, Minnesota.

In the St. Croix River, total organic plus ammonia nitrogen concentrations did not vary significantly along its length. At sampling sites along the St. Croix River from Danbury to Prescott, Wisconsin, median concentrations ranged from 0.4 to 0.7 mg/L.

Total ammonia nitrogen

Total ammonia nitrogen concentrations (fig. 10) were significantly greater at the Minnesota River near the mouth and the Mississippi River at Newport and Grey Cloud Island, Minnesota, than all other sites except the Mississippi River at Nininger and the Straight River near Clinton Falls, Minnesota. Median concentrations at these five sites ranged from 0.17 to 0.27 mg/L. At all other sites, median concentrations were less, 0.04 to 0.16 mg/L.

The variability in total ammonia nitrogen concentrations also were greatest at the Minnesota River near the mouth and the Mississippi River at Newport and Grey Cloud Island, Minnesota, relative to the other sites. Interquartile ranges at these sites were from 0.37 to 0.85 mg/L. At all other sites, interquartile ranges were less, 0.04 to 0.32 mg/L.

In contrast to the results for the other nitrogen constituents, total ammonia nitrogen concentrations in the Vermillion River showed no significant difference from Farmington to Empire, Minnesota. Median concentrations near Farmington and Empire, Minnesota were 0.04 and 0.05 mg/L, respectively. The lack of any downstream increase in total ammonia concentrations in the stream was possibly the result of advanced secondary treatment with nitrification at an upstream wastewater treatment plant (fig. 4) (Metropolitan Waste Control Commission, 1990).

Total Nitrogen

Total nitrogen concentrations (fig. 9) in the Mississippi River and its tributaries generally paralleled nitrate. Concentrations were significantly greater in the Minnesota, Straight, and Cannon Rivers and in the Vermillion River near Empire, Minnesota, than in the Sauk, Rum, St. Croix, Kettle, and Namekagon Rivers. In the Mississippi River, concentrations were significantly greater at sites downstream of the Minnesota River (sites 11–15, 22, 27; table 2; fig. 9) than at sites upstream (sites 1, 3–5, 7, 8; table 2; fig. 9).

Loads and Yields

The stream load is the amount of a constituent, such as nitrate, that has been carried past a point on the stream in a given amount of time, usually 1 year. Yield is load per unit drainage area. In this report, total nitrogen, nitrate nitrogen, and total organic plus ammonia nitrogen loads were calculated at 21 sites on the Mississippi, Minnesota, St. Croix, Kettle, Rum, Vermillion, and Straight Rivers (table 5) for water years 1984–93.

Tributaries that contributed most of the nitrogen to the Mississippi River were the Minnesota and St. Croix Rivers (table 5; fig. 11). Total organic plus ammonia nitrogen was the predominant form of nitrogen loading in tributaries draining areas with primarily forested or mixed forest and cropland land cover. Nitrate nitrogen was the predominant form of nitrogen loading in tributaries draining areas that have primarily agricultural land cover. Total organic plus ammonia nitrogen comprised 70, 84, and 90 percent of the median total nitrogen load, respectively, in the Rum River near Isanti, Minnesota; St. Croix River near Danbury, Wisconsin; and Kettle River near Hinckley, Minnesota. In contrast, nitrate nitrogen comprised 80, 85, and 88 percent of the median total nitrogen load, respectively, in the Vermillion River near Farmington, Minnesota; Straight River near Clinton Falls, Minnesota; and Minnesota River near Jordan, Minnesota.

In the Minnesota River, total nitrogen and nitrate loads decreased in the downstream direction from Jordan, Minnesota, to the mouth, and total organic plus ammonia nitrogen loads increased (table 5). Annual nitrate loads decreased, and annual total organic plus ammonia nitrogen loads increased in every water year analyzed in this report. Annual total nitrogen loads decreased in every water year analyzed except 1990. Decreases in nitrate and total nitrogen loads may have been the result of denitrification or the biological conversion of nitrate or ammonia. Increases in total organic plus ammonia nitrogen load possibly were the result of uptake of nitrate or ammonia by stream biota.

In the St. Croix River, median total nitrogen, nitrate, and total organic plus ammonia nitrogen loads increased in the downstream direction from Danbury, Wisconsin, to Prescott, Wisconsin (table 5). Annual nitrogen-constituent loads increased in every water year analyzed in this report. Increases in nitrogen-constituent loads possibly were the result of increased streamflow or

Table 5.--Median nitrogen constituent loads at selected stream sites in the study area, water years 1984–93
[listed in downstream order]

Site number (fig. 4)	Water-quality site: Location	Median load, in tons per year: Total nitrogen	Total nitrite plus nitrate nitrogen	Total organic plus ammonia nitrogen
1	Mississippi River near Royalton, Minnesota	4,515	985	3,530
5	Mississippi River downstream of bridge on U.S. Highway 169 at Anoka, Minnesota	19,145	10,598	8,547
6	Rum River near Isanti, Minnesota	961	284	677
7	Mississippi River at the city of Minneapolis waterworks intake at Fridley, Minnesota	17,210	7,932	9,278
8	Mississippi River above Lock and Dam 1, Minnesota	16,009	7,367	8,642
9	Minnesota River downstream of bridge on County Road 9 near Jordan, Minnesota	72,777	63,917	8,860
10	Minnesota River near mouth in Fort Snelling State Park, Minnesota	63,629	52,679	10,950
11	Mississippi River at St. Paul, Minnesota	76,079	53,804	22,276
12	Mississippi River at automonitor site in Newport, Minnesota	72,371	50,984	21,387
13	Mississippi River at automonitor site near J.L. Shiely Company, Grey Cloud Island, Minnesota	75,174	53,311	21,863
14	Mississippi River at Nininger, Minnesota	66,261	49,071	17,191
15	Mississippi River at Lock and Dam 2, Hastings, Minnesota	75,507	54,236	21,271
17	St. Croix River at bridge on Minnesota State Highway 48 near Danbury, Wisconsin	855	141	714
18	Kettle River at bridge on Minnesota State highway 48 near Hinckley, Minnesota	758	73	685
19	St. Croix River downstream from Chestnut Street bridge at Stillwater, Minnesota	4,626	1,566	3,061
21	St. Croix River downstream from U.S. Highway 10 bridge at Prescott, Wisconsin	5,575	2,582	2,993
22	Mississippi River at Lock and Dam 3, Red Wing, Minnesota	90,418	63,475	26,944
23	Vermillion River at Biscayne Avenue bridge, Farmington, Minnesota	170	136	34
24	Vermillion River at bridge on County Road 9 near Empire, Minnesota	279	227	53
25	Straight River at bridge on County Road 1 near Clinton Falls, Minnesota	2,427	2,055	372
27	Mississippi River near the mouth of Lake Pepin	87,439	60,708	26,731

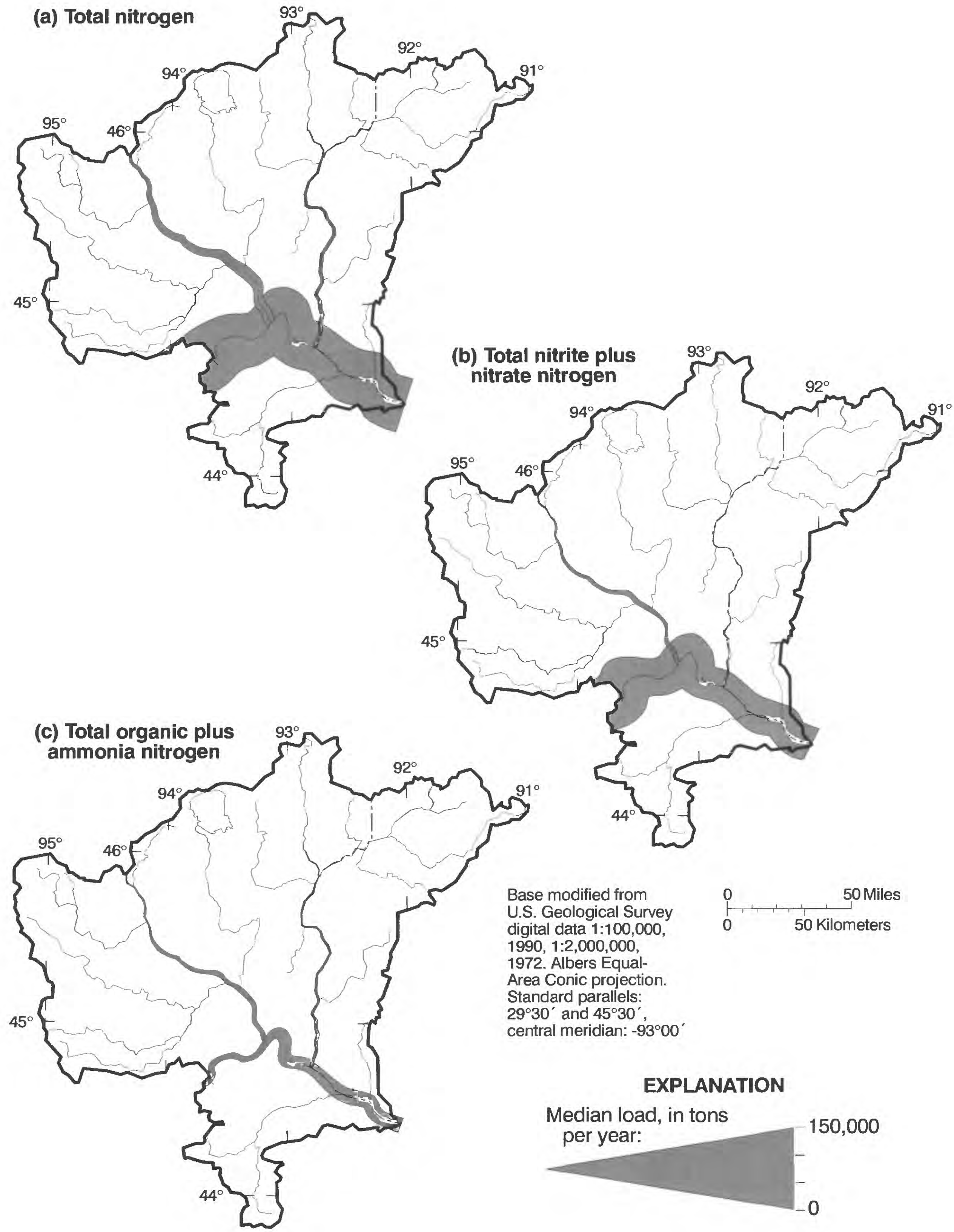

Figure 11.--(a) Total nitrogen, (b) total nitrite plus nitrate nitrogen, and (c) total organic plus ammonia nitrogen loads in the study area, water years 1984-93.

inflow from tributaries draining areas with larger proportions of mixed forest and agricultural land cover.

The proportion of nitrate comprising the total nitrogen load in the St. Croix River also increased in the downstream direction (table 5). Increases from Danbury to Prescott, Wisconsin were observed in every water year analyzed. Near Danbury, Wisconsin, nitrate comprised approximately 16 percent of the median total nitrogen load. Approximately 100 miles downstream from Danbury, Wisconsin, the proportion of nitrate comprising the median total nitrogen load increased to 33 percent at Stillwater, Minnesota. Near the confluence with the Mississippi River near Prescott, Wisconsin, nitrate nitrogen comprised approximately 46 percent of the median total nitrogen load.

Total nitrogen and nitrate yields were greater in the watersheds draining areas with predominantly agricultural land cover than forested areas or areas with mixed forest and agriculture land cover (fig. 3; table 6). Median total nitrogen and nitrate yields were greatest in the Minnesota, Vermillion, and Straight Rivers. Total organic plus ammonia nitrogen yields generally showed less variability than total nitrogen or nitrate yields.

Total nitrogen loads in the Mississippi River increased from Royalton to Anoka, Minnesota, possibly the result of contributions from tributaries such as the Sauk and Crow Rivers or wastewater discharges (fig. 4). The greatest increase in nitrogen loading occurred downstream of the Minnesota River (fig. 11; table 5). Loads further increased at Lock and Dam 3, possibly the result of increased streamflow.

Median loads (table 5) indicated nitrate losses from the water column in the pooled reaches of the Mississippi River above Locks and Dams 1 and 2, and in Lake Pepin. Annual nitrate loads decreased in the downstream direction in every water year analyzed in this report in the reach from Anoka to Fridley, Minnesota. Part of the nitrate may have been removed by conversion to organic forms by stream biota or denitrification. Annual total organic plus ammonia nitrogen loads increased in this same reach in every water year analyzed except 1985.

In the Mississippi River reach above Lock and Dam 2 from Grey Cloud Island to Nininger, Minnesota, annual nitrate loads decreased in all water years analyzed except 1987 and 1992. Part of the nitrate load may have been converted to organic forms by stream biota.

Table 6.--Median total nitrogen, total nitrite plus nitrate nitrogen, and total organic plus ammonia nitrogen yields at selected sites in the study area, water years 1984–93.
[listed in downstream order]

Site number (fig. 4)	Water-quality site	Yield, units are in tons/square mile/year		
	Location	Total nitrogen	Total nitrite plus nitrate nitrogen	Total organic plus ammonia nitrogen
6	Rum River at bridge on County State Aid Highway 5 near Isanti, Minnesota	0.81	0.24	0.57
9	Minnesota River downstream of bridge on County Road 9 near Jordan, Minnesota	4.49	3.95	0.55
10	Minnesota River near the mouth in Fort Snelling State Park, Minnesota	3.77	3.12	0.65
17	St. Croix River at bridge on Minnesota State Highway 48 near Danbury, Wisconsin	0.54	0.08	0.45
18	Kettle River at bridge on Minnesota State Highway 48 near Hinckley, Minnesota	0.88	0.08	0.79
19	St. Croix River downstream from Chestnut Street bridge at Stillwater, Minnesota	0.66	0.22	0.43
21	St. Croix River downstream from U.S. Highway 10 bridge at Prescott, Wisconsin	0.72	0.33	0.39
23	Vermillion River at Biscayne Avenue bridge, Farmington, Minnesota	1.55	1.24	0.31
24	Vermillion River at bridge on County Road 79 near Empire, Minnesota	2.02	1.64	0.38
25	Straight River at bridge on County Road 1 near Clinton Falls, Minnesota	9.71	8.22	1.49

However, annual total organic plus ammonia nitrogen loads also decreased in the downstream direction along this same reach in every water year analyzed.

Annual nitrate loads in the Mississippi River reach from Lock and Dam 3 to near the outlet of Lake Pepin decreased in every water year analyzed. Denitrification and uptake by stream biota are two possible removal mechanisms for nitrate. Conversion to organic nitrogen by biota may not have removed all of the nitrate from the water column. Annual total organic plus ammonia nitrogen loads in this reach decreased in all water years analyzed except 1988–90 and 1992. When increases in total organic plus ammonia nitrogen occurred in the downstream direction along this reach, the net gains in organic nitrogen were, at most, about one-half the amount of nitrate lost. Results indicated a median annual net loss of 6.1 percent of the total nitrogen from the water column in the lake from water years 1984–93. The median annual net loss of total nitrogen and nitrate from the water column in the lake was larger from water years 1991–93, 13 and 17 percent, respectively. These results are consistent with a mass balance study by Maurer and others (1995) that determined that Lake Pepin acted as a net sink for nitrogen from June 1987 through June 1988 and removed 14 percent of the total nitrogen from the water column.

In the Mississippi River at the inflow to the study area near Royalton, Minnesota, the nitrogen load was 20 percent nitrate and 80 percent organic plus ammonia nitrogen. The percentage of nitrate increased to 50 percent in the reach between Anoka, Minnesota, and Lock and Dam 1. This increase may have been the result of increased nitrate contributions from streams draining areas that have a greater proportion of agricultural land cover (fig. 3). Downstream of the confluence with the Minnesota River, which carries a greater nitrate load than other streams analyzed in this report, the percentage of nitrate in the Mississippi River further increased to approximately 70 at all sites from St. Paul, Minnesota, and persisted in that proportion.

Nitrate loads in the Mississippi River similarly increased substantially downstream of the confluence with the Minnesota River (fig. 11; table 5). Total nitrogen loads followed a similar longitudinal pattern, largely because nitrate comprises the majority of the nitrogen loading downstream of the Minnesota River. In contrast, organic plus ammonia nitrogen load in the Mississippi River primarily was contributed by the drainage upstream of the TCMA and the Minnesota River. Total organic plus ammonia nitrogen load decreased upstream of the confluence with the Minnesota River at Lock and Dam 1. The decrease was possibly due to the sedimentation of organic nitrogen sorbed to particulates in the pool upstream of the dam. Downstream of the confluence with the Minnesota River at St. Paul, Minnesota, the load in the Mississippi River approximately doubled. The load in the Mississippi River further increased at Newport, Minnesota. Loads remained at approximately this amount to Lock and Dam 2. Total organic plus ammonia nitrogen loads further increased downstream of the confluence with the St. Croix River at Lock and Dam 3 and remained at approximately the same amount to the outlet of the study area in Lake Pepin.

