Nutrients, Suspended Sediment, and Pesticides in Streams in the Red River of the North Basin, Minnesota, North Dakota, and South Dakota, 1993–95

By L.H. Tornes, M.E. Brigham, and D.L. Lorenz

U.S. GEOLOGICAL SURVEY

Water-Resources Investigations Report 97-4053

Contribution from the

National Water-Quality Assessment Program

Mounds View, Minnesota

1997

U.S. DEPARTMENT OF THE INTERIOR

BRUCE BABBITT, Secretary

U.S. GEOLOGICAL SURVEY

Gordon P. Eaton, Director

For additional information write to:

District Chief
U.S. Geological Survey
2280 Woodale Drive
Mounds View, MN 55112

Copies of this report can be purchased from:

U.S. Geological Survey
Branch of Information Services
Box 25286
Denver, CO 80225

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

Contents

List of Illustrations

List of Illustrations—continued

List of Tables

Conversion Factors and Abbreviations

Multiply	By	To obtain
cubic foot per second (ft^3/s)	.02832	cubic meter per second
foot per second (ft/s)	0.3048	meter per second
pound per day (lb/d)	.4536	kilogram per day
pound per square mile per day ($lb/mi^2/d$)	1.175	kilogram per square kilometer per day
mile (mi)	1.609	kilometer
square mile (mi^2)	2.590	square kilometer
degree Fahrenheit (°F)∞	(°F–32)/1.8	degree Celsius

Abbreviated water-quality units used in this report: Chemical concentrations are given in metric units. Chemical concentration is given in milligrams per liter (mg/L) or micrograms per liter (µg/L). Milligrams per liter and micrograms per liter are units expressing the concentration of chemical constituents in solution as mass (milligrams or micrograms) of solute per unit volume (liter) of water. For concentrations less than 7,000 mg/L, the numerical value of milligrams per liter is the same as for concentrations in parts per million. The numerical value of micrograms per liter is the same as for concentrations in parts per billion.

Nutrients, Suspended Sediment, and Pesticides in Streams in the Red River of the North Basin, Minnesota, North Dakota, and South Dakota, 1993–95

By L.H. Tornes, M.E. Brigham, *and* D.L. Lorenz

Abstract

Fifteen stream sites in the Red River of the North Basin were sampled during 1993–95 to assess levels of nutrients, organic carbon, and suspended sediment, and five sites were sampled for pesticides. Concentrations varied seasonally and were related to periods of fertilizer and pesticide application, and to runoff. Concentrations of several constituents were related to the physiographic area the stream drains, but other factors such as local land use frequently complicated that relation.

Median dissolved nitrogen concentrations were highest in streams influenced by the Red River Valley Lake Plain physiographic area. Organic nitrogen comprised the largest part of the dissolved nitrogen in streams. Ammonia was negligible most of the year, but accumulated under ice in late winter. Nitrate concentrations generally were highest during snowmelt and rainfall runoff.

Phosphorus in streams mostly was in the dissolved form, which is readily available to biota. Streams draining the Moraine and Lake-Washed Till Plain had the lowest concentrations of total phosphorus, while Drift Prairie and Red River Valley Lake Plain streams had the highest concentrations. Concentrations of both dissolved and suspended phosphorus increased substantially during runoff of snowmelt and rainfall.

The Bois de Sioux River Basin had the highest nitrogen yield. High nitrogen and phosphorus yields probably were related to agricultural practices in the Bois de Sioux River Basin. High phosphorus concentrations in the Pembina River probably result from agricultural practices and runoff from the steep terrain in the basin.

Improved wastewater treatment appears to have reduced ammonia concentrations in streams, but has resulted in increased nitrate concentrations. The loads of nitrogen and phosphorus in the Red River of the North during this study were about twice as high as historical loads, but still were only about 4.1 and 2.4 percent, respectively, of the amounts introduced to the study unit.

Dissolved organic carbon concentrations above 15 mg/L were common in streams draining peatlands. Suspended organic carbon concentrations were highly variable and generally were highest during runoff.

Most suspended sediment in streams was clay and silt sized particles. The Pembina River had the highest concentrations and yields of suspended sediment, probably the result of erosion along this relatively high-gradient stream. Streams having an abundance of lakes, reservoirs, and wetlands in their watersheds had the lowest sediment concentrations and yields.

Several pesticides were frequently detected. Atrazine and other triazine compounds were detected in most stream-water samples throughout the study. Concentrations of triazine herbicides were highest in streams draining southern parts of the study unit where they are applied to corn. Triallate was commonly detected in northern streams where it is applied to small grains and sunflowers. Simazine and prometon were commonly detected, but generally are used only for nonagricultural purposes. Few insecticides were detected in stream-water samples. Carbofuran was the most commonly detected insecticide and was found in 16 percent of the samples.

The most heavily used herbicides, 2,4-D and MCPA, were infrequently detected in stream-water samples. Of the estimated applications of atrazine, triallate, and 2,4-D, about 0.9, 0.06, and 0.02 percent of each of these compounds, respectively, was carried out of the study unit by the Red River of the North during 1993–95.

Introduction

The Red River of the North (hereinafter referred to as Red River) Basin study unit (fig. 1) encompasses areas of rich agricultural lands, forests, grasslands, and large numbers of lakes, wetlands, and prairie potholes. The Red River was selected as a study unit under the U.S. Geological Survey's National Water-Quality Assessment (NAWQA) Program because (1) the study unit represents an important hydrologic region where good quality water is a valued resource vital to the region's economy, (2) the quality of the Red River, which flows north into Manitoba, Canada, is of international concern, (3) the study unit is an important agricultural area and provides opportunities to review nutrient, suspended-sediment, and pesticide data through the national assessment part of NAWQA, and (4) the northern location and potential interaction of surface water and ground water are essential physical factors necessary for a complete national assessment of water quality.

The NAWQA Program began full implementation in 1991 at 20 major hydrologic areas called study units throughout the United States. Data are collected through a multidisciplinary (surface water, ground water, ecology, and supporting data including land use) study of water quality. The purposes of the NAWQA Program are to (1) describe current water-quality conditions for a large part of the Nation's streams, rivers, and aquifers, (2) describe how water quality is changing over time, and (3) improve understanding of the primary natural and human factors that affect water-quality conditions. As part of the NAWQA design, it is planned that the 3-year period of intensive data collection at each of the study units will be followed by about 6 years of a long-term, low-intensity phase, in which fewer sites will be sampled at a reduced frequency. This cycling of high-intensity and low-intensity cycles will be repeated to assess trends in water quality.

Objectives

The objectives of this report are to (1) describe nutrient, suspended-sediment, and pesticide concentrations in streams spatially and temporally during the sampling period, (2) describe loads and yields of selected constituents for selected sampling sites, and (3) identify trends in nutrient concentrations where sufficient historical data exist; and relate concentrations, loads, and yields to physiography, land use and land cover, and to possible sources and sinks.

This report provides the results of sampling for nutrients, suspended sediment, and pesticides in selected streams in the Red River Basin study unit during 1993–95. During March and December 1992, samples were collected near the mouth of major streams in the study unit to determine concentrations of selected constituents during low-flow conditions. Intense data collection was started in March 1993 and completed in August 1995. Many other constituents were sampled from streams in the study unit, but these data will be discussed only as needed to explain the presence and distribution of nutrients, suspended sediment, and pesticides.

Tornes and Brigham (1994) summarized selected data from streams and ground water collected by Federal, state, and local agencies throughout the

Figure 1. Location of the Red River of the North Basin study unit.

Red River Basin. This report updates findings on nutrients, suspended sediments, and pesticides in streams using consistent sampling and analytical methods.

Description of Study Unit

The general physical, hydrological, and ecological setting of the Red River Basin study unit is diverse in ways that could significantly affect the areal distribution and flow of water and, therefore, the distribution and concentration of constituents that affect water quality (Stoner and others, 1993). Continental glaciers and glacial lakes deposited 150 to 300 feet of unconsolidated material over much of the basin and shaped a landscape of flat plains near the center of the basin, and gently rolling uplands, lakes, and wetlands along the margins. The fertile, black, fine-grained soils are conducive to cropland agriculture (fig. 2). The 1990 study unit population of 511,000 represents an 8 percent increase since 1980 (U.S. Bureau of Census, 1991). Almost one-third of the population lives in the cities of Fargo and Grand Forks, North Dakota, and Moorhead, Minnesota.

For this assessment, the study unit is divided into the major physiographic areas shown in figure 2. The Drift Prairie to the west is an area of low, rolling hills and prairie, with many prairie-pothole wetlands. The Red River Valley Lake Plain is an extensive area of flat land mostly comprised of clays and silts deposited by glacial Lake Agassiz. To the northeast is the Lake-Washed Till Plain, a relatively flat upland area having extensive wetlands and peat deposits. The Moraine area to the east is comprised mostly of lakes and woodlands.

From its origin, the Red River meanders northward for 394 mi to the United States-Canadian border, a path that is nearly double the straight-line distance. The main focus of this study ends at the Canadian border, but part of the 35,600 mi^2 drainage area extends into Canada. The Pembina River starts in Manitoba then crosses south into North Dakota before joining the Red River a few miles south of the U.S.-Canadian border. The Roseau River drains parts of northern Minnesota and southern Manitoba and crosses north into Canada where it flows into the Red River.

The climate of the study unit is continental and ranges from dry subhumid in the west to subhumid in the east. The mean monthly temperature ranges from –1°F in January near the United States-Canadian border to 73°F in July in the southern part of the study unit.

Mean annual precipitation in the Red River Basin ranges from less than 18 inches in the west to about 26 inches in the east (fig. 3). Loss of water to evapotranspiration increases from east to west across the study unit. Because of these changes, the Red River receives over 75 percent of its annual flow from its eastern tributaries; about one-third of the streamflow measured where the Red River flows into Canada at Emerson, Manitoba, comes from the Red Lake River. The Sheyenne River, a western tributary, has a much larger drainage area than other tributary streams in the study unit, but supplies less than 5 percent of the water flowing into Canada.

Streamflow varies greatly throughout the year. Largest streamflow occurs in spring and early summer as a result of rains falling on melting snow or heavy rains falling on saturated soils. Flooding is a major problem that is aggravated by the very gentle slope of the Red River and the flatness of the overbank areas. An extensive system of drainage ditches has been constructed in parts of the Red River Valley Lake Plain and the Lake-Washed Till Plain to promote rapid drainage of clay-rich soils.

Ground water is found primarily in sand and gravel aquifers near land surface or buried within glacial deposits that mantle the entire study unit. Water also moves through a system of bedrock and glacial-drift aquifers in a regional system generally towards the Red River. Many of these bedrock and glacial-drift aquifers are hydraulically connected to streams in the region and affect the flow and water quality of the streams. During dry periods, ground water, in addition to water from lakes and reservoirs, is an important source of flow in many streams.

The total water use in 1990, about 196 million gallons, was mostly for public supply and irrigation. About 48 percent of the water used in 1990 came from surface-water sources. The largest cities (Fargo and Grand Forks, North Dakota; and Moorhead, Minnesota) have surface-water sources, and most of this water is obtained from the Red River.