Trends

Within the study area, concentrations of nitrogen compounds in streams are expected to vary seasonally due to seasonal application of fertilizers, decreased runoff in the winter when most of the precipitation is in the form of snow, and variations in streamflow. Fertilizers, which typically contain nitrogen in the form of ammonium, urea, and nitrate, generally are applied to the study area during the spring and fall. During winter, the lack of liquid precipitation restricts the transport of nitrogen from the land surface to streams. The seasonal variations in precipitation and streamflow affect the concentrations of nitrogen compounds by increasing runoff or enhancing dilution.

Changes in wastewater-treatment practices and fertilizer use may have affected nitrogen-constituent concentrations during the 10-year analysis period. Many of the municipal wastewater treatment facilities permitted to discharge in the study unit were constructed or upgraded during the analysis period. In addition, 99 percent of the combined sanitary and storm sewers in the City of Minneapolis (Leonard Krumm, City of Minneapolis, oral commun., 1996) and all of the combined sanitary and storm sewers in the City of St. Paul (Pat Byrne, City of St. Paul, oral commun., 1996) have been separated.

Seasonal Variations

Nitrate concentrations in the Minnesota River near Jordan, Minnesota (fig. 12), generally were greatest in the spring and summer based on 1984–93 data. Seasonal variations in concentrations in the Straight River near Clinton Falls, Minnesota, and Cannon River near Welch, Minnesota, were similar to those at Jordan, except the greatest concentrations typically occurred about 1 month earlier.

In contrast, the greatest nitrate concentrations in the St. Croix River at Stillwater, Minnesota, and Sauk River at Sauk Rapids, Minnesota, occurred during the winter

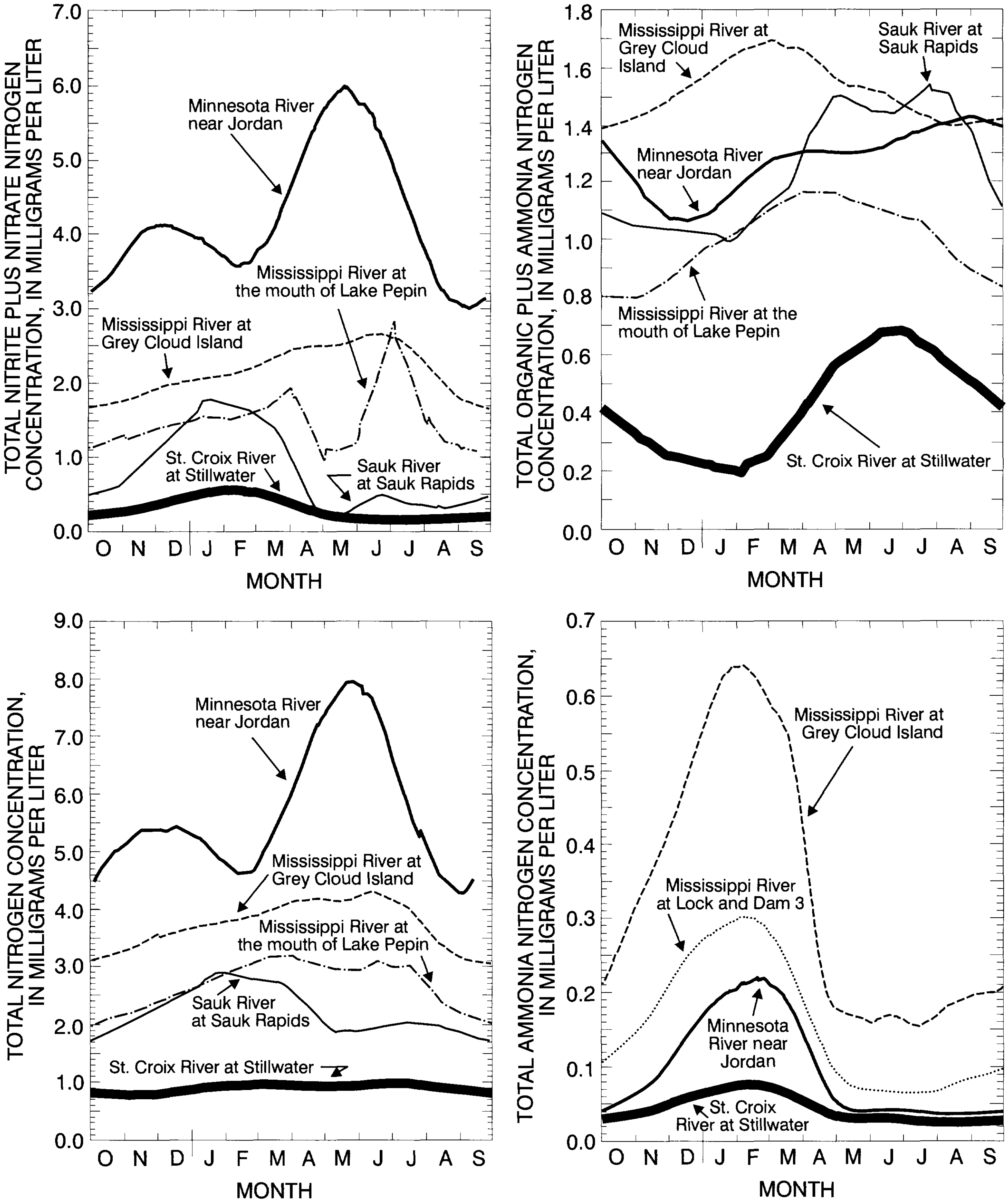

Figure 12.--Seasonal variations in total nitrite plus nitrate nitrogen, total organic plus ammonia nitrogen, total nitrogen, and total ammonia nitrogen concentrations at selected sites in the study area, water years 1984-93.

from December through March. Seasonal variations in concentrations were similar at sites on the St. Croix, Namekagon, Kettle, Rum, and Vermillion Rivers and in the Mississippi River upstream of the TCMA near Royalton, Sauk Rapids, and Monticello, Minnesota.

Total organic plus ammonia nitrogen concentrations generally were greatest in the spring and summer in the Minnesota River near Jordan, Minnesota, Sauk River, and St. Croix River at Stillwater, Minnesota. Total organic plus ammonia nitrogen concentrations in the Minnesota River near Jordan, Minnesota, showed less seasonal variability than nitrate. Seasonal variations were similar at sites on the Minnesota, St. Croix, Rum, Namekagon, Kettle, Straight, Cannon, and Vermillion Rivers.

Seasonal variations in total nitrogen concentrations generally paralleled those observed for nitrate, a result of the nitrogen load in many of these streams being comprised predominantly of nitrate. In the St. Croix River at Stillwater, Minnesota, seasonal variations in total nitrogen concentrations were less compared to the other stream sites. Seasonal variations were similar at sites on the St. Croix, Namekagon, and Kettle Rivers, and in the Mississippi River upstream of the TCMA near Royalton, Sauk Rapids, and Monticello, Minnesota.

In the Mississippi River upstream of the TCMA near Royalton, Sauk Rapids, and Monticello, Minnesota, total nitrogen, nitrate, and total organic plus ammonia nitrogen concentrations showed similar seasonal variations to those observed in the St. Croix River at Stillwater, Minnesota. However, total nitrogen concentrations at Monticello typically were greater in the winter months.

Downstream of the confluence with the Minnesota River, nitrogen-constituent concentrations in the Mississippi River generally showed seasonal patterns similar to those observed in the Minnesota River near Jordan, Minnesota. However, total organic plus ammonia nitrogen concentrations in the Mississippi River at Grey Cloud Island, Minnesota, were greatest during the winter (fig. 12). Seasonal variations in total organic plus ammonia nitrogen concentrations at Newport, Minnesota, and Lock and Dam 2 were similar to those at Grey Cloud Island.

Total ammonia nitrogen concentrations were greatest from December through March in all the streams analyzed in this report. However, the seasonal variation in concentrations was more distinct at sites located within the TCMA such as the Mississippi River at Lock and Dam 3 (fig. 12) than at sites located upstream of the TCMA such as the Minnesota River near Jordan, Minnesota.

Temporal Trends

Total ammonia nitrogen concentrations decreased at 24 of 25 stream sites with available data from water years 1984–93 (table 7), possibly a result of improvements in municipal wastewater treatment within the study unit. Data collected by the Minnesota Pollution Control Agency (1991) showed that 131 of the 292 municipal wastewater treatment plants in Minnesota that were discharging within the study unit in 1993 were constructed or upgraded between 1984 and 1991. Conventional secondary wastewater treatment processes typically remove as much as 30 percent of the total nitrogen in municipal wastewaters, and most of the nitrogen in the effluent is in the form of ammonia (Metcalf and Eddy, Inc., 1991).

Despite increases in nitrogen fertilizer usage from 286,200 tons in fertilizer year 1982 to 384,160 tons in fertilizer year 1991; most stream sites outside of the TCMA showed no increase in total nitrogen, nitrate, or total organic nitrogen concentrations (table 7), possibly the result of improvements in farming practices. The only site outside of the TCMA with significant trends in these constituents was located on the St. Croix River at Prescott, Wisconsin, which showed a slight increase in nitrate concentrations.

Within the TCMA, nitrate concentrations increased, and total ammonia concentrations decreased in the Mississippi and Minnesota Rivers (table 7; fig. 13), probably a result of recent improvements in municipal wastewater treatment. In 1985 and 1991, the three largest municipal wastewater treatment facilities on the Mississippi and Minnesota Rivers within the study unit, modified their systems to include nitrification. These three facilities together treat approximately 275 million gallons of effluent per day. In 1985, installation of nitrification systems was completed at the largest facility on the Mississippi River within the study unit (Metropolitan Waste Control Commission, 1990), and installation of nitrification systems was completed at the two largest facilities on the Minnesota River in 1991 (Metropolitan Waste Control Commission, 1994).

Streambed Sediment

Nitrogen enters the sediment in depositional zones within stream reaches and reservoirs through the settling of phytoplankton and other aquatic biota, nitrogenous organic matter, and particles with sorbed nitrogen. Clay particles in the sediments also can sorb ammonia from the water column. Once in the sediments, ammonia can be released to the water column by the decomposition of nitrogenous organic matter in the sediments. If the decomposition of organic matter produces anaerobic

Table 7.--Results of Seasonal Kendall tests for trends in total nitrogen, total nitrite plus nitrate nitrogen, total organic nitrogen, and total ammonia nitrogen concentrations at stream sites in the study area, water years 1984–93

[N/A, data were not available. Arrows indicate the direction of trend. Small arrows indicate a magnitude less than 5 percent of the median concentration per year. Medium arrows indicate a magnitude between five and 10 percent of the median concentration per year. Large arrows indicate a magnitude greater 10 percent of the median concentration per year. Horizontal lines indicate no significant trend at the 0.05 significance level]

Site number (fig. 4)	Location	Total nitrogen	Total nitrite plus nitrate nitrogen	Total organic nitrogen	Total ammonia nitrogen
1	Mississippi River near Royalton, Minnesota	—	—	—	—
2	Sauk River downstream of bridge on County State Aid Highway 1 at Sauk Rapids, Minnesota	—	—	—	↓
3	Mississippi River upstream of bridge on Minnesota State Highway 15 at Sauk Rapids, Minnesota	—	—	—	↓
4	Mississippi River at bridge on Minnesota State Highway 25 at Monticello, Minnesota	—	—	—	↓
5	Mississippi River downstream of bridge on U.S. Highway 169 at Anoka, Minnesota	—	—	—	↓
6	Rum River at bridge on County State Aid Highway 5 near Isanti, Minnesota	—	—	—	↓
7	Mississippi River at the city of Minneapolis waterworks intake at Fridley, Minnesota	—	—	—	↓
8	Mississippi River above Lock and Dam 1, Minnesota	—	—	—	↓
9	Minnesota River downstream from County Road 9 near Jordan, Minnesota	—	—	—	↓
10	Minnesota River near mouth in Fort Snelling State Park, Minnesota	↑	↑	—	↓
11	Mississippi River at St. Paul, Minnesota	↑	↑	—	↓
12	Mississippi River automonitor at Newport, Minnesota	↑	↑	—	↓
13	Mississippi River at Grey Cloud Island, Minnesota	↑	↑	—	↓
14	Mississippi River at Nininger, Minnesota	↑	↑	—	↓
15	Mississippi River at Lock and Dam 2, Hastings, Minnesota	↑	↑	—	↓
16	Namekagon River near Minong, Wisconsin	—	—	—	N/A

Table 7.--Results of Seasonal Kendall tests for trends in total nitrogen, total nitrite plus nitrate nitrogen, total organic nitrogen, and total ammonia nitrogen concentrations at stream sites in the study area, water years 1984–93--Continued

[N/A, data were not available. Arrows indicate the direction of trend. Small arrows indicate a magnitude less than 5 percent of the median concentration per year. Medium arrows indicate a magnitude between five and 10 percent of the median concentration per year. Large arrows indicate a magnitude greater 10 percent of the median concentration per year. Horizontal lines indicate no significant trend at the 0.05 significance level]

Site number (fig. 4)	Location	Total nitrogen	Total nitrite plus nitrate nitrogen	Total organic nitrogen	Total ammonia nitrogen
17	St. Croix River at bridge on Minnesota State Highway 48 near Danbury, Wisconsin	—	—	—	↓
18	Kettle River at bridge on Minnesota State Highway 48 near Hinckley, Minnesota	—	—	—	↓
19	St. Croix River downstream from Chestnut Street bridge at Stillwater, Minnesota	—	—	—	↓
20	St. Croix River at Hudson, Wisconsin	—	—	—	↓
21	St. Croix River downstream from U.S. Highway 10 bridge at Prescott, Wisconsin	—	↑	—	↓
22	Mississippi River at Lock and Dam 3, Red Wing, Minnesota	↑	↑	—	↓
23	Vermillion River at Biscayne Avenue bridge, Farmington, Minnesota	—	—	↓	↓
24	Vermillion River at bridge on County Road 79 near Empire, Minnesota	—	—	—	↓
25	Straight River at bridge on County Road 1 near Clinton Falls, Minnesota	—	—	—	↓
26	Cannon River at bridge on County State Aid Highway 7 near Welch, Minnesota	—	—	—	↓
27	Mississippi River near the outlet of Lake Pepin	↑	↑	N/A	N/A

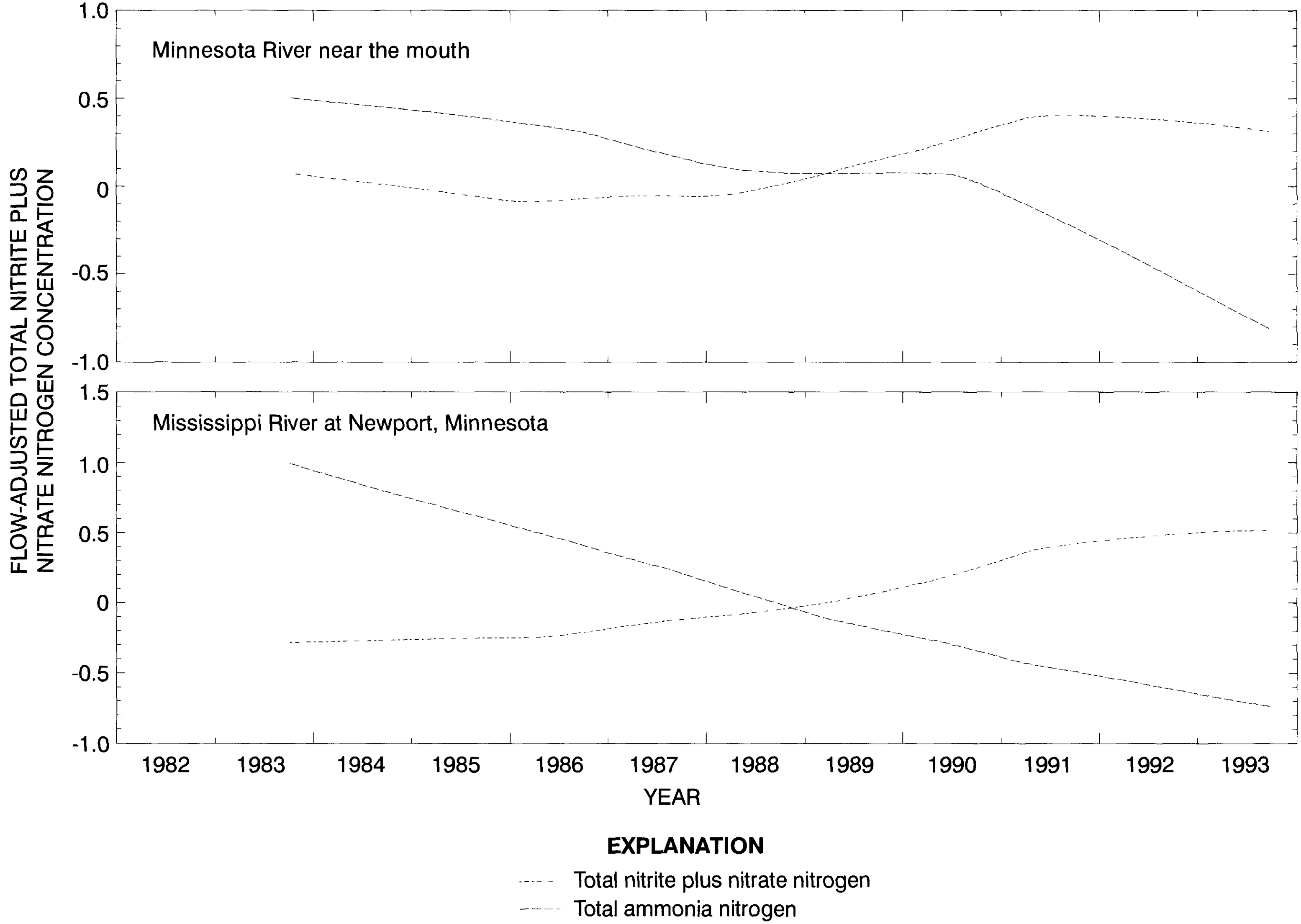

Figure 13.--Temporal trends in total nitrite plus nitrate nitrogen, and total ammonia nitrogen concentrations at selected stream sites in the study area, water years 1984-93.

conditions, nitrogenous organic matter can be denitrified to release nitrogen gas into the water column.