Agriculture predominates the land use in the study unit; about 64 percent of the area is cropland, and about 16 percent is pasture, farmsteads, and local roads (data interpreted from U.S. Geological Survey, 1986; Minnesota Agricultural Statistics Service, 1991; and North Dakota Agricultural Statistics Service,

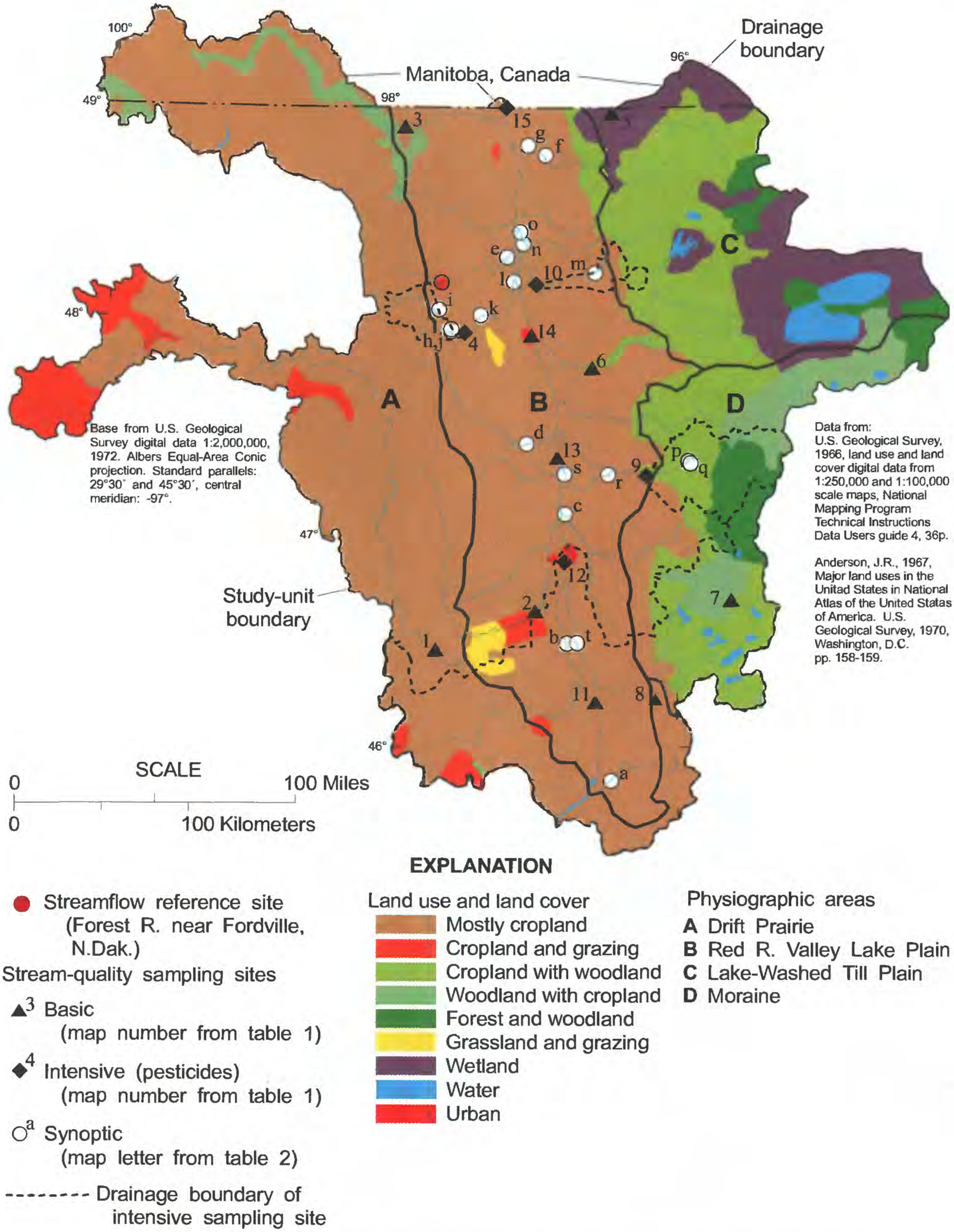


Figure 2. Study area, stream-quality sampling sites, land use and land cover, and physiographic areas in the Red River of the North Basin study unit.

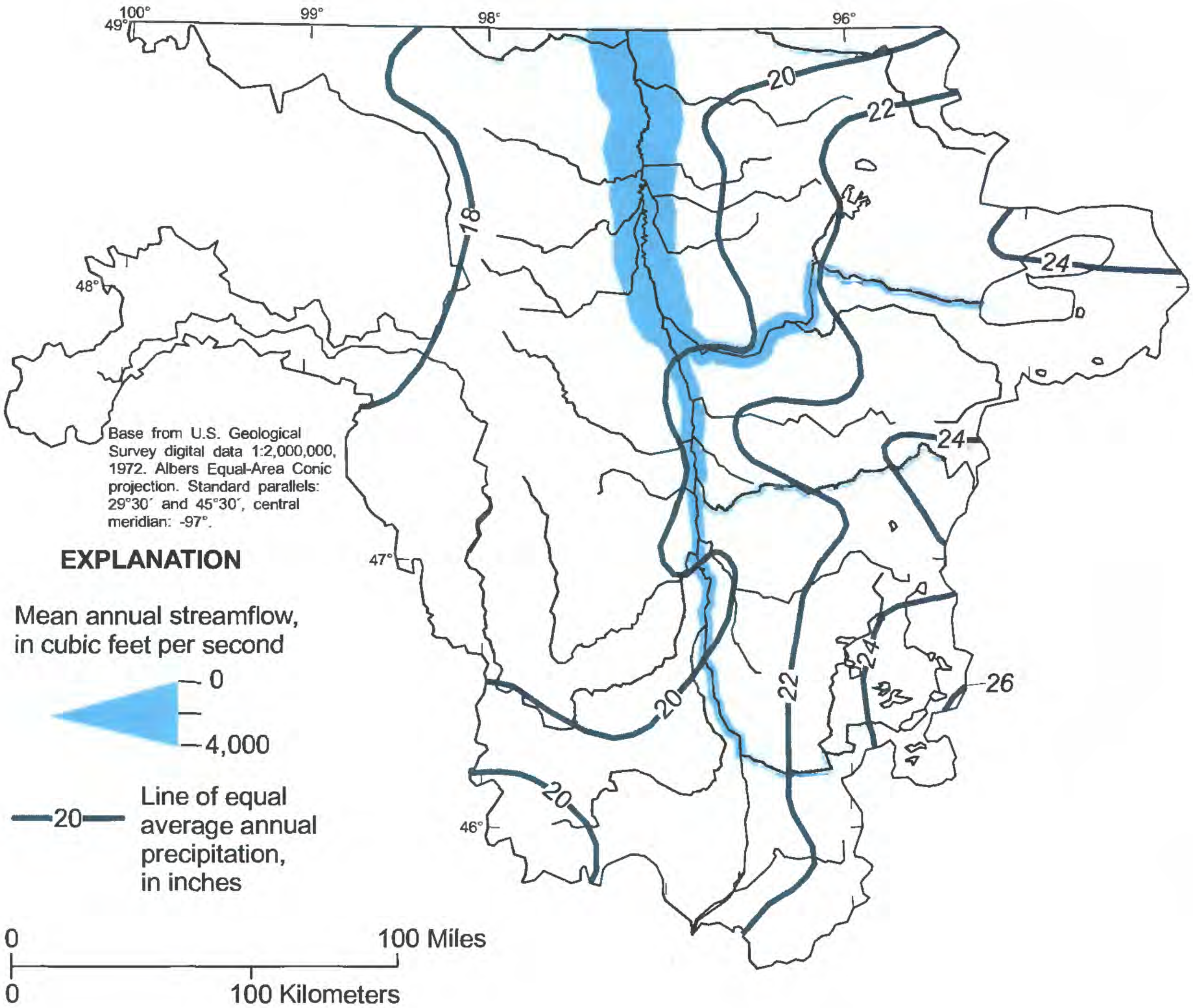


Figure 3. Average annual precipitation and streamflow in the Red River of the North Basin study unit.

1992). The rest of the study unit is comprised of grassland, forest, open water, and wetland. Cropland is most extensive in the Red River Valley Lake Plain. Small grains including wheat, oats, rye, and barley are grown throughout most of the study unit. These grains often are rotated with other crops in regional patterns based on differences in soils, topography, and climate. Corn primarily is grown in the southern part of the study unit, but small fields of corn also are planted in other parts of the study unit. Sunflowers, hay, and small grains are grown on the Drift Prairie. Sugar beets, small grains, and soybeans are grown in the Red River Valley Lake Plain. These areas, especially in the northern one-half of the study unit, are flanked by narrow bands where potatoes are rotated with small grains. In the northern Red River Valley Lake Plain, edible beans (excludes soybeans) are rotated with small grains.

Study Design

This study was designed to evaluate water quality in the entire Red River Basin study unit, so stream-sampling sites were selected to represent subbasins within the study unit while avoiding local point and nonpoint inputs. Several factors, including land cover and land use, cropping patterns, precipitation and runoff patterns, were considered during site selection. The sites commonly were located at existing stream gaging sites and sites where water-quality data had been collected historically, to help evaluate trends and to determine how data collected during this study might be different because of differences in streamflow. Most of these factors were described generally by Stoner and others (1993). Details of the study unit stratification scheme and the logic behind sampling site selection were described by Lorenz and Stoner (1996). The location of stream quality sampling sites selected for this study are shown in figure 2.

Physiography and several other factors influence the type of crops grown and the agricultural practices used in different regions. Physiographic areas were a useful way to group sampling sites based on relatively homogeneous characteristics of land cover and land use, slope, soil groups, runoff characteristics, and crops. Table 1 lists the sites routinely sampled for this study and the predominant physiographic area that each site represents. Some sites integrate multiple physiographic areas. The sites along the mainstem of the Red River are shown in downstream order and do not clearly represent any one physiographic area, although they probably are most influenced by the Red River Valley Lake Plain.

The stream sites sampled for this study are categorized by sampling strategy: basic, intensive, and synoptic. Basic sites were sampled 20–26 times, intensive sites were sampled 32–43 times, and synoptic sites (table 2) were sampled once or twice during the 3-year period. Sampling frequency at the basic and intensive sites was greatest during 1993.

Basic and intensive sites were further classified as indicator or integrator sites (Lorenz and Stoner, 1996). Indicator sites represent a particular combination of physiographic area, soil, and land cover and land use. Integrator sites receive flow from a mixture of physiographic areas, soils, and land covers and land uses. The Red River at Emerson, Manitoba, integrates flow from the entire basin, except for the Roseau River.

The basic stream sites were sampled for concentrations of dissolved major ions, dissolved and total nutrients (various forms of nitrogen and phosphorus), dissolved and suspended organic carbon, and suspended sediment. Water temperature, pH, specific conductance, alkalinity, and dissolved oxygen also were measured with each sampling. Samples were collected over a range of conditions, including under-ice, low-flow, and high-flow conditions. Special emphasis was placed on trying to collect samples during snowmelt and rainfall-runoff events when constituent transport is most variable. Streamflow was measured continuously at basic and intensive stream sites during all or most of the sample-collection program.