Organic plus ammonia nitrogen concentrations generally were greatest in the Minnesota River sediments and least in the St. Croix River sediments based on 1974–89 data (table 8). Concentrations ranged from a minimum of 0.01 mg/kg in the Lower St. Croix River sediments to a maximum of 48,600 mg/kg in the sediments of Navigation Pool 1. Median concentrations ranged from 21 mg/kg in the Lower St. Croix River sediments to 1,300 mg/kg in the Lower Minnesota River sediments. In the Mississippi River, streambed-sediment total organic plus ammonia nitrogen concentrations were greatest in Navigation Pools 2 and 4 (table 8), probably a result of sedimentation in Spring Lake and Lake Pepin.

Ammonia nitrogen concentrations were greatest in the Minnesota and Mississippi River sediments within the TCMA (table 9). Concentrations ranged from a minimum of 0.1 mg/kg at several locations to a maximum of 698 mg/kg in Navigation Pool 4. Median concentrations ranged from 0.6 mg/kg in the Lower St. Croix River sediments to 16 mg/kg in the Lower Minnesota River sediments. In Mississippi River Navigation Pool 2, the median concentration also was greater relative to the other reaches, 14 mg/kg.

Ground Water

Ground water is the source of drinking water to about 75 and 70 percent of the populations of Minnesota and Wisconsin, respectively (Wisconsin Department of Natural Resources and Wisconsin Geological and Natural History Survey, 1987; Leete, 1991). Because of concern for health effects of elevated concentrations of nitrate in drinking water, nitrate concentrations have been analyzed by Federal and state agencies in water from numerous wells completed in major aquifers in the study area. The aquifers most commonly sampled for nitrate include unconfined sand and gravel, buried sand and gravel, and the Prairie du Chien-Jordan aquifer(fig. 14; tables 10–12).

For unconfined sand and gravel aquifers, the greatest nitrate concentrations generally were detected in water samples from wells in the Anoka Sand Plain and in alluvial aquifers located to the west and north of the

Table 8.--Summary statistics for total organic plus ammonia nitrogen concentrations in streambed sediments in selected reaches of the Mississippi, Minnesota, and St. Croix Rivers in the study area, 1974–89
[Units are in milligrams per kilogram]

River reach	Median	Interquartile range	Minimum	Maximum
Mississippi River Navigation Pool 0	400	370	150	800
Mississippi River Navigation Pool 1	300	430	10	48,600
Lower Minnesota River	1,300	1,280	150	4,100
Mississippi River Navigation Pool 2	447	2,567	64	9,800
Lower St. Croix River	21	45	.01	48
Mississippi River Navigation Pool 3	247	110	18	9,700
Mississippi River Navigation Pool 4	410	1,400	27	11,300

Table 9.--Summary statistics for total ammonia nitrogen concentrations in streambed sediments in selected reaches of the Mississippi, Minnesota, and St. Croix Rivers in the study area, 1974–89
[Units are in milligrams per kilogram]

River reach	Median	Interquartile range	Minimum	Maximum
Mississippi River Navigation Pool 0	3.1	5.1	0.7	12.0
Mississippi River Navigation Pool 1	4.5	5.6	0.6	130
Lower Minnesota River	16	21	5.5	115
Mississippi River Navigation Pool 2	14	79	0.1	490
Lower St. Croix River	0.6	2.0	0.1	5.6
Mississippi River Navigation Pool 3	2.2	17	0.1	119
Mississippi River Navigation Pool 4	6.2	41	0.1	698

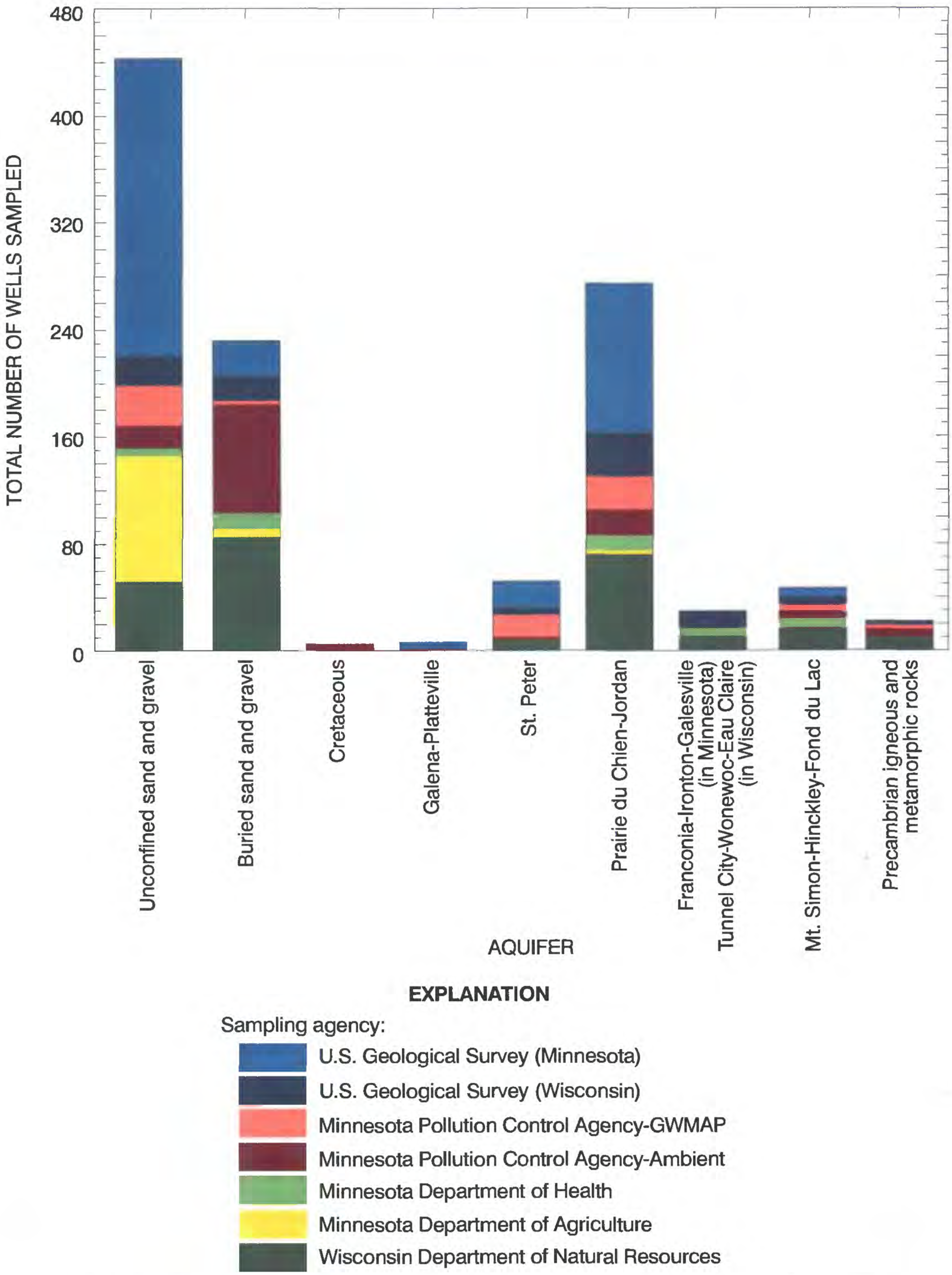

Figure 14.--Number of wells sampled for nitrate nitrogen in the study area, by aquifer.

Table 10.--Summary statistics of nitrate concentrations by sampling agency in unconfined sand and gravel aquifers in the study area, 1974–94
[Units are in milligrams per liter]

Agency	Dates sampled	Number of wells sampled	Reporting limits	Median	Range
U.S. Geological Survey (Minnesota)	1976–93	222	0.01, 0.05, 0.1	1.7	<0.01–39
U.S. Geological Survey (Wisconsin)	1974–86	22	0.01, 0.1	2.3	0.01–4.5
Minnesota Pollution Control Agency—Ground-Water Monitoring and Assessment Program	1994	17	0.02	1.5	<0.5–9.3
Minnesota Department of Health	1990–93	7	0.01	1.0	0.11–7.9
Minnesota Department of Agriculture	1987–93	94	1.0	5.5	<1–44.5
Wisconsin Department of Natural Resources	1988–94	63	0.1, 0.5, 1.0	0.85	0.27–17

Table 11.--Summary statistics of nitrate concentrations by sampling agency in buried sand and gravel aquifers in the study area, 1974–94
[Units are in milligrams per liter]

Agency	Dates sampled	Number of wells sampled	Reporting limits	Median	Range
U.S. Geological Survey (Minnesota)	1984–93	27	0.05, 0.1	<0.1	<0.05–20
U.S. Geological Survey (Wisconsin)	1974–86	20	0.01, 0.1	0.26	0.01– 6.6
Minnesota Pollution Control Agency—Ground-Water Monitoring and Assessment Program	1992–94	80	0.02, 0.5	<0.05	<0.02–16.8
Minnesota Pollution Control Agency—Ambient Ground-Water Monitoring Network	1981–91	3	0.01	0.01	<0.01–3.9
Minnesota Department of Health	1989–94	12	0.01	0.58	0.02– 4.8
Minnesota Department of Agriculture	1986–93	6	1.0	<1.0	<1.0–2.0
Wisconsin Department of Natural Resources	1980–94	85	0.5, 1.0	1.0	<0.5–13.9

Table 12.--Summary statistics of nitrate concentrations by sampling agency in the Prairie du Chien-Jordan aquifer in the study area, 1971–94
[Units are in milligrams per liter]

Agency	Dates sampled	Number of wells sampled	Reporting limits	Median	Range
U.S. Geological Survey (Minnesota)	1971–91	112	0.001, 0.01, 0.05, 0.1, 0.4	0.1	<0.001–40
U.S. Geological Survey (Wisconsin)	1974–80	31	0.01, 0.1	3.2	0.01–18
Minnesota Pollution Control Agency—Ground-Water Monitoring and Assessment Program	1992–94	19	0.02, 0.1	<0.1	<0.1–8.2
Minnesota Pollution Control Agency—Ambient Ground-Water Monitoring Network	1979–91	25	0.01, 0.5	0.03	<0.01–6.5
Minnesota Department of Health	1989–94	11	0.01	0.46	0.02– 3.2
Minnesota Department of Agriculture	1988	3	1.0	6.4	<1–19.6
Wisconsin Department of Natural Resources	1984–94	72	0.5, 1.0	4.75	<1–55.6

Anoka Sand Plain (fig. 15). Nitrate concentrations in both of these areas generally were greater than 3 mg/L, which typically indicates anthropogenic effects on ground-water quality (Madison and Brunett, 1985). Agriculture is the most likely source of nitrate in those areas because the land covers overlying those areas were mixed agricultural and forested (fig. 3). Forested areas generally receive little or no fertilizers, and nutrients in rainfall are taken up before reaching ground water. Nitrate concentrations exceeded the MCL in one-third of the water samples from 94 wells completed in unconfined sand and gravel aquifers, which were sampled by the MDA (fig. 16). Almost 25 percent of the 222 wells sampled by the USGS in Minnesota in this aquifer had concentrations exceeding the MCL (fig. 16). The greater percentage of exceedances of the nitrate MCL in wells sampled by MDA may have been a result of well selection. The MDA generally sampled wells with shallower depths that were located in agricultural areas. Nitrate concentrations in water samples from unconfined sand and gravel aquifers were related to well depth. The agencies that measured the greatest nitrate concentrations, the MDA and USGS in Minnesota, sampled the shallowest wells, with median well depths of 24 and 25 ft, respectively (fig. 16). Deeper wells, such as those sampled by the Ground-Water Monitoring and Assessment Program (GWMAP) of the MPCA and by the WDNR, had lesser nitrate concentrations (fig. 16). Wells sampled by the MPCA as part of the GWMAP Program and by the WDNR had median depths of 52 and 60 feet, respectively.

Water samples from wells completed in buried sand and gravel aquifers, which were sampled by the USGS in Minnesota, GWMAP, MDA, and WDNR commonly did not have detectable concentrations of nitrate (figs. 17, 18). Clays and tills overlying buried sand and gravel aquifers tend to confine these aquifers and retard leaching of nitrate from the land surface. Median nitrate concentrations in water samples from this aquifer, were less than 1 mg/L (fig. 18), indicating relatively little effect by anthropogenic activities. Most of the wells completed in buried sand and gravel aquifers, which had nitrate concentrations greater than 3 mg/L, were located in Wisconsin and northwest of the TCMA (fig. 18). Both of those areas have agricultural or mixed forested and agricultural land covers, indicating that agriculture is the potential source of nitrate detected in ground water in those areas. In contrast to unconfined sand and gravel aquifers, nitrate concentrations in water samples from buried sand and gravel aquifers in the study area do not appear to be related to well depth (fig. 18).

For the Prairie du Chien-Jordan aquifer, the greatest nitrate concentrations occurred in the water samples from the portion of the aquifer in Wisconsin and in the vicinity of the Cannon River in Minnesota (figs. 2, 19). The greater nitrate concentrations in water samples from this aquifer in those areas probably were due to the predominance of agricultural land uses, lack of confinement, and close proximity of the aquifer to the land surface in those areas (figs. 2, 3, 19). The wells sampled in Wisconsin were noticeably shallower than those sampled in Minnesota (fig. 20). Median depths of the wells completed in Wisconsin ranged from 140 to 175 feet. In contrast, the wells completed in Minnesota were much deeper, with median depths ranging from 250 to 350 feet. In Wisconsin and southern Minnesota, the aquifer also tends to be either exposed at the land surface or very shallowly buried by glacial deposits (Mudrey and others, 1987; Wisconsin Department of Natural Resources and Wisconsin Geological and Natural History Survey, 1987; Brown, 1988).

To evaluate trends in nutrient concentrations in ground water in the study area, a widespread network of wells would have to be sampled on a regular basis for several years. Within the study area, the MDA has collected about 20 samples per well from a set of 21 individual wells in unconfined sand and gravel aquifers located in agricultural areas from 1987–93. Evaluation of trends in nitrate concentrations from those wells, using the nonparametric Kendall trend test (Hirsch and others, 1982), indicated a significant positive trend in nitrate concentrations with time in water samples from four of those wells. Because local changes in cropping and other land practices can dramatically change nitrate concentrations in water from shallow monitoring wells completed in unconfined aquifers (Andrews, 1994), trends in nitrate concentrations in water samples from such a limited number of wells cannot be extrapolated to apply to the entire study area.

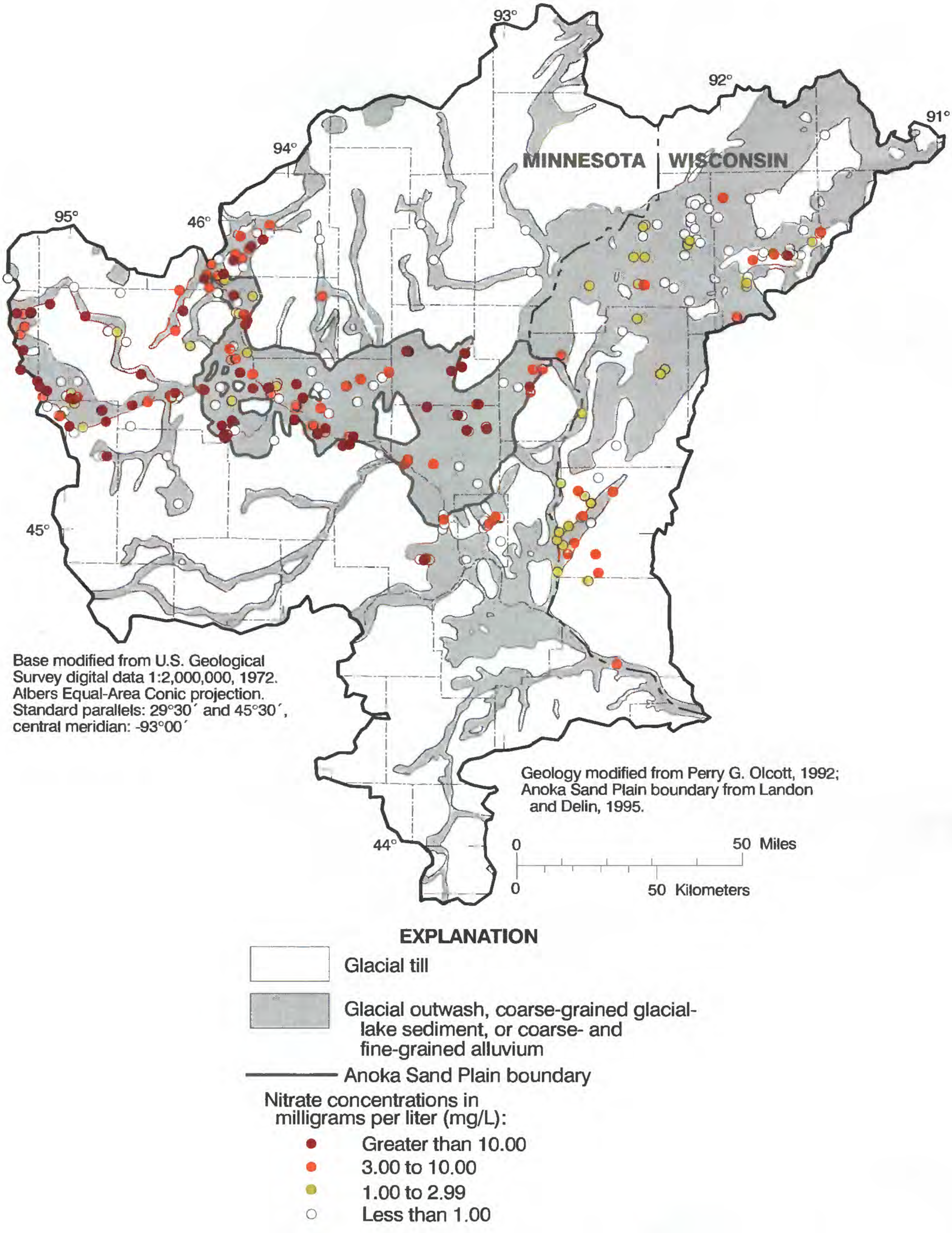

Figure 15.--Nitrate nitrogen concentrations in samples from unconfined sand and gravel aquifers in the study area, 1974-94.

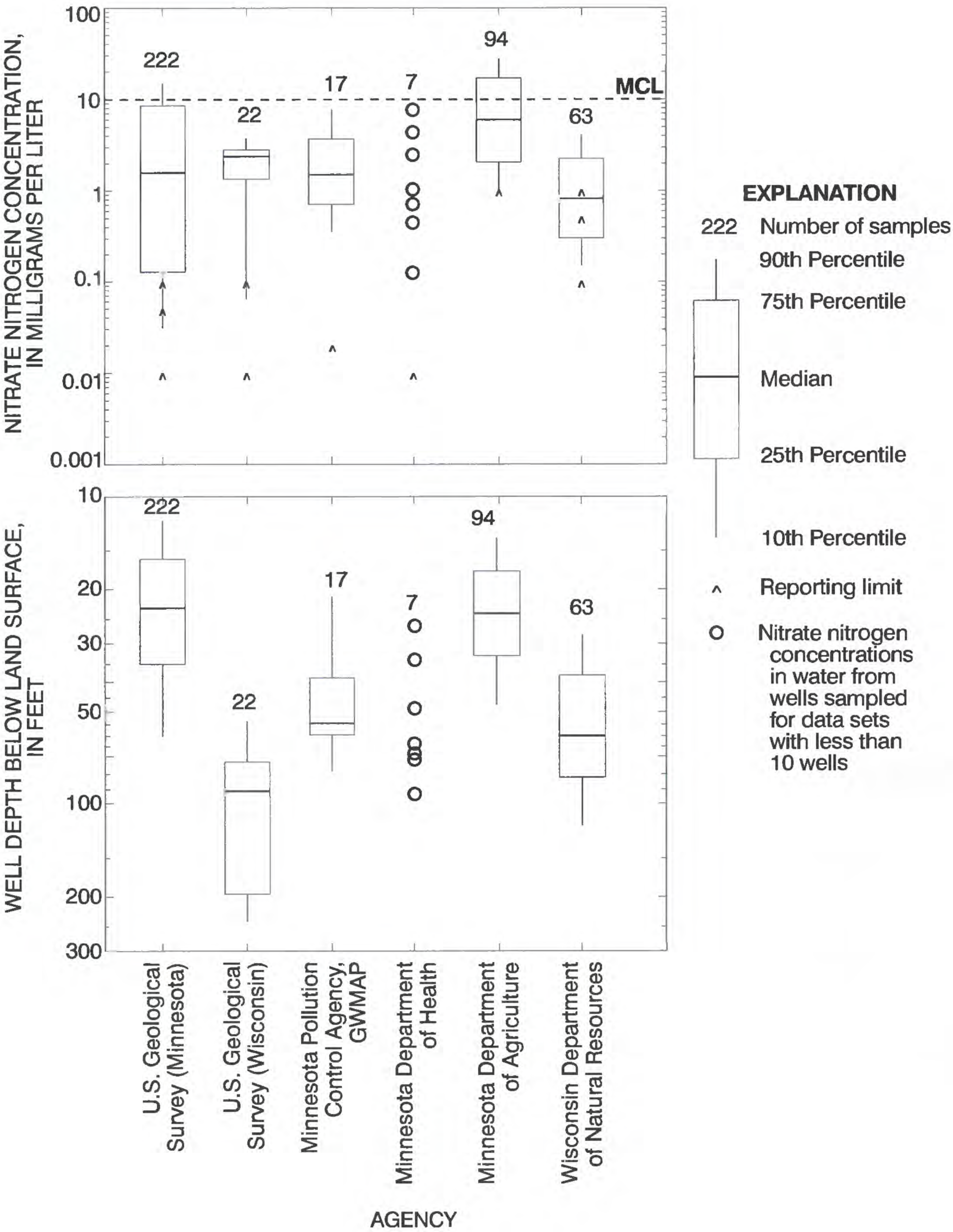

Figure 16.--Nitrate nitrogen concentrations in water from wells and depth of wells completed in unconfined sand and gravel aquifers in the study area, by sampling agency, 1974-94.

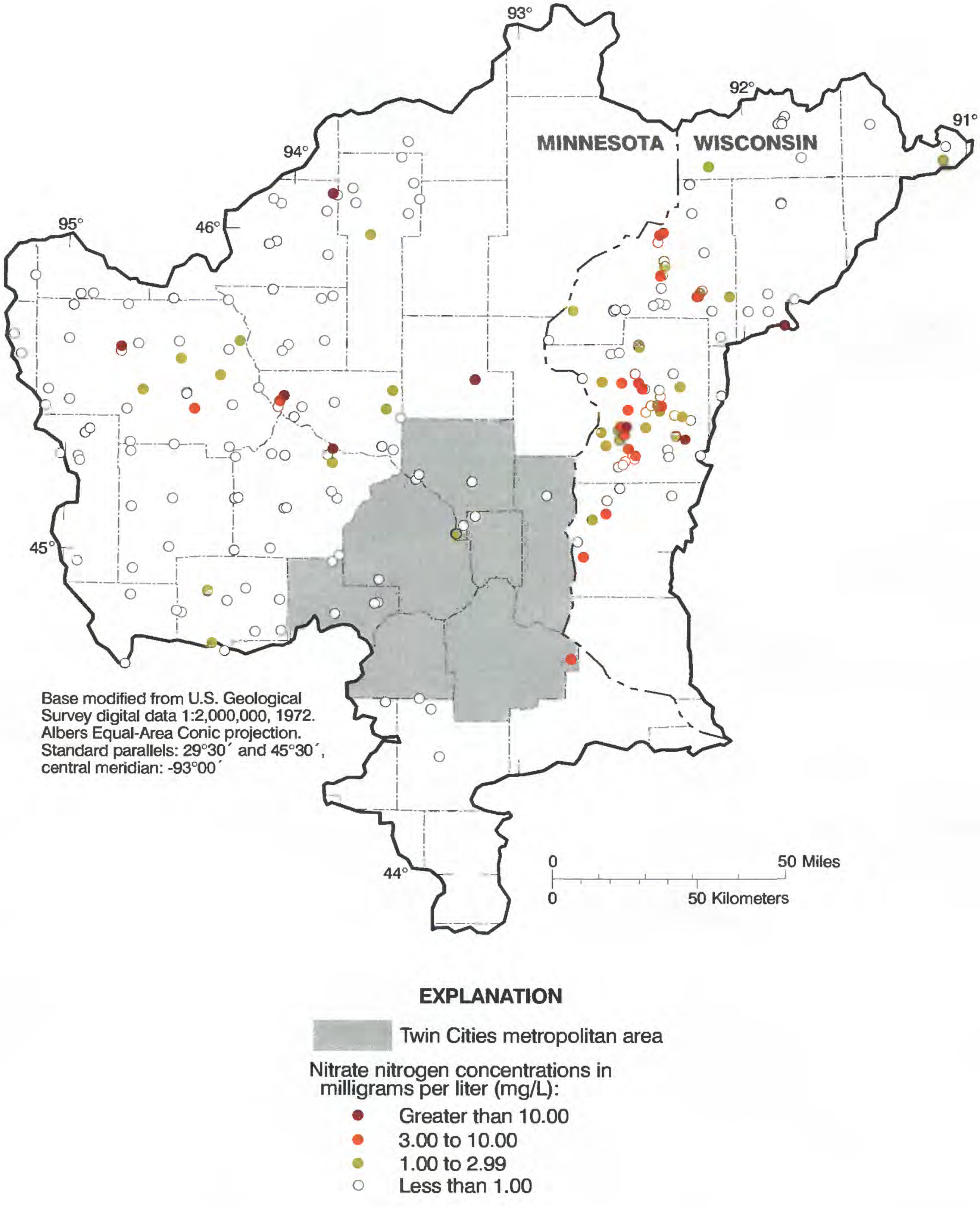

Figure 17.--Nitrate nitrogen concentrations in samples from buried sand and gravel aquifers in the study area, 1974-94.

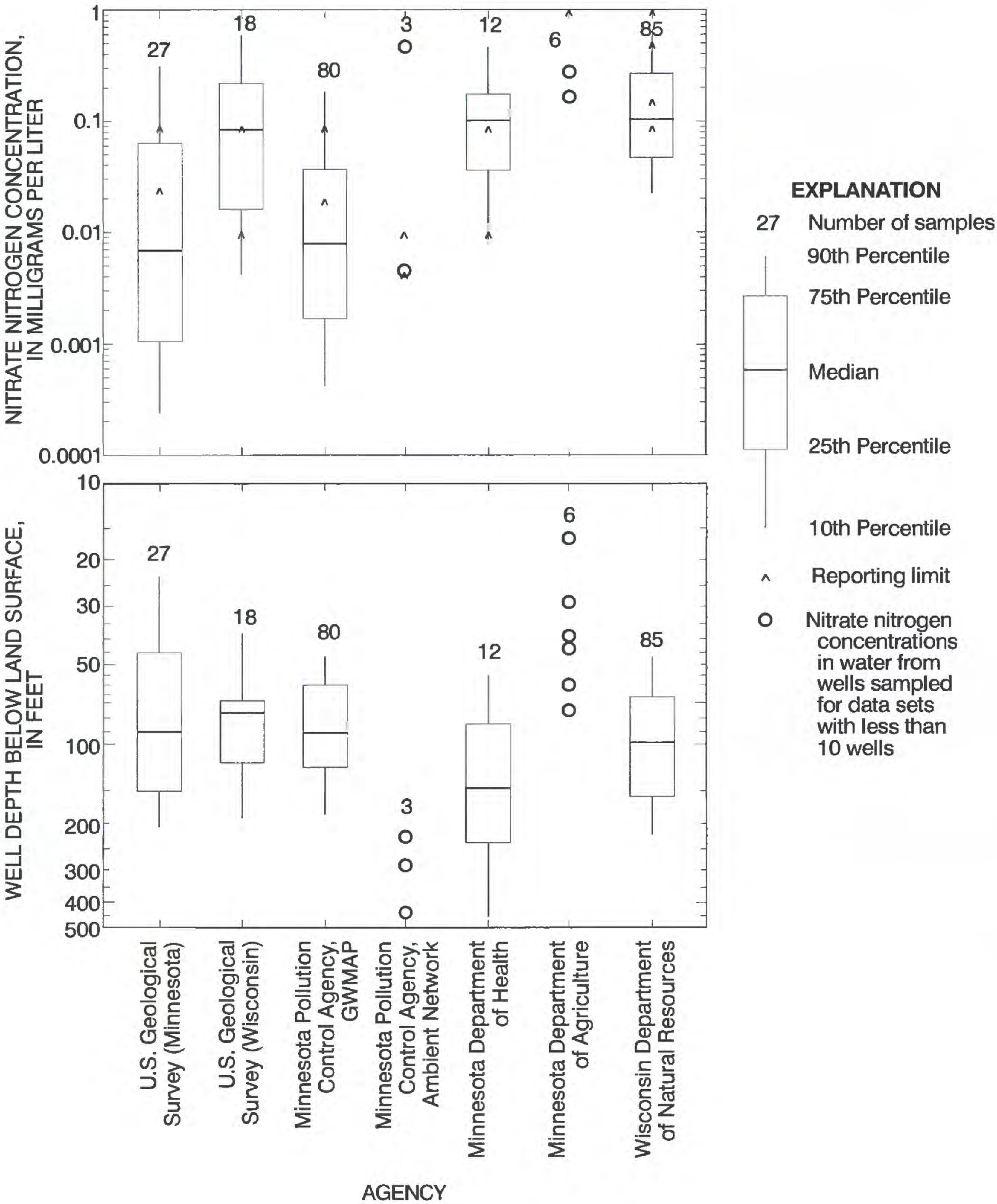

Figure 18.--Nitrate nitrogen concentrations in water from wells and depth of wells completed in buried sand and gravel aquifers in the study area, by sampling agency, 1974-94.

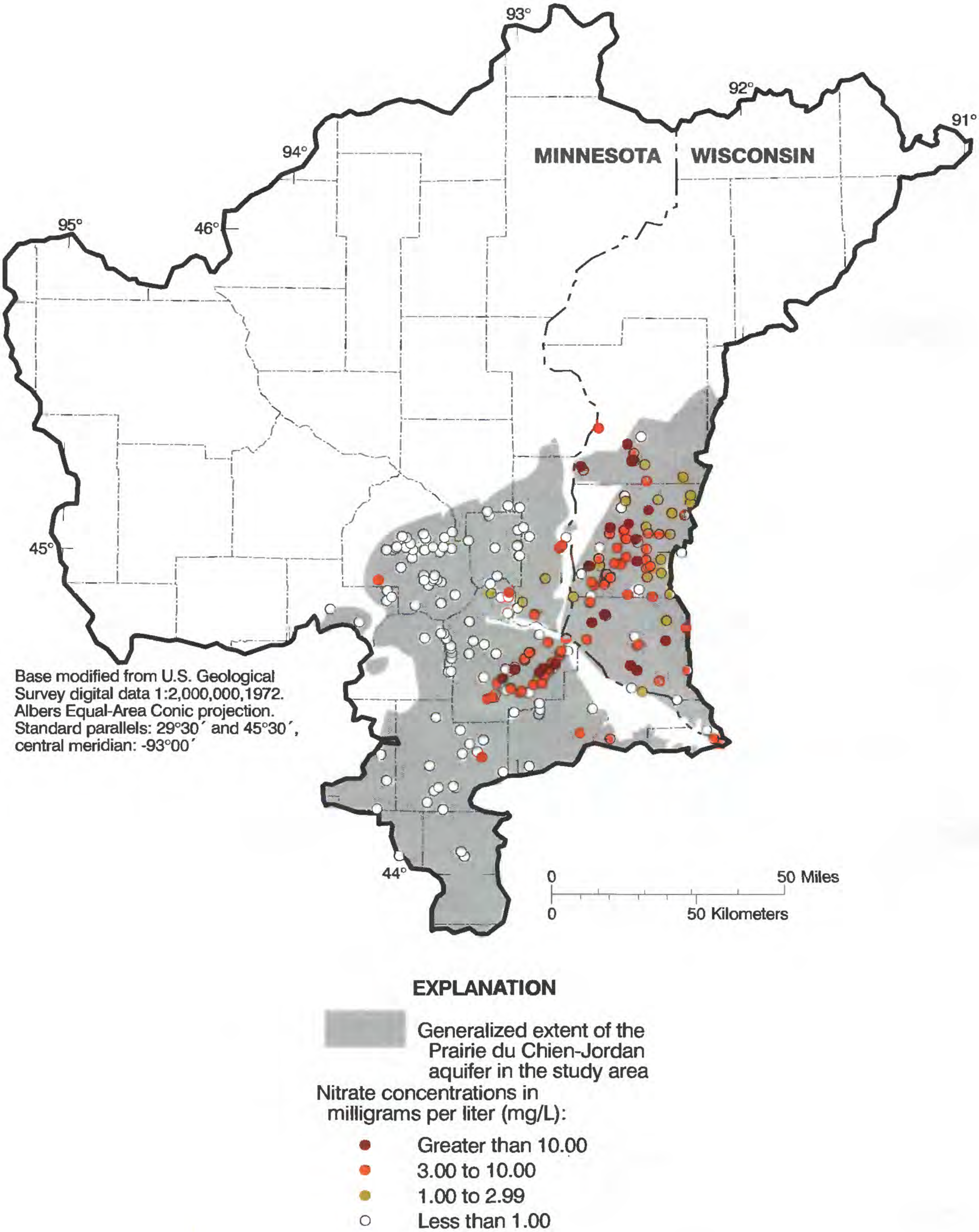

Figure 19.--Nitrate nitrogen concentrations in samples from the Prairie du Chien-Jordan aquifer in the study area, 1971-94.