The intensive stream sites were sampled at about twice the frequency and for the same constituents as the basic stream sites. Additionally, many of the samples were analyzed for about 80 water-soluble pesticides. Special effort also was made to collect some samples during runoff events. In addition to continuous measurement of streamflow, water temperature and specific conductance were measured continuously at three of the intensive stream sites for at least 1 year.

Initially, four intensive-sampling sites were selected. Three of these were at sites having relatively homogeneous land use that were considered indicative of the major crops grown in the study unit. The fourth intensive-sampling site was established on the Red River at Emerson, Manitoba. To help determine the general source of pesticides found at the Red River at Emerson, Manitoba, a fifth site was sampled on the Red River of the North above Fargo, North Dakota, during 1994–95 and analyzed for the same constituents as the intensive-site samples.

Synoptic sites were sampled to evaluate how well the basic and intensive sites represented conditions in each basin and in other parts of the Red River Basin study unit (fig. 2, table 2). Within-stream synoptic sites were located along the tributary streams having intensive sites and were sampled in a downstream order during a rainfall-runoff event following agricultural-chemical application. These sites were sampled to determine how samples collected at each intensive site represented conditions along the rest of that stream. Basin-wide synoptic samples were collected from near the mouth of each of the major tributary streams in the study unit to determine whether samples collected at the intensive-sampling sites were representative of conditions across the study unit. Synoptic samples were analyzed for the same suite of constituents analyzed for the intensive-sampling sites including water-soluble pesticides.

Acknowledgments

We gratefully thank several people that contributed significantly to the coordination of sampling and collection of data contained in this report. Robert N. Woychuck from Environment Canada helped collect concurrent and split samples. Valel T. Chacko from

Table 1.—Sites routinely sampled for stream-water quality in the Red River of the North Basin study unit

[USGS, U.S. Geological Survey; dd, degree; mm, minute; ss, second; mi^2, square mile; B, basic sampling; I, intensive sampling; int, integrator; ind, indicator]

Site number (figure 2)	USGS site identification	Site name	Site type	Latitude/ longitude (dd mm ss)	Drainage area (mi^2)	Physiographic area		Land use and major crops
						Major	Minor	
1	05058700	Sheyenne River at Lisbon, N. Dak.	B, ind	46 26 49/ 07 40 44	4,490	Drift Prairie		small grains, field crops, pasture
2	05059000	Sheyenne River near Kindred, N. Dak.	B, int	46 37 54/ 97 00 01	5,000	Drift Prairie	Red River Valley Lake Plain	small grains, field crops
3	05099600	Pembina River at Walhalla, N. Dak.	B, int	48 54 50/ 97 55 00	3,200	Drift Prairie		small grains
4	05082625	Turtle River at Turtle River State Park near Arvilla, N. Dak.	I, ind	47 56 18/ 97 30 00	254	Drift Prairie	Red River Valley Lake Plain	small grains, some potatoes
5	05112000	Roseau River near Caribou, Minn.	B, ind	48 58 54/ 96 27 46	1,560	Lake-Washed Till Plain		small grains, field crops
6	05079000	Red Lake River at Crookston, Minn.	B, int	47 46 32/ 96 36 33	5,270	Lake-Washed Till Plain	Moraine	about 50 percent agriculture, small grains
7	05030150	Otter Tail River near Perham, Minn.	B, ind	46 38 34/ 95 36 15	336	Moraine		less than 50 percent agriculture; small grains, alfalfa, some potatoes
8	05046000	Otter Tail River below Orwell Dam near Fergus Falls, Minn.	B, int	46 12 35/ 96 11 05	1,740	Moraine		corn, alfalfa, small grains
9	05062500	Wild Rice River at Twin Valley, Minn.	I, ind	47 16 00/ 96 14 40	929	Moraine		about 50 percent agriculture, small grains
10	05085900	Snake River above Alvarado, Minn.	I, ind	48 10 27/ 96 59 55	218	Red River Valley Lake Plain		small grains
11	05051300	Bois de Sioux River near Doran, Minn.	B, ind	46 09 08/ 96 34 44	1,550	Red River Valley Lake Plain	Drift Prairie	corn, soybeans, small grains
12	05053800	Red River of the North above Fargo, N. Dak.	I, int	46 48 14/ 96 47 47	6,610	mix (several)	Red River Valley Lake Plain	small grains, corn, soybeans
13	05064500	Red River of the North at Halstad, Minn.	B, int	47 21 10/ 96 50 50	17,300	mix (several)	Red River Valley Lake Plain	small grains
14	05082500	Red River of the North at Grand Forks, N. Dak.	B, int	47 56 34/ 97 03 10	25,700	mix (several)	Red River Valley Lake Plain	small grains
15	05102500	Red River of the North at Emerson, Man.	I, int	49 00 30/ 97 12 40	35,600	mix (several)	Red River Valley Lake Plain	small grains

Table 2.—Basinwide and instream synoptic sampling sites

[USGS, U.S. Geological Survey; dd, degree; mm, minute; ss, second; map letters refer to figure 2. Basinwide synoptic sites also include all sites shown on table 1. Instream synoptic sites also include intensive sites from table 1.]