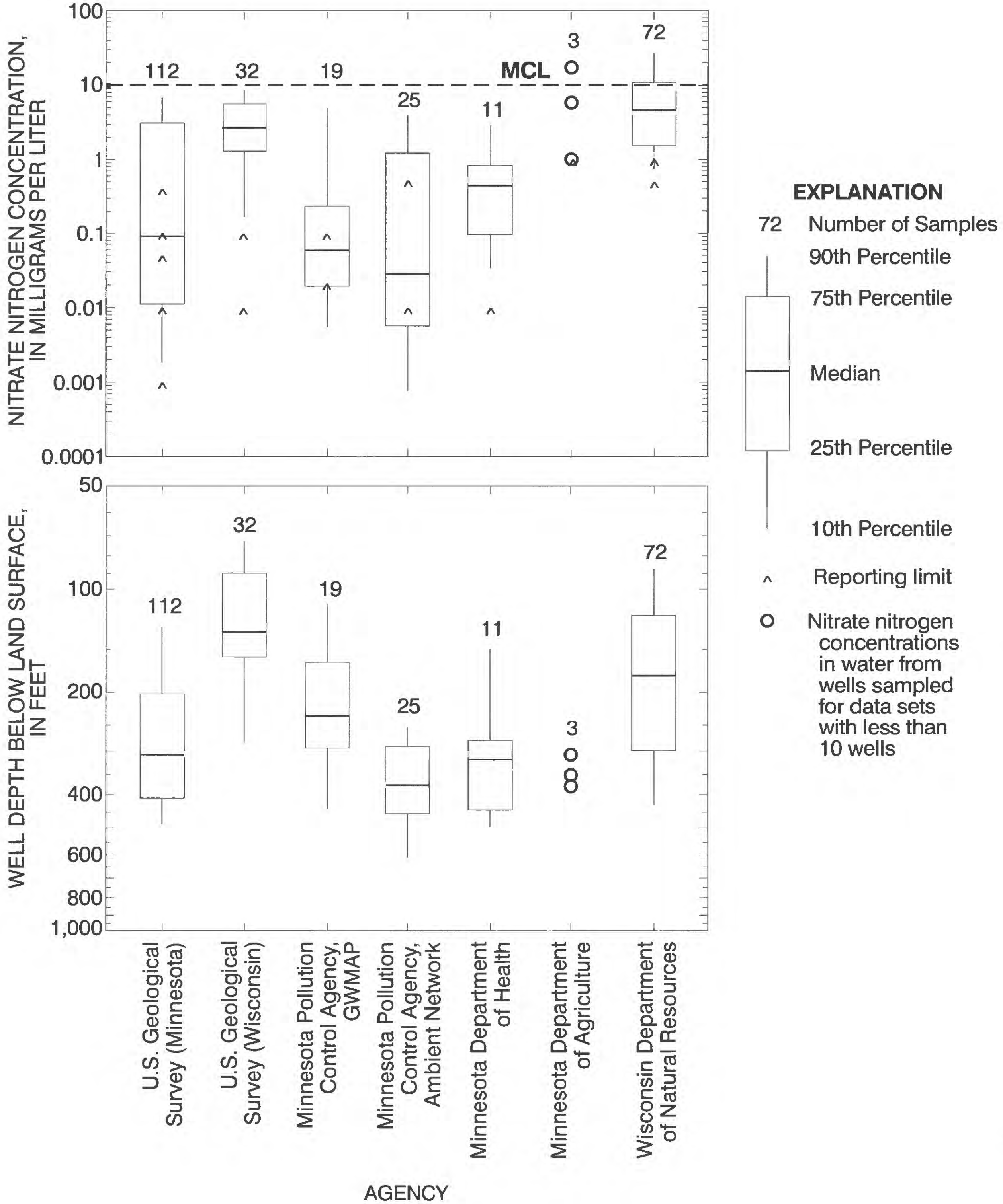

Figure 20.--Nitrate nitrogen concentrations in water from wells and depth of wells completed in the Prairie du Chien-Jordan aquifer in the study area by sampling agency, 1971-94.

PHOSPHORUS DISTRIBUTION AND TRENDS

Phosphorus generally enters streams by the transport of sediment from the land surface and direct point-source discharges. Phosphorus enters ground water through leaching from the land surface. Sources of phosphorus include discharges from municipal and industrial wastewater treatment facilities, combined sewer overflows, storm sewers, livestock feedlot operations, improperly functioning septic systems, runoff of fertilizers applied to agricultural and urban areas, and soil erosion from construction sites, agricultural land and logging areas. In fertilizers, phosphorus is primarily in the form of water-soluble orthophosphates (PO_4^{3-}, HPO_4^{2-}, and $H_2PO_4^{-}$).

Streams

Phosphorus in streams primarily occurs as orthophosphates, organic phosphorus, and phosphorus sorbed to clay particles and organic matter. Orthophosphate is readily available to stream biota. Orthophosphate concentrations and their distribution within the water column are dependent upon stream pH and the relative concentrations of metals, major cations, and other ligands. Trace metals and common cations can precipitate orthophosphates from the water column.

Concentrations

Dissolved orthophosphate and total phosphorus are the constituents summarized in this section of the report. Dissolved orthophosphate data were only available from the MCES, WDNR, and USGS; therefore, analyses for this constituent are from stream sites predominantly within the TCMA.

Dissolved Orthophosphate

The greatest dissolved orthophosphate concentrations (fig. 21) occurred within the TCMA in the Mississippi, Minnesota, and Vermillion Rivers. Concentrations in the Mississippi River from Newport, Minnesota, to Lock and Dam 2, near the outlet of the study area at Lake Pepin, the Minnesota River near the mouth, and the Vermillion River near Empire, Minnesota, were significantly greater than at all other stream sites.

Total Phosphorus

Total phosphorus concentrations in the tributaries to the Mississippi River (fig. 21) generally were greatest in streams draining intensively farmed agricultural areas and were least in the St. Croix River Basin. In some streams, median concentrations were greater than the suggested criteria of 0.1 mg/L (U.S. Environmental Protection Agency, 1986). Concentrations in the Sauk, Minnesota, Straight, and Cannon Rivers, and in the Vermillion River near Empire, Minnesota, were significantly greater than the St. Croix, Namekagon, and Kettle Rivers.

Total phosphorus concentrations in the Vermillion River near Empire, Minnesota, were significantly greater than in all other streams summarized within the study area, possibly the result of wastewater discharges. Upstream of a wastewater discharge near Farmington, Minnesota, concentrations were much less.

In the Mississippi River, total phosphorus concentrations were greatest, on average, from Newport, Minnesota, to Lock and Dam 3. Median concentrations from Newport, Minnesota, to Lock and Dam 3 exceeded the recommended criteria of 0.1 mg/L set by the USEPA (1986). Concentrations from Royalton to St. Paul, Minnesota, were significantly less than concentrations measured within the TCMA from Newport, Minnesota, to Lock and Dam 3. Farther downstream near the outlet of the study area in Lake Pepin, the median concentration decreased slightly (fig. 21).

Total phosphorus concentrations in the Mississippi River within the TCMA have been strongly influenced by streamflow conditions. Studies by the Metropolitan Waste Control Commission (1993c) and Kroening (1994) showed that during extreme low-flow conditions in the Mississippi River, the greatest total phosphorus concentrations occurred downstream of a large wastewater discharge. However, under average and high-flow conditions, the greatest total phosphorus concentrations in the Mississippi River occurred downstream of the confluence with the Minnesota River.

Loads and Yields

The Minnesota and St. Croix Rivers were the tributaries that contributed most of the total phosphorus and dissolved orthophosphate loads to the Mississippi River during water years 1984–93 (fig. 22; table 13). In the remaining tributaries that had adequate data to calculate loads, total phosphorus and orthophosphate loads were much less, and orthophosphate comprised about one-half of the phosphorus load.

Of the streams analyzed in this report, the greatest phosphorus yields (table 14) were from the Minnesota and Straight Rivers, and the Vermillion River near Empire, Minnesota. Greater yields in the Minnesota and Straight Rivers may be the result of drainage from intensively-farmed agricultural areas. However, in the Vermillion River near Empire, Minnesota, greater phosphorus yields were probably a result of a relatively large wastewater discharge (fig. 4) to a relatively small stream. Approximately 5 miles upstream of the

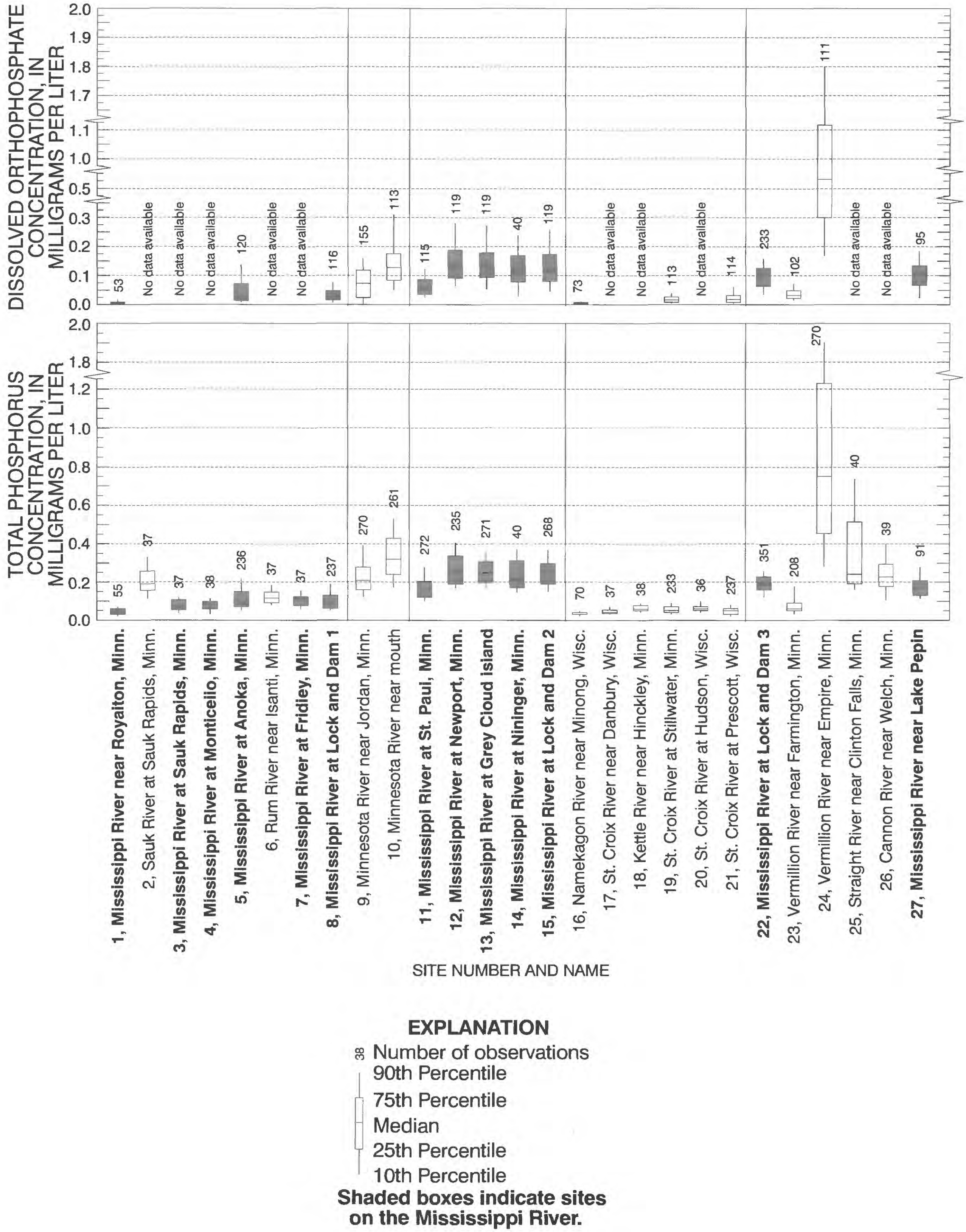

Figure 21.--Dissolved orthophosphate and total phosphorus concentrations at selected stream sites in the study area, water years 1984-93 (shown in downstream order).

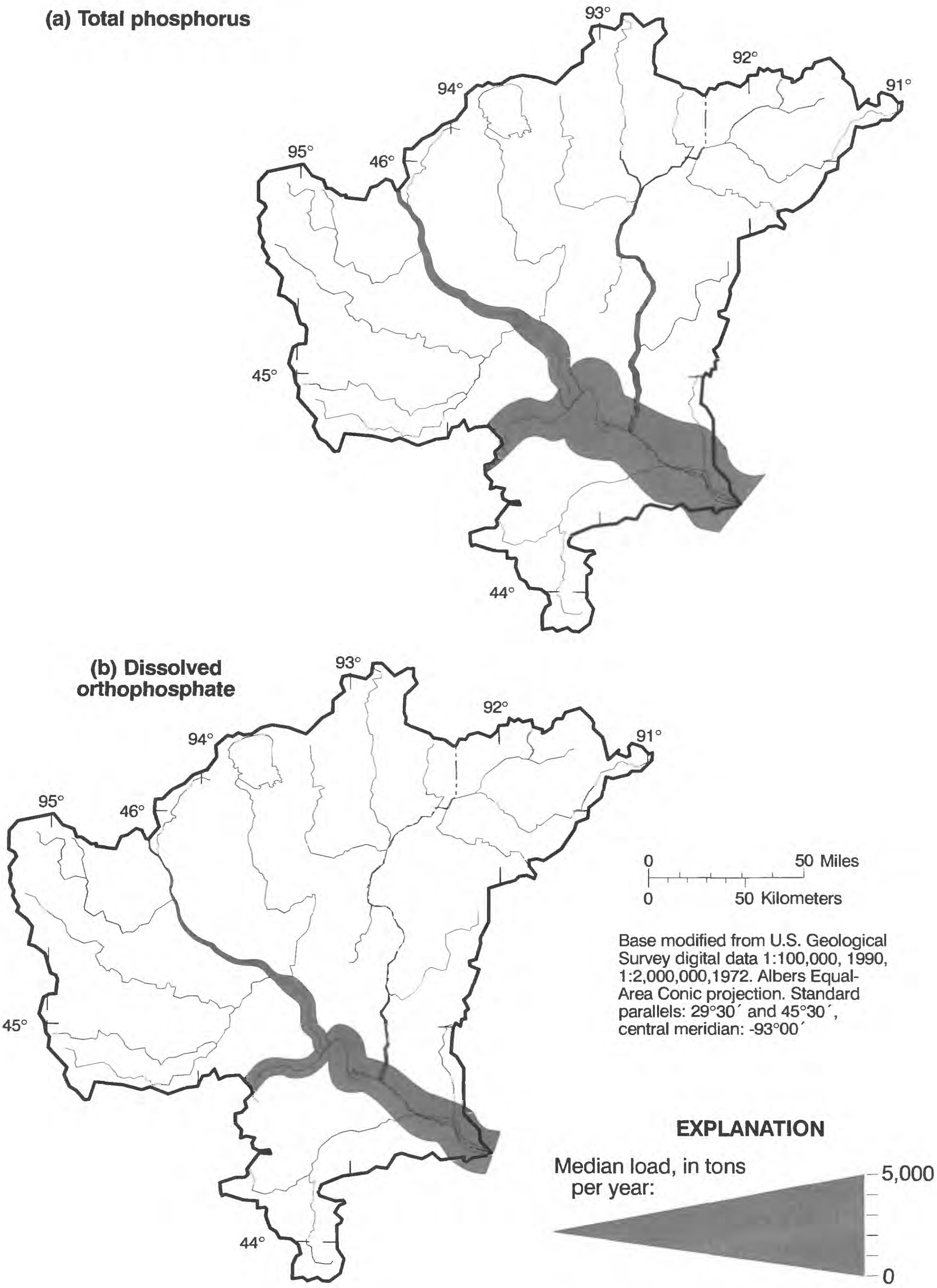

Figure 22.--(a) Total phosphorus (b) dissolved orthophosphate loads in the study area, water years 1984-93.