Site name	Site identification (figure 2)	USGS site identification	Latitude (dd mm ss)	Longitude (dd mm ss)
Basinwide synoptic sites				
Forest River near Warsaw, N. Dak.	e	05085080	48 17 44	97 11 55
North Branch Two Rivers near Northcote, Minn.	g	05097500	48 49 06	97 03 11
Two Rivers below Hallock, Minn.	f	05095500	48 46 50	97 02 25
Goose River at Hillsboro, N. Dak.	d	05066500	47 24 34	97 03 39
Mustinka River above Wheaton, Minn.	a	05049000	45 49 15	96 29 25
Wild Rice River near Abercrombie, N. Dak.	b	05053000	46 28 05	96 47 00
Buffalo River near mouth at Georgetown, Minn.	c	05062100	47 04 43	96 47 50
Instream synoptic sites				
South Branch Turtle River below dam near Larimore, N. Dak.	h	475611097351801	47 56 11	97 35 18
Turtle River near Mekinock, N. Dak.	k	05082650	48 00 51	97 23 05
North Branch Turtle River near Mccanna, N. Dak.	i	480137097411501	48 01 37	97 41 15
North Branch Turtle River near Larimore, N. Dak.	j	475650097350401	47 56 50	97 35 04
Turtle River at mouth near Manvel, N. Dak.	l	05083100	48 10 28	97 08 52
Snake River near Radium, Minn.	m	481311096345501	48 12 45	96 36 32
Snake River above Middle River near Big Woods, Minn.	n	05086500	48 21 30	97 04 00
Snake River near mouth near Big Woods, Minn.	o	05087600	48 24 42	97 06 26
White Earth River near Mahnomen, Minn.	p	05062435	47 18 53	95 55 58
Wild Rice River near Mahnomen, Minn.	q	471931095564601	47 19 31	95 56 46
Wild Rice River near Ada, Minn.	r	05063000	47 15 50	96 30 00
Wild Rice River at Hendrum, Minn.	s	05064000	47 16 05	96 47 50
Wild Rice River near Abercrombie, N. Dak.	b	05053000	46 28 05	96 47 00
Red River of the North near Abercrombie, N. Dak.	t	462959096441401	46 29 59	96 44 14

Environment Canada arranged for analysis of those samples. Members of the Red River National Water-Quality Assessment Program Liaison Committee provided valuable local and regional input and concurrence in selecting sampling sites and in interpreting some of the study findings. In particular, we thank Bruce Seelig, North Dakota State University Extension Service, and Gerald Van Amberg, Concordia College, Moorhead, Minnesota, for their review comments, which improved the quality of this report. Finally, Kelvin L. Boespflug of the U.S. Geological Survey dedicated extraordinary effort and time to this study and collected a majority of the data presented here, often working under adverse conditions. He is responsible for the high quality of samples collected.

Methods

Most of the data discussed in this report were collected and analyzed by the U.S. Geological Survey (USGS) for the NAWQA Program. Supplementary data were collected for the National Stream Quality Accounting Network (NASQAN) Program. The NASQAN data are considered comparable to the NAWQA data because data-collection, analytical methods, and the analytes determined from samples usually were similar.

Samples were collected, processed, and preserved; and field measurements generally were made following the guidelines and equipment specified in Shelton (1994) and Sandstrom (1995). Generally, samples from all sites were collected from multiple vertical sections using a depth-integrating suspended-sediment sampler. Deviations from those guidelines, such as collection of "grab" samples, sometimes were necessary because of challenging field conditions.

When pesticides were to be analyzed, samples for all constituents were collected from multiple vertical sections using an epoxy-coated D-77 or DH-81 sampler (Ward and Harr, 1990) with a Teflon bottle and Teflon nozzle. Samples from each vertical section were composited and split into separate sample bottles using a Teflon cone splitter. When stream velocities were slow (considerably less than 2 ft/s) or under ice cover, samples were collected using a glass bottle in a weighted holder that was plunged into the water to sample as much of each vertical section as possible.

When pesticides were not to be analyzed, it was more common to use a polypropylene bottle and nozzle to collect the sample than to use the Teflon equipment because that equipment required additional cleaning. Also, a D-74 depth-integrating suspended-sediment sampler often was used to collect the sample in a one-quart or one-pint glass bottle. During most of 1993, multiple vertical-section samples for all constituents, except suspended sediment, were composited in and split from a polypropylene churn splitter; suspended-sediment samples were collected directly into the sample bottle using a D-74, DH-59, DH-48, or DH-81 sampler. Since October 1993, samples to be analyzed for all constituents except pesticides and organic carbon were composited and split using a polycarbonate or Teflon cone splitter (Capel and Larson, 1996).

Samples to be analyzed for dissolved constituents were filtered in the field within two hours of collection. Each nutrient and major ion sample was filtered using a 142-millimeter (mm) diameter, 0.45-micrometer (µm) pore size nitrocellulose filter on a polycarbonate filter holder, or a polypropylene encapsulated filter containing a polyether-sulfone medium having a 0.45-µm pore size (Gelman Sciences, #12175). The encapsulated filter has a much larger effective surface area (600 cm^2) than the 142-mm diameter filter. A peristaltic pump with Tygon and polypropylene tubing forced water through these filters. Pesticide samples were filtered in the field or laboratory through a 142-mm diameter, 0.7-µm baked glass-fiber filter on an aluminum filter holder using the method outlined by Sandstrom (1995).

Samples for dissolved and suspended organic carbon (DOC and SOC) were collected separately from other samples to avoid contamination from methanol and detergent used to clean pesticide sampling equipment. A weighted, open-glass bottle was plunged into the centroid of flow to collect the sample water. Samples were nitrogen-pressure filtered using a stainless-steel filter assembly fitted with a 47-mm diameter, 0.45-µm pore-size, silver filter (Osmonics). The filtrate was chilled and analyzed for DOC. The material retained on the filter was chilled and analyzed for SOC.

Samples were preserved immediately after collection and processing. Before October 1994, nutrient samples were preserved using mercuric chloride (a biocide) and chilling; thereafter, nutrient samples were preserved by chilling only. Pesticide samples were preserved by chilling and extracting onto a solid-phase material in the field or in the laboratory. The pesticides stabilized on the solid phase were eluted in the laboratory for subsequent analysis.

With occasional exception, all samples were analyzed for concentrations of dissolved major ions, dissolved and total nutrients, and suspended sediment. The suspended sediment was further analyzed to determine how much was finer than sand (less than 63 µm). DOC and SOC concentrations were determined on slightly more than one-half of the samples. Pesticides were analyzed in most samples from the intensive stream sites and in most of the synoptic samples.

Table 3 lists the nutrients and major ions analyzed for this study, using the methods of Fishman (1993), Guy (1969), Patton and Truitt (1992), and Wershaw and others (1987). Two methods were used for the analysis of dissolved (0.7-µm-filterable) pesticides. Table 4 lists pesticides determined by gas chromatography with mass spectroscopy (GC/MS) (Zaugg and others, 1995; Lindley and others, 1996). Table 5 lists pesticides determined by high-performance liquid chromatography (HPLC) (Werner and others, 1996). Selected quality-control data are discussed later in this report.

Table 3.—Nutrients and major ions, with a summary of selected stream-water and quality-control data

[MDL, method detection limit; N, number of samples; N≥MDL, number of samples with concentrations equal to or greater than the MDL; CV, coefficient of variation; <, less than. All concentrations in milligrams per liter. For all nitrogen forms, concentrations in milligrams per liter as nitrogen; for all phosphorus forms, concentrations in milligrams per liter as phosphorus.]

		Stream samples				Blank samples			Replicate samples		
Constituent	MDL	Number of samples	Minimum concentration	10th percentile concentration	Maximum concentration	Number of samples	N≥MDL	Maximum concentration	Number of replicate samples	Number of replicate sets	Pooled CV
A. Dissolved nutrients											
Ammonia nitrogen	0.01	511	<0.01	0.02	1.60	7	3	0.03	31	15	[1]12.6
Nitrite nitrogen	.01	511	<.01	<.01	.31	7	0	<.01	12	6	40.4
Ammonia plus organic nitrogen	.20	496	.30	.50	3.1	6	0	<.20	35	17	11.3
Nitrite plus nitrate nitrogen	.05	511	<.05	.05	5.8	7	2	.08	27	13	[2]17.0
Dissolved phosphorus	.01	510	<.01	<.01	.81	6	2	.01	33	16	9.2
Orthophosphate	.01	511	<.01	.01	.74	7	0	<.01	29	14	7.5
B. Total (unfiltered water) nutrients											
Ammonia plus organic nitrogen	.20	529	<.20	.60	3.3	7	0	<.20	37	18	9.4
total phosphorus	.01	529	<.01	.03	1.7	7	0	<.01	37	18	10.5
C. Dissolved major ions and silica											
Calcium	.02	457	26	39	220	7	6	1.8	26	13	1.8
Magnesium	.01	457	9.3	18	140	7	3	.73	26	13	2.9
Sodium	.20	457	1.7	4.9	530	7	4	1.3	26	13	2.9
Potassium	.10	457	.10	2.6	29	7	0	<.10	26	13	2.2
Chloride	.10	457	1.5	3.9	740	7	2	.10	28	14	2.6
Sulfate (as SO_4)	.10	458	1.0	12	790	7	2	.70	28	14	.9
Fluoride	.10	457	<.10	.10	.60	7	1	.10	26	13	0
Silica (as SiO_2)	.01	455	.52	8.1	41	7	5	.25	26	13	1.7

[1]For ammonia nitrogen concentrations greater than or equal to five times the MDL, the pooled CV was 6.9 (based on nine sets of duplicate samples).

[2]For dissolved ammonia plus organic nitrogen concentrations greater than or equal to five times the MDL, the pooled CV was 4.9 (based on four sets of duplicate samples).

Table 4.—Pesticides measured and method detection limits (MDL) for samples analyzed by gas chromatography/mass spectroscopy (GC/MS)

[units in micrograms per liter; H, herbicide; I, insecticide; M, metabolite; --, no data]

Compound name	Type	MDL	Mean percent recovery	Coefficient of variation (percent)	Compound name	Type	MDL	Mean percent recovery	Coefficient of variation (percent)
Acetochlor	H	0.002	105	2.3	Malathion	I	0.005	93.9	22.7
Alachlor	H	.002	101	16.9	Metolachlor	H	.002	109	1.3
Atrazine, desethyl-[1]	M	.002	43.4	35.4	Metribuzin	H	.004	87.3	11.4
Atrazine	H	.001	95.2	5.5	Molinate	H	.004	92.9	11.9
Azinphos-methyl[1]	I	.001	287	44.4	Napropamide	H	.003	109	19.6
Benfluralin	H	.002	81.2	23.7	Parathion, ethyl-	I	.004	--	--
Butylate	H	.002	95.8	9.0	Parathion, methyl-	I	.006	--	--
Carbaryl[1]	I	.003	210	47.4	Pebulate	H	.004	91.2	11.3
Carbofuran[1]	I	.003	157	27.5	Pendimethalin	H	.004	91.1	31.5
Chlorpyrifos	I	.004	88.3	21.3	Permethrin, *cis*-	I	.005	20.4	91.4
Cyanazine	H	.004	122	17.3	Phorate	I	.002	56.1	32.6
Dacthal (DCPA)	H	.002	108	13.4	Pronamide	H	.003	99.7	15.9
p,p'-DDE	M	.006	48.7	40.5	Prometon	H	.018	98.0	18.8
Diazinon	I	.002	98.8	15.6	Propachlor	H	.007	105	9.1
Dieldrin	I	.001	92.6	24.6	Propanil	H	.004	103	24.1
2,6-diethylaniline	M	.003	86.0	10.0	Propargite	I	.013	95.5	34.8
Disulfoton	I	.017	59.0	77.3	Simazine	H	.005	103	17.3
EPTC	H	.002	93.7	10.0	Thiobencarb	H	.002	100	15.1
Ethalfluralin	H	.004	121	26.6	Tebuthiuron	H	.010	111	23.1
Ethoprop	I	.003	110	15.9	Terbacil[1]	H	.007	113	24.6
Fonofos	I	.003	93.9	15.5	Terbufos	I	.013	83.6	18.0
α-HCH	M	.002	96.3	9.5	Triallate	H	.001	96.9	13.0
γ-HCH (lindane)	I	.004	103	17.0	Trifluralin	H	.002	82.2	22.1
Linuron	H	.002	127	17.5					