Table 13.--Median phosphorus constituent loads at selected stream sites in the study area, water years 1984–93
[listed in downstream order, N/A, data were not available]

Site number (fig. 4)	Water-quality site	Median load, in tons per year	
	Location	Total phosphorus	Dissolved orthophosphate
1	Mississippi River near Royalton, Minnesota	190	50
5	Mississippi River downstream of bridge on U.S. Highway 169 at Anoka, Minnesota	989	550
6	Rum River at bridge on County State Aid Highway 5 near Isanti, Minnesota	72	N/A
7	Mississippi River at the city of Minneapolis waterworks intake at Fridley, Minnesota	954	N/A
8	Mississippi River above Lock and Dam 1, Minnesota	877	367
9	Minnesota River downstream of bridge on County Road 9 near Jordan, Minnesota	1,681	918
10	Minnesota River near mouth in Fort Snelling State Park, Minnesota	2,114	699
11	Mississippi River at St. Paul, Minnesota	3,293	1,286
12	Mississippi River at automonitor site in Newport, Minnesota	3,835	1,949
13	Mississippi River near J.L. Shiely Company, Grey Cloud Island, Minnesota	3,912	1,694
14	Mississippi River at Nininger, Minnesota	2,921	1,632
15	Mississippi River at Lock and Dam 2, Hastings, Minnesota	3,578	1,578
17	St. Croix River at bridge on Minnesota State Highway 48 near Danbury, Wisconsin	42	N/A
18	Kettle River at bridge on Minnesota State Highway 48 near Hinckley, Minnesota	43	N/A
19	St. Croix River downstream from Chestnut Street bridge at Stillwater, Minnesota	263	210
21	St. Croix River downstream from U.S. Highway 10 bridge at Prescott, Wisconsin	219	117
22	Mississippi River at Lock and Dam 3, Red Wing, Minnesota	4,388	2,080
23	Vermillion River at Biscayne Avenue bridge, Farmington, Minnesota	5	3
24	Vermillion River at bridge on County Road 79 near Empire, Minnesota	42	37
25	Straight River at bridge on County Road 1 near Clinton Falls, Minnesota	76	N/A
27	Mississippi River near the outlet of Lake Pepin	3,646	2,339

Table 14.--Median annual total phosphorus and dissolved orthophosphate yields for selected tributaries to the Mississippi River in the study area, water years 1984–93
[listed in downstream order; units are in pounds/square mile/year]

Site number (fig. 4)	Water-quality site	Yield	
	Location	Total phosphorus	Dissolved orthophosphate
6	Rum River at bridge on County State Aid Highway 5 near Isanti, Minnesota	121	Not available
9	Minnesota River at bridge on County Road 9 near Jordan, Minnesota	208	113
10	Minnesota River near mouth in Fort Snelling State Park, Minnesota	250	83
17	St. Croix River at bridge on Minnesota State Highway 48 near Danbury, Wisconsin	53	Not available
18	Kettle River at bridge on Minnesota State Highway 48 near Hinckley, Minnesota	100	Not available
19	St. Croix River downstream from Chestnut Street bridge at Stillwater, Minnesota	75	60
21	St. Croix River downstream from U.S. Highway 10 bridge at Prescott, Wisconsin	56	30
23	Vermillion River at Biscayne Avenue bridge, Farmington, Minnesota	91	55
24	Vermillion River at bridge on County Road 79 near Empire, Minnesota	609	536
25	Straight River at bridge on County Road 1 near Clinton Falls, Minnesota	608	Not available

wastewater discharge near Farmington, Minnesota, phosphorus yields were much less.

Total phosphorus loads in the Minnesota and Vermillion Rivers, and in the St. Croix River from Danbury to Stillwater increased in the downstream direction (table 13). Loads increased in every year summarized in this report in the Minnesota and Vermillion Rivers, and in the St. Croix River from Danbury to Stillwater. In the Minnesota River, increases in phosphorus load were probably a result of wastewater discharges and urban runoff from the TCMA, and tributary loads from streams draining into the lower Minnesota River. The increase in loading to the Vermillion River was probably the result of a relatively large wastewater discharge (fig. 4) to a relatively small stream. However, runoff from agricultural lands in the Vermillion River watershed may have also affected phosphorus loads between Farmington and Empire, Minnesota. The increase in phosphorus load in the St. Croix River probably was the result of contributions from tributaries, which generally have greater total phosphorus concentrations than the St. Croix River (Wisconsin Department of Natural Resources, 1994).

Dissolved orthophosphate loads in the lower reaches of the Minnesota and St. Croix Rivers decreased in the downstream direction. In the Minnesota River, orthophosphate loads decreased from Jordan to near the confluence with the Mississippi River in every year except 1988–90. In the St. Croix River, loads decreased in every year summarized in this report from Stillwater, Minnesota, to Prescott, Wisconsin.

In the Mississippi River, total phosphorus loads (fig. 22; table 13) were greatest downstream of the Minnesota River. Decreased phosphorus loads at Lock and Dam 1 may be the result of sedimentation in the pool immediately upstream of the dam. Downstream of the confluence with the Minnesota River, at St. Paul, Minnesota, the total phosphorus load in the Mississippi River increased substantially. Phosphorus loads further increased at Newport, Minnesota, which is located downstream from a large wastewater discharge from the TCMA (fig. 4). Average phosphorus loads remained at approximately this level to Lock and Dam 2. Downstream of the confluence with the St. Croix River and other smaller tributaries, the average phosphorus load in the Mississippi River further increased at Lock and Dam 3. Near the outlet of the study area in Lake Pepin, the phosphorus load in the Mississippi River decreased slightly, probably a result of sedimentation in the lake.

Results of previous investigations of historical total phosphorus data collected within the study area (Metropolitan Waste Control Commission, 1993a; Kroening, 1994) showed during higher streamflow conditions, the Minnesota River Basin contributed approximately 50 percent of the total phosphorus load to the Mississippi River. During extreme low-flow conditions, point sources contributed 73 percent of the total phosphorus load to the Mississippi River.

Dissolved orthophosphate loads in the Mississippi River increased substantially downstream from the confluence with the Minnesota River (fig. 22, table 13). Downstream from wastewater discharges within the TCMA, the dissolved orthophosphate load in the Mississippi River further increased at Newport, Minnesota. From Newport to Lock and Dam 2, the load in the Mississippi River decreased, possibly the result of algal uptake in Spring Lake. Downstream of the confluence with the St. Croix River, the dissolved orthophosphate load in the Mississippi River increased at Lock and Dam 3. Near the outlet of the study area in Lake Pepin, the dissolved orthophosphate load in the Mississippi River increased further. Increased dissolved orthophosphate loads in this reach were probably a result of drainage from the Vermillion, Cannon, and Straight Rivers, and other smaller tributaries and input from the sediments of Lake Pepin. During summers with an average flow below 26,500 ft^3/s, Lake Pepin is a source of dissolved orthophosphate, with most of the releases occurring in the late summer (Heiskary and others, 1993).

Trends

Within the study unit, phosphorus concentrations in streams are expected to vary seasonally due to seasonal application of fertilizers, decreased runoff in the winter, and variations in streamflow. In addition, phosphorus-fertilizer use has increased during the analysis period.

Seasonal Variations

In the Mississippi River and its tributaries, total phosphorus concentrations generally peaked during the spring and summer based on 1984–93 data. LOWESS-smoothed time series of total phosphorus concentration from selected sites on the Mississippi, Minnesota, St. Croix, and Vermillion Rivers (fig. 23) showed this relation. Similar seasonal variations in total phosphorus concentrations were observed at the remaining stream sites. In the environment, phosphorus is often associated with clay particles. Greater concentrations observed during the spring and summer may have been the result of runoff and erosion in the study area. In the Vermillion River near Empire, Minnesota (fig. 23), the greatest concentrations were observed during January, possibly the result of the increased concentration of wastewater effluent from an upstream facility, which at times dominates the flow of the stream (Mitton and others, 1995). Streamflow in the Vermillion River near Empire, Minnesota was, on average, lowest during January (Mitton and others, 1995).

Total phosphorus concentrations were least during the winter and during April and May near the mouth of the Minnesota River and in the Mississippi River at Grey Cloud Island, Minnesota. Seasonal variations at these sites were consistent with results from previous analyses of historical data in the study area (Kroening, 1994), which reported no significant seasonal variations in total phosphorus concentrations in the Minnesota River near the mouth and in the Mississippi River from Newport, Minnesota, to Lock and Dam 2.

In the Mississippi River near Royalton, Minnesota, dissolved orthophosphate concentrations showed little seasonal variability (fig. 23). However, farther downstream at Anoka, Minnesota, dissolved orthophosphate concentrations were greatest during the summer. Greater concentrations during summer may have been the result of surface runoff transporting fertilizers. Downstream of wastewater discharges at Grey Cloud Island, Minnesota, dissolved orthophosphate concentrations were greatest during the winter and least in the spring following snowmelt. Greater concentrations in the winter may have been the result of decreased dilution of wastewater effluents during the winter low-flow period and diminished uptake by biota. Lower concentrations during the spring may have been the result of increased dilution from snowmelt.

In the Minnesota, Namekagon, St. Croix, and Vermillion Rivers, the seasonal variations in dissolved orthophosphate concentrations generally were similar to those observed for total phosphorus. However, in the St. Croix River at Stillwater, Minnesota, dissolved orthophosphate concentrations generally had little seasonal pattern (fig. 23).

Temporal Trends

Despite the increased sales of fertilizers from 62,710 tons in fertilizer year 1982 to 66,842 tons in fertilizer year 1991, most stream sites had no long-term temporal change in total phosphorus or dissolved orthophosphate concentrations during water years 1984–93. A statistically significant decrease at the 0.05 significance level in total phosphorus concentrations was detected at one site, Mississippi River at Monticello, Minnesota. Dissolved orthophosphate concentrations had a statistically significant increase at one site, the Mississippi River at Grey Cloud Island. However, long-term changes in total phosphorus

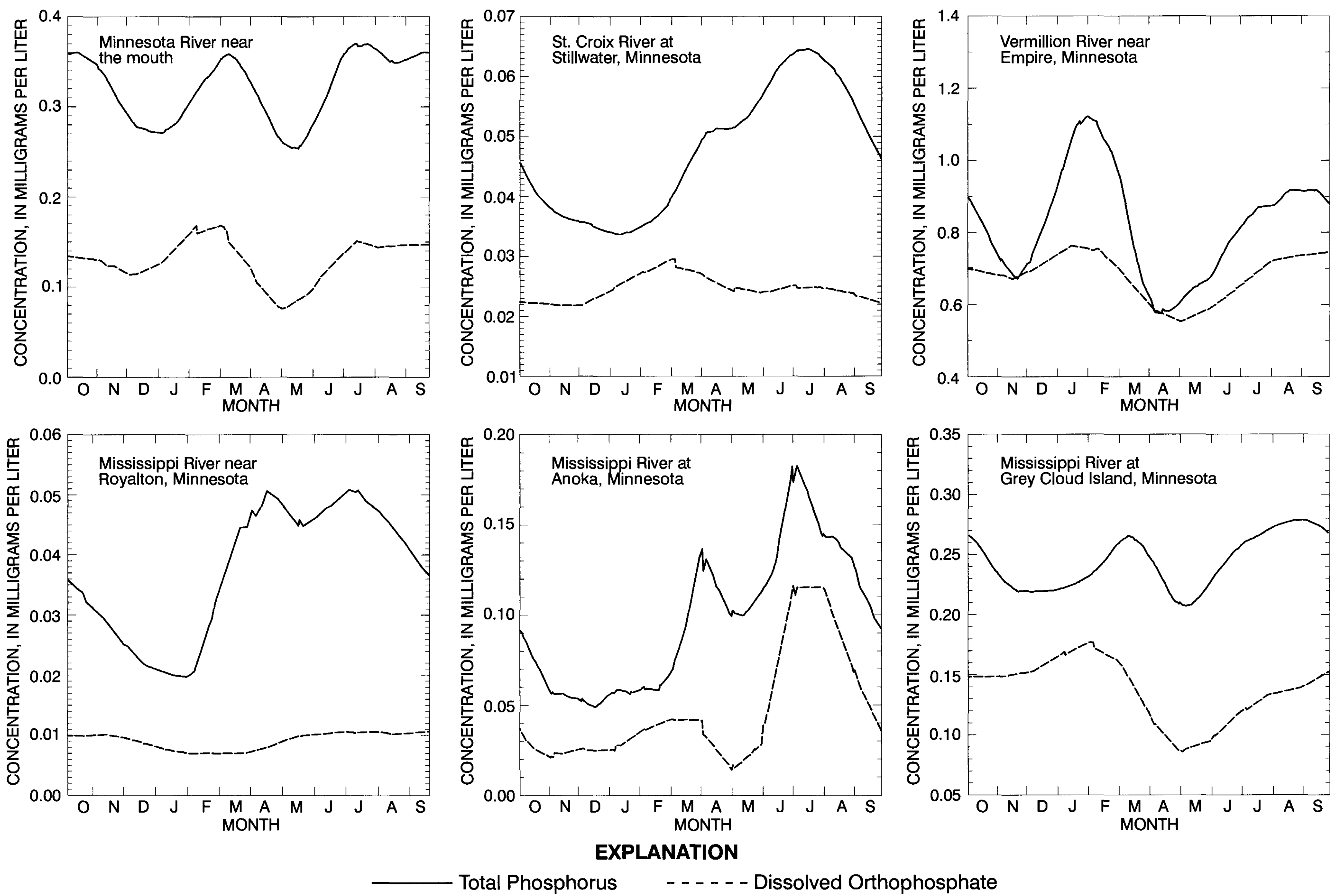

Figure 23.--Seasonal trends in total phosphorus and dissolved orthophosphate concentrations at selected stream sites in the study area, water years 1984-93.

concentrations were very slight. In the Mississippi River at Monticello, Minnesota, median total phosphorus concentrations decreased from 0.10 mg/L in 1984 to 0.08 mg/L in 1993.

Streambed Sediment

Phosphorus is added to streambed sediments through deposition of particles in slow-moving reaches or reservoirs. Concentrations in the sediments typically are several orders of magnitude greater than in the water column. Phosphorus in sediments generally is inorganic and is adsorbed to iron hydroxides or clays. Phosphorus can be released from sediments to the water column under both anaerobic and aerobic conditions. Under anaerobic conditions, phosphorus adsorbed to iron hydroxides in the sediment can be mobilized into the water after iron and manganese in sediments is reduced. The microbial degradation of organic matter in sediments, which lowers the pH, can result in phosphorus release from sediments by the dissolution of carbonate minerals. Phosphorus also may be released into the water column under aerobic conditions by desorption, which can occur when sediments are in contact with water that has a lesser orthophosphate concentration.

Streambed-sediment total phosphorus data for 1974–89 were available from the USACOE. Total phosphorus concentrations in the sediments (table 15) ranged from a minimum of 14 mg/kg in the Lower St. Croix River to a maximum of 3,141 mg/kg in Navigation Pool 4 (Lake Pepin). Median concentrations were greatest in the lower Minnesota River and in the Mississippi River Navigation Pools 2, 3, and 4. However, the interquartile range in streambed-sediment concentrations in Navigation Pools 2 and 4 was very great, 810 and 841 mg/kg, respectively.

The pattern in total phosphorus concentrations in the streambed sediments of the Mississippi River was generally consistent with results from a study by the Metropolitan Waste Control Commission (1993b). That study reported total phosphorus concentrations in the Mississippi River sediments increased from 157 mg/kg at Anoka, Minnesota, to 956 mg/kg in Navigation Pool 2 and remained at about the same concentration. In Lake Pepin (Navigation Pool 4), the total phosphorus concentration was 954 mg/kg.

Ground Water

Phosphorus is less likely than nitrate to leach in substantial concentrations to ground water. In soils, phosphorus readily sorbs to clays and metallic oxides. Phosphorus may leach from soils to underlying aquifers when phosphorus-rich substances such as fertilizers or livestock wastes have been applied at rates exceeding the sorption capacity of soils and the vadose zone. Sandy soils do not sorb phosphorus compounds as effectively as clayey soils, which are less permeable, have slower percolation rates, and have more positively charged sorption sites.

In this section of the report, only dissolved (filtered) phosphorus concentrations in ground water were summarized, because the dissolved form is more likely than the particulate form to be transported over distances of several miles from aquifer recharge areas to points of discharge to surface water. Most of the water-quality data bases summarized in this report contained total (unfiltered) phosphorus concentrations. The USGS was the only agency that analyzed ground-water samples for dissolved phosphorus in the study area, and only a relatively limited number of ground-water samples were

Table 15.--Summary statistics for total phosphorus concentrations in streambed sediments in selected reaches of the Mississippi, Minnesota, and St. Croix Rivers in the study area, 1974–89
[Concentrations are in units of milligrams per kilogram].

River Reach	Median	Interquartile Range	Minimum	Maximum
Mississippi River Navigation Pool 0	120	81	50	173
Mississippi River Navigation Pool 1	143	106	82	990
Lower Minnesota River	400	220	230	561
Mississippi River Navigation Pool 2	250	810	85	1,770
Lower St. Croix River	99	185	14	220
Mississippi River Navigation Pool 3	247	130	46	1,100
Mississippi River Navigation Pool 4	225	841	37	3,141

analyzed for dissolved phosphorus concentrations. Only the unconfined sand and gravel and Prairie du Chien-Jordan aquifers have been sampled more than a few times for dissolved phosphorus by the USGS in the study area (table 16, fig. 24).

Dissolved phosphorus concentrations in water samples from unconfined sand and gravel aquifers generally were near reporting limits (fig. 24, table 16). Concentrations ranged from less than the reporting limits (0.002 to 0.01 mg/L) to a maximum of 0.77 mg/L. In water samples from unconfined sand and gravel aquifers, phosphorus concentrations were greatest in the TCMA (fig. 24). Dissolved phosphorus concentrations also generally were below the reporting limits in the Prairie du Chien-Jordan aquifer. Water samples from the Prairie du Chien-Jordan aquifer had lesser median concentrations of dissolved phosphorus than water samples from unconfined sand and gravel aquifers (fig. 25)—probably a result of phosphorus sorption in overlying unconsolidated and consolidated units. The greatest median concentrations in water samples from the Prairie du Chien-Jordan aquifer were from wells located in the TCMA (figs. 1, 3, 24). A few wells with greater dissolved phosphorus concentrations also were located in agricultural areas on sandy soils in the southeast part of the TCMA in Minnesota and east of the TCMA in Wisconsin (fig. 24). Well depths were not strongly associated with differences in dissolved phosphorus concentrations in water in the major aquifers in the study area (fig. 25).

No wells were sampled for dissolved phosphorus for sufficient periods of time to assess temporal trends in dissolved phosphorus concentrations in ground water in the study area.

Table 16.--Summary statistics for dissolved phosphorus concentrations in the ground water in the study area, 1976–91

[listed by sampling agency and aquifer. Concentrations are given in units of milligrams per liter]

Agency	Aquifer	Dates sampled	Number of wells sampled	Reporting limits	Range in concentrations
U.S. Geological Survey (Minnesota)	Unconfined sand and gravel	1977–91	62	0.01	<0.01 - 0.77
U.S. Geological Survey (Minnesota)	Buried sand and gravel	1985	5	0.01	0.03 - 0.10
U.S. Geological Survey (Minnesota)	Galena-Platteville	1983	4	0.01	<0.01 - 0.11
U.S. Geological Survey (Minnesota)	St. Peter	1983–90	8	0.01	<0.01 - 0.21
U.S. Geological Survey (Minnesota)	Prairie du Chien-Jordan	1980–91	74	0.01	<0.01 - 0.60
U.S. Geological Survey (Minnesota)	Franconia-Ironton-Galesville	1979	1	0.01	<0.01
U.S. Geological Survey (Minnesota)	Mt. Simon-Hinckley-Fond du Lac	1979	1	0.01	<0.01
U.S. Geological Survey (Wisconsin)	Unconfined sand and gravel	1979	13	0.002, 0.01	<0.002 - 0.06
U.S. Geological Survey (Wisconsin)	Buried sand and gravel	1976–88	5	0.01	0.01 - 0.04
U.S. Geological Survey (Wisconsin)	Prairie du Chien-Trempealeau	1976	1	0.01	0.02
U.S. Geological Survey (Wisconsin)	Tunnel City-Wonewoc-Eau Claire	1976–80	5	0.01	0.04 - 0.16
U.S. Geological Survey (Wisconsin)	Mt. Simon-Hinckley-Fond du Lac	1976	1	0.01	0.01
U.S. Geological Survey (Wisconsin)	Precambrian igneous and metamorphic	1976	1	0.01	0.04

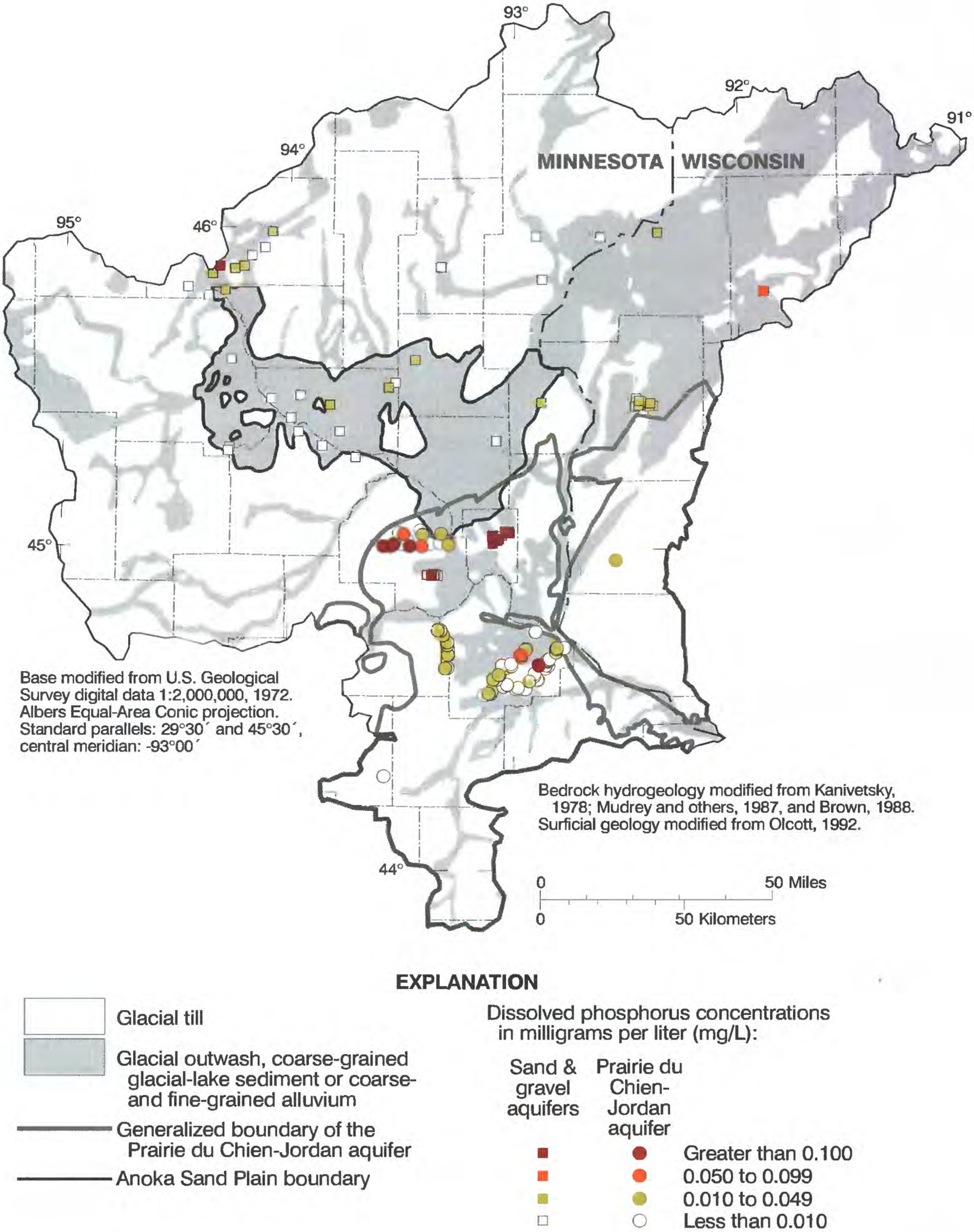

Figure 24.--Dissolved phosphorus concentrations in samples from unconfined sand and gravel aquifers and the Prairie du Chien-Jordan aquifer in the study area, 1976-91.

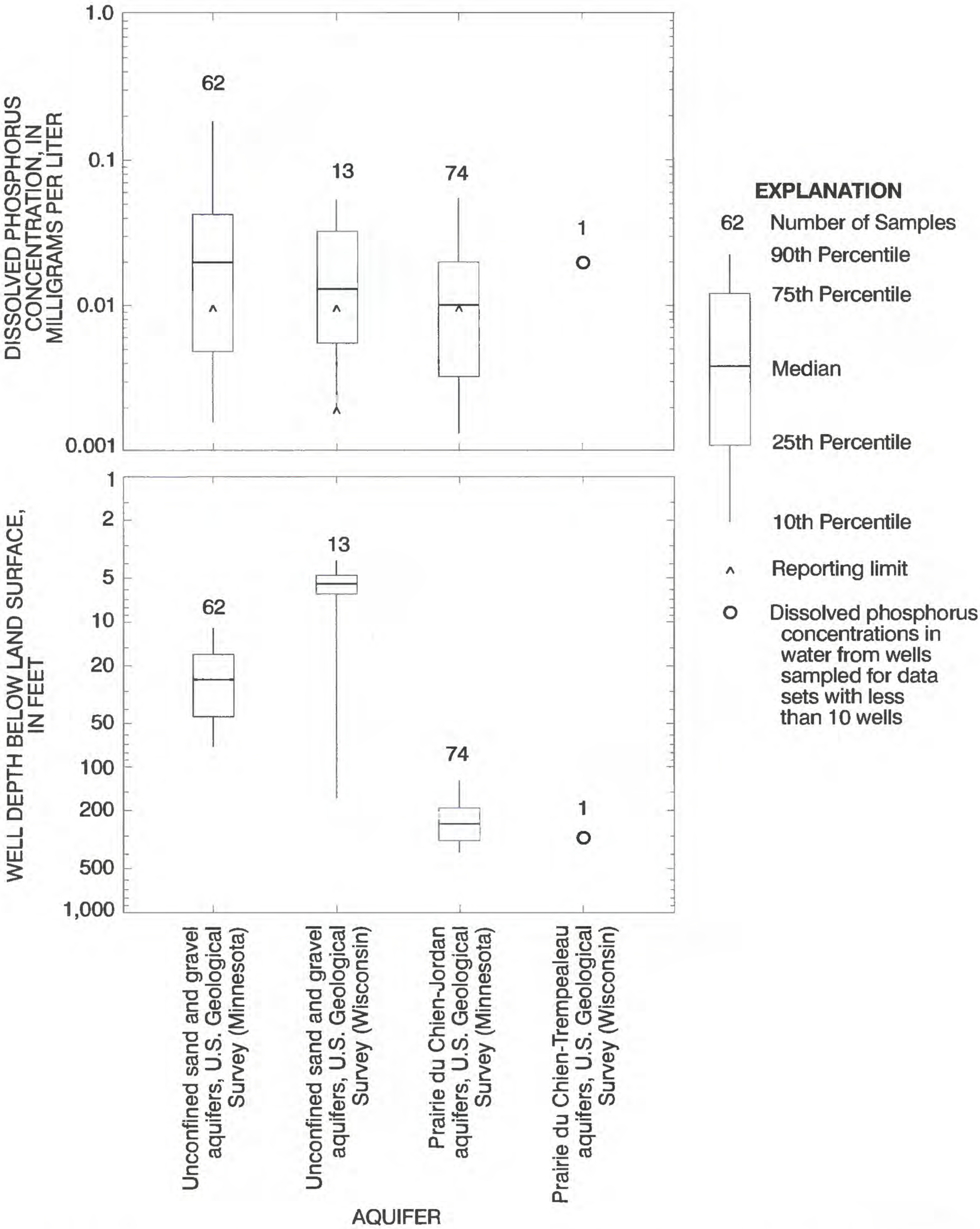

Figure 25.--Dissolved phosphorus concentrations in water from wells and depth of wells completed in unconfined sand and gravel aquifers and the Prairie du Chien-Jordan aquifer in the study area, 1976-91.

SUMMARY AND CONCLUSIONS

Nitrogen and phosphorus in streams, streambed sediment, and ground water were summarized as part of an analysis of historical water-quality data for the Upper Mississippi River Basin study unit of the U.S. Geological Survey's National Water-Quality Assessment Program. The Upper Mississippi River Basin study unit encompasses the entire drainage of the Mississippi River from the source at Lake Itasca to the outlet of Lake Pepin. For this report, data were obtained from Federal, state and local agencies. Sources of water-quality data used for these analyses included the Metropolitan Council Environmental Services, Minnesota Department of Agriculture, Minnesota Department of Health, Minnesota Pollution Control Agency, Wisconsin Department of Natural Resources, and the U.S. Geological Survey.

This report focused on an area of about 19,500 mi^2 in the eastern part of the study unit. The study area includes the part of the Upper Mississippi River Basin from Royalton, Minnesota, to the outlet of Lake Pepin, the Minnesota River Basin from Jordan, Minnesota, to the confluence with the Mississippi River, and the entire drainage basins of the St. Croix, Cannon, and Vermillion Rivers. Land use and land cover in the study area is diverse and ranges from areas of rich agricultural lands to forests, wetlands, and a major urban area. The Twin Cities metropolitan area, with a population of approximately 2.3 million people, is located in the south-central part of the study area.

Fertilizers and livestock manure were the principal sources of nitrogen and phosphorus applied to the land surface of the study unit. These two sources comprised 72 percent of the nitrogen and 98 percent of the phosphorus applied. The majority of the fertilizers, approximately 60 percent, were applied to the Minnesota River Basin, which drains agricultural areas in the southern and western parts of the study unit.

Concentrations of total nitrite plus nitrate nitrogen, total nitrogen, and total phosphorus generally were greatest in streams draining agricultural areas in the western and southern portion of the study area and at sites on the Mississippi River downstream of the confluence with the Minnesota River and the Twin Cities metropolitan area. Concentrations of these constituents generally were least at sites draining forested land. Total nitrite plus nitrate nitrogen concentrations generally were greatest in the spring and summer in the streams draining agricultural areas and were greatest in the winter in the streams draining forested areas. In all tributaries of the Mississippi River that were summarized in this report, total phosphorus concentrations were greatest in the spring and summer.

In the Mississippi River, concentrations of these constituents increased in the downstream direction and increased substantially downstream from the Minnesota River and downstream of wastewater discharges from the Twin Cities metropolitan area. Similarly, total ammonia and dissolved orthophosphate concentrations generally were greatest at sites downstream from municipal wastewater discharges on the Mississippi and Minnesota Rivers in the Twin Cities metropolitan area.

Total nitrite plus nitrate nitrogen concentrations in streams generally were below the primary drinking water standard of 10 mg/L (as nitrogen) established by the U.S. Environmental Protection Agency. Total phosphorus concentrations in streams generally were above the 0.1 mg/L concentration recommended by the U.S. Environmental Protection Agency at sites located in agricultural areas, on the Mississippi River, downstream from its confluence with the Minnesota River and downstream from wastewater discharges.

Phosphorus and nitrogen yields were greatest in watersheds primarily draining agricultural land. The majority of the nitrogen and phosphorus loading to the Mississippi River was from the Minnesota River. In the Minnesota River, the nitrogen load primarily was total nitrite plus nitrate nitrogen.

Despite increases in fertilizer usage from 1982 through 1991, most stream sites outside of the Twin Cities metropolitan area had no trends in total nitrite plus nitrate nitrogen, total phosphorus, or dissolved orthophosphate concentrations. However, most sites had a decrease in total ammonia nitrogen concentrations from water years 1984–93, possibly a result of improvements in wastewater treatment. In the Twin Cities metropolitan area, decreases in total ammonia concentrations in the Mississippi and Minnesota Rivers coincided with increases in total nitrite plus nitrate nitrogen concentrations, probably a result of wastewater treatment plants initiating nitrification processes.

Nitrite plus nitrate nitrogen concentrations in ground water reflect land uses and hydrogeologic settings of major aquifers in the study area. Unconfined sand and gravel, buried sand and gravel, and the Prairie du Chien-Jordan were the aquifers most frequently sampled for nitrite plus nitrate nitrogen because they are the principal sources of ground water in the study area. Unconfined sand and gravel aquifers are highly susceptible to contamination from chemicals applied at the land surface. Some of the greatest nitrite plus nitrate nitrogen concentrations in the study area were in water from shallow wells in agricultural and mixed forested and agricultural areas. The greatest nitrite plus nitrate nitrogen concentrations reported by Federal and state agencies, some exceeding the U.S. Environmental Protection Agency's Maximum Contaminant level of 10 mg/L by a factor of four, were in water from shallow wells in agricultural and mixed forested and agricultural areas. Water sampled from buried sand and gravel aquifers, which are more shielded from substances leaching from the land surface by layers of clay or till, generally had lesser nitrite plus nitrate nitrogen concentrations and lower frequencies of detection of nitrite plus nitrate nitrogen than unconfined sand and gravel aquifers. Nitrite plus nitrate nitrogen concentrations in water sampled from the Prairie du Chien-Jordan aquifer were greatest in the Wisconsin portion of the study area and in the vicinity of the Cannon River, where the aquifer is commonly unconfined, exposed at the land surface, and overlain by agricultural or by mixed forested and agricultural land.

Dissolved phosphorus concentrations in ground water in the study area generally were near detection limits of 0.01 mg/L or less, indicating that surface-water eutrophication from phosphorus may be more likely to occur from overland runoff of phosphorus compounds and from direct discharges of treated wastewater than from ground-water base flow. The greatest concentrations of dissolved phosphorus in ground water generally were detected in water samples from wells in urban portions of the study area.

REFERENCES

Adolphson, D.G., Ruhl, J.F., and Wolf, R.J., 1981, Designation of principal water-supply aquifers in Minnesota: U.S. Geological Survey Water-Resources Investigations Report 81–51, 19 p.

Almendinger, J.E., and Mitton, G.B., 1995, Hydrology and relation of selected water-quality constituents to selected physical factors in Dakota County, Minnesota: U.S. Geological Survey Water-Resources Investigations Report 94–4207, 26 p.

Anderson, H.W., Jr., 1986, Hydrogeologic and water-quality characteristics of crystalline-rock aquifers of Archean and Proterozoic Age, Minnesota: U.S. Geological Survey Water-Resources Investigations Report 86–4033, 3 sheets.

Anderson, J.R., Hardy, E.E., Roach, J.T., and Witmer, R.E., 1976, A land use and land cover classification system for use with remote sensor data: U.S. Geological Survey Professional Paper 964, 28 p.

Andrews, W.J., 1994, Nitrate in ground water and spring water near four dairy farms in North Florida, 1990–93: U.S. Geological Survey Water-Resources Investigations Report 94–4162, 63 p.

Andrews, W.J., Trotta, L.C., and Schoenberg, M.E., 1995, Water-level declines from 1980–90 in major aquifers in the Twin Cities areas: Proceedings of the 31st annual conference and symposia of the American Water Resources Association, Houston, Texas, November 5–9, 1995, p. 63–72.

Baker, D.G., Nelson, W.W., and Kuehnast, E.L., 1979, Climate of Minnesota Part XII—The hydrologic cycle and soil water: Agricultural Experiment Station Technical Bulletin 322, University of Minnesota, 24 p.

Battaglin, W.A., and Goolsby, D.A., 1995, Spatial data in geographic information system format on agricultural chemical use, land use, and cropping practices in the United States: U.S. Geological Survey Water-Resources Investigation Report 94–4176, 87 p.

Brown, B.A., 1988, Bedrock geology of Wisconsin: Wisconsin Geological and Natural History Survey Map 88–7, 1 sheet.

Bundy, L.G., Kelling, K.A., Schulte, E.E., Combs, S., Wolkowski, R.P., and Sturgul, S.J., 1992, Nutrient management—Practices for Wisconsin corn production and water-quality protection: University of Wisconsin-Extension, College and Agriculture and Life Sciences, University of Wisconsin, Madison, 27 p.

Burns, R.C., and Hardy, R.F., 1975, Nitrogen fixation in bacteria and higher plants: Springer-Verlag, Berlin, Germany, 186 p.

Crawford, C.G., Slack, J.R., and Hirsch, R.M., 1983, Nonparametric tests for trends in water-quality data using the Statistical Analysis System: U.S. Geological Survey Open-File Report 83–550, 102 p.

Delin, G.N., and Woodward, D.G., 1984, Hydrogeologic setting and the potentiometric surfaces of the regional aquifers of the Hollandale Embayment, southeastern Minnesota, 1970–80: U.S. Geological Survey Water-Supply Paper 2219, 56 p.

Gleit, A., 1985, Estimation for small normal data sets with detection limits: Environmental Science and Technology, v. 19, no. 12, p. 1201–1206.

Green, J.C., 1977, Keweenawan plateau volcanism in the Lake Superior region, *in* Baragen, W.R., Coleman, L.C., and Hall, J.M. (eds.), Volcanic Regimes in Canada: Geological Association of Canada Special Paper 15, p. 407–422.

Gunard, K.T., Hess, J.H., and Zirbel, J.L., 1992, Water resources data Minnesota water years 1991—Volume 2. Upper Mississippi and Missouri River Basins: U.S. Geological Survey Water-Data Report MN-91-2, 271 p.

______1993, Water resources data Minnesota water years 1992—Volume 2. Upper Mississippi and Missouri River Basins: U.S. Geological Survey Water-Data Report MN-92-2, 372 p.

Heiskary, Steve, Vavrika, Mike, and Walker, W.W., 1993, Mississippi River Phosphorus Study—Section 7, Lake Pepin and Mississippi River BATHTUB modeling: Minnesota Pollution Control Agency, Water-Quality Division, St. Paul, Minnesota, 62 p.

Helsel, D.R., 1990, Less than obvious—Statistical treatment of data below the detection limit: Environmental Science and Technology, v. 24, no. 12, p. 1766–1774.

Helsel, D.R., and Cohn, T.A., 1988, Estimation of descriptive statistics for multiply censored water-quality data: Water Resources Research, v. 24, no. 12, p. 1997–2004.

Helsel, D.R., and Hirsch, R.M., 1992, Statistical methods in water resources: Studies in Environmental Science 49, Elsevier, 529 p.

Hem, J.D., 1985, Study and interpretation of the chemical characteristics of natural water: U.S. Geological Survey Water-Supply Paper 2254, 263 p.

Hirsch, R.M., Slack, J.R., and Smith, R.A., 1982, Techniques of trend analysis for monthly water-quality data: Water Resources Research, v. 18, no. 18, p 107–121.

Iowa Department of Natural Resources, 1989, Geologic Map of Iowa, Iowa City, Iowa, Scale 1:500,000.

Iowa State University, 1994, Iowa Agricultural Statistics: Iowa State University, Ames, Iowa, 112 p.

Justic, D., Rabalais, N.N., Turner, E.R., and Wiseman, W.J., 1993, Seasonal coupling between riverborne nutrients, net productivity, and hypoxia: Marine Pollution Bulletin, v. 26, no. 4. p. 184–189.

Kanivetsky, Roman, 1978, Hydrogeologic map of Minnesota, Bedrock Hydrogeology: Minnesota Geological Survey, State Map Series S–3.

King, P.B., and Beikman, H.M., compilers, 1974, Geologic map of the United States: U.S. Geological Survey, scale 1:2,500,000, 2 sheets.

Kroening, S.E., 1994, Phosphorus trends in the Upper Mississippi River Basin: University of Minnesota, M.S. Thesis, 220 p.

Landon, M.K., and Delin, G.N., 1995, Ground-water quality in agricultural areas, Anoka Sand Plain aquifer, east-central Minnesota: U.S. Geological Survey Water-Resources Investigations Report 95–4024, 25 p.

Leete, J.H., 1991, Ground-water quality and management in Minnesota: Journal of the Minnesota Academy of Science, v. 56, no. 1, p. 34–43.

Madison, R.J., and Brunett, J.O., 1985, Overview of the occurrence of nitrate in ground water of the United States, *in* National water summary 1984, Hydrologic events, selected water-quality trends and ground-water resources: U.S. Geological Survey Water-Supply Paper 2275, p. 93–105.

Maurer, W.R., Claflin, T.O., Rada, R.G., and Rogala, J.T., 1995, Volume loss and mass balance for selected physicochemical constitutents in Lake Pepin, Upper Mississippi River, USA: Regulated Rivers—Research and Management, v. 2, p. 175–184.

Metcalf and Eddy, Inc., 1991, Advanced wastewater treatment, *in* Tchobanoglous, George and Burton, Frank, eds., Wastewater Engineering—Treatment, disposal, and reuse (3rd ed.): McGraw-Hill, Inc., New York, 1334 p.

Metropolitan Waste Control Commission, 1990, 1990 annual wastewater treatment plant report, volume I: Laboratory Services Division, Quality Control Department and Operations Planning and Engineering Section, Operations and Maintenance Department, St. Paul, Minnesota, 99 p.

______1993a, Mississippi River phosphorus study report— Summary and recommendations: St. Paul, Minnesota, 43 p.

______1993b, Mississippi River phosphorus study report—River and lake sediment: St. Paul, Minnesota.

______1993c, Mississippi River Phosphorus study report—Water quality of the Mississippi River and its tributaries 1976–1991, St. Paul, Minnesota.

______1994, Water-quality analysis of the Lower Minnesota River and selected tributaries—River (1976–1991) and nonpoint source (1989–1992) monitoring, volume I: Water-Quality Division, Quality Control Department, Report No. QC-93–267, St. Paul, Minnesota, 142 p.

Minnesota Agricultural Statistics Service, 1995, Minnesota agricultural statistics: St. Paul, Minnesota, 103 p.

Minnesota Pollution Control Agency, 1985, Lower Minnesota River waste load allocation study: St. Paul, Minnesota, 190 p.

______1989, Review of water-quality conditions in Lake Pepin for the summer of 1988: St. Paul, Minnesota, 50 p.

______1991, Wastewater disposal facilities inventory: St. Paul, Minnesota, 89 p.

______1992, Minnesota water quality—Water years 1990-1991— The 1992 report to the Congress of the United States: St. Paul, Minnesota, 59 p.

Minnesota State Statutes, November 1996, Chapter 7050.0211, subpart 1.

Mitton, G.B., Hess, J.H., and Guttormson, K.G., 1994, Water resources data Minnesota water year 1993: U.S. Geological Survey Water-Data Report MN-93–2, 311 p.

______1995, Water resources data Minnesota water year 1994: U.S. Geological Survey Water-Data Report MN-94°–1, 478 p.

Mudrey, M.G., Jr., LaBarge, G.A., Myers, P.E., and Cordua, W.S., 1987, Bedrock geology of Wisconsin: Wisconsin Geological and Natural History Survey, Map 87–11a, 2 sheets.

Mueller, D.K., Hamilton, P.A., Helsel, D.R., Hitt, K.J., and Ruddy, B.C., 1995, Nutrients in ground water and surface water of the United States—An analysis of data through 1992: U.S. Geological Survey Water-Resources Investigations Report 95–4031, 74 p.

Myers, C.F., Meek, J., Tuller, S., and Weinberg, A., 1985, Nonpoint sources of water pollution: Journal of Soil and Water Conservation, v. 40, no. 6, p. 14–18.

National Oceanic and Atmospheric Administration, 1993, Point source methods document, Appendix II: Silver Spring, MD

National Research Council, 1978, The health effects of nitrate, nitrite, and N-nitroso compounds: Washington, D.C., National Academy Press, 723 p.

North Dakota Agricultural Statistics Service, 1994, North Dakota Agricultural Statistics: Fargo, North Dakota, 104 p.

Olcott, P.G., 1992, Ground water atlas of the United States, Segment 9; Iowa, Michigan, Minnesota, Wisconsin: U.S. Geological Survey Hydrologic Investigations Atlas 730–J, 31 p.

Omernik, J.M., 1976, The influence of land use on stream nutrient levels: U.S. Environmental Protection Agency Report EPA-600/3–76–014, 68 p.

Ott, R.L., 1993, An introduction to statistical methods and data analysis: Belmont, California, Duxbury Press, 1051 p.

Puckett, L.J., 1995, Identifying the major sources of nutrient water pollution: Environmental Science and Technology, v. 29, no. 9, p. 408–414.

Rabalais, N.N., Turner, R.E., Wiseman, W.J., Justic, D., Dortch, Q., and Gupta, B.S., 1994, Hypoxia on the Louisiana Shelf and system responses to nutrient changes in the Mississippi River—A brief synopsis, *in* National Oceanic and Atmospheric Administration, Nutrient-enhanced coastal ocean productivity: Proceedings of the 1994 synthesis workshop, Baton Rouge, LA.

Scragg, R.K.R., Dorsch, M.M., McMicheal, A.J., and Baghurst, P.A., 1982, Birth defects and household water supply: Medical Journal of Australia, v. 2, p. 577–579.

Sisterson, D.L., 1990, Detailed SO_x-S and NO_x-N mass budgets for the United States and Canada, *in* Venkatram, A. and others, eds., Acidic deposition—State of science and technology, appendix A: National Acid Precipitation Assessment Program, Washington D.C., p. 8A1–8A10.

South Dakota Agricultural Statistics Service, 1994, South Dakota Agricultural Statistics: Sioux Falls, South Dakota, 84 p.

Stark, J.R., Andrews, W.J., Fallon, J.D., Fong, A.L., Hanson, P.E., Lee, K.E., Kroening, S.E., and Goldstein, R.M., 1996, Water-quality assessment of the Upper Mississippi River Basin study unit, Minnesota and Wisconsin—Environmental setting and study design: U.S. Geological Survey Water-Resources Investigations Report 96–4098, 62 p.

Stewart, J.C., 1990, Drinking water hazards: Hiram, Ohio, Envirographics Publishing, 323 p.

Strange, M., and Krupicka, L., 1984, Farming and cancer, *in* It's not all sunshine and fresh air: Center for Rural Affairs, p. 41–53.

Thomann, R.V., and Mueller, J.A., 1987, Eutrophication, chap. 7, *in* Principles of surface water-quality modeling and control: New York, Harper and Row Publishers, 644 p.

Trotta, L.C., and Cotter, R.D., 1973, Depth to bedrock in Wisconsin: University of Wisconsin-Extension, Geological and Natural History Survey, 1 sheet.

Turner, Eugene, and Rabalais, N.N., 1994, Coastal eutrophication near the Mississippi River delta: Nature, v. 368, p. 619–621.

U.S. Environmental Protection Agency, 1986, Quality criteria for water 1986: U.S. Environmental Protection Agency, EPA 440–5–86–001.

U.S. Geological Survey, 1990, USGeoData 1:250,000- and 1:100,000 scale land use and land cover maps digital data.

Wall, D.B., Montgomery, B.R., Deluca, D., Meyers, G., and Thomas, D., 1991, Nitrogen in Minnesota ground water, prepared for the Legislative Water Commission: Minnesota Pollution Control Agency and Minnesota Department of Agriculture, variously paged.

Wayne, R.P., 1993, Nitrogen and nitrogen compounds in the atmosphere, *in* Burt, T.P., Heathewaite, A.L., and Trudgill, S.T., eds., Nitrate—Process, patterns, and management: Chichester, England, John Wiley and Sons, p. 23–38.

Wei, T.C., and McGuinness, J.L., 1973, Reciprocal distance squared method, a computer technique for estimating area precipitation, ARS-NC–8: U.S. Agricultural Research Service, North Central Region, Coshocton, Ohio, 29 p.

Wisconsin Agricultural Statistics Service, 1994, Wisconsin Agricultural Statistics: Madison, Wisconsin, 98 p.

Wisconsin Department of Natural Resources and Wisconsin Geological and Natural History Survey, 1987, Groundwater contamination susceptibility in Wisconsin: Wisconsin Department of Natural Resources and Wisconsin Geological and Natural History Survey, 1 sheet.

Wisconsin Department of Natural Resources, 1994, The St. Croix River—Water-quality management plan: PUBL-WR-270–94-REV, 269–p.

Woodward, D.G., 1986, Hydrogeologic framework and properties of regional aquifers in the Hollandale Embayment, southeastern Minnesota: U.S. Geological Survey Hydrologic Investigations Atlas HA–677, 2 sheets.

Woodward, D.G., and Anderson, H.W., Jr., 1986, Hydrogeologic and water-quality characteristics of the Cretaceous aquifer in southwestern Minnesota: U.S. Geological Survey Hydrologic Investigations Report 84–4153, 2 sheets.

World Health Organization, 1977, Nitrates, nitrites, and N-nitroso compounds: World Health Organization Environmental Health Criteria Document no. 5, 252 p.

Zublena, J.P., 1991, Nutrient removal by crops in North Carolina: The North Carolina Cooperative Extension Service, Raleigh, North Carolina, 4 p.

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