[1]Concentrations of these compounds are reported as estimated. See Zaugg and others, 1995.

Annual loads for selected constituents were estimated using a multiple regression approach, a U.S. Geological Survey program called Estimator (G.E. Schwarz, U.S. Geological Survey, written commun., 1996; Cohn and others, 1992a; Cohn and others, 1992b). The general approach was to model constituent concentrations or instantaneous loads (the product of streamflow and the measured constituent concentration) as a function of streamflow and, for some constituents, season. With these relations the program is used to calculate estimated daily loads using a mean-daily streamflow. Adjusted maximum likelihood estimates (AMLE) (Cohn and others, 1992b) were used in the program to assign values to censored (below the detection level) data.

The instructions for using Estimator (G. Baier, T. Cohn, and E. Gilroy, U.S. Geological Survey, written commun., 1995) note a "rule of thumb" of at least 25 observations per year for 2 years for load estimation. Although we had fewer samples for all the sampling sites during 1993–95, we feel the samples adequately represent conditions during this period, including all seasons, low-flow, and high-flow conditions.

Many pesticide data were below method detection limits (MDL). Occasionally, poor performance and/or recovery during analysis caused some pesticide concentrations to be reported as estimated. For this report, estimated values generally were treated as actual values. Censored values were usually set

Table 5.—Pesticides measured and method detection limits (MDL) for samples analyzed by high performance liquid chromatography (HPLC)

[units in micrograms per liter; H, herbicide: I, insecticide; M, metabolite; F, fungicide; --, no data]

Compound	Type	MDL	Mean recovery (percent)	Coefficient of variation (percent)	Compound	Type	MDL	Mean recovery (percent)	Coefficient of variation (percent)
Acifluorfen	H	0.035	68.1	46.6	Esfenvalerate[2]	I	0.019	41.7	17.7
Aldicarb	I	.016	36.0	46.2	Fenuron	H	.013	68.6	15.1
Aldicarb sulfone[1]	M	.016	0	--	Fluometuron	H	.035	69.0	18.7
Aldicarb sulfoxide[1]	M	.021	24.6	36.1	Carbofuran,3-hydroxy[1]	M	.014	61.6	--
Bentazon	H	.014	63.0	64.9	Linuron	H	.018	66.1	22.5
Bromacil	H	.035	75.7	14.4	MCPA	H	.050	47.8	46.3
Bromoxynil	H	.035	73.1	17.9	MCPB	H	.035	85.1	5.4
Carbaryl[1]	I	.008	25.8	109	Methiocarb[1]	I	.026	32.3	100
Carbofuran[1]	I	.028	54.7	45.3	Methomyl	I	.017	72.1	3.9
Clopyralid	H	.050	--	--	1-Naphthol[1,2]	I	.007	1.5	149
Chloramben	H	.011	62.6	18.4	Neburon	H	.015	48.5	58.7
Chlorothalonil[1,2]	F	.035	13.2	174	Norflurazon	H	.024	77.1	19.9
2,4-D	H	.035	51.4	39.6	Oryzalin	H	.019	85.4	7.0
Dacthal (DCPA)	H	.017	32.7	88.4	Oxamyl[1]	I	.018	4.4	200
2,4-DB	H	.035	48.2	77.0	Picloram[1]	H	.050	37.3	51.7
Dicamba[3]	H	.035	4.9	117	Propham	H	.035	67.6	18.7
Dichlobenil[2]	H	.020	58.0	14.2	Propoxur	I	.035	42.1	42.6
Dichlorprop	H	.032	68.4	45.5	Silvex	H	.021	59.8	42.8
Dinoseb	H	.035	71.8	19.7	2,4,5-T	I	.035	70.0	21.4
Diuron	H	.020	59.8	27.9	Triclopyr[1]	H	.050	74.5	29.7
DNOC[2]	H,I	.035	81.5	16.3					

[1]Analyte is heat and light sensitive and, therefore, susceptible to degradation. This may result in low recovery and precision (NAWQA/NWQL Quality Assurance Committee for the Schedule 2050/2051 Pesticide Analysis Method, written commun., 1995).

[2]Concentrations of these compounds are reported as estimated. See Werner and others, 1996.

[3]Recovery much lower than that reported for dicamba by Werner and others, 1996.

equal to the detection level, with exceptions noted in the text or illustrations (a notable exception is calculation of loads).

Quality Control

Replicate samples, field-equipment blank samples, and field matrix spike samples were processed through sampling equipment to assess the variability and bias of water-quality data (tables 3-5). In addition to quality-control samples prepared in the field, numerous quality-control tests were run internally at the laboratory, as described by Pritt and Raese (1995).

Quality Control Sample Types and Data Analysis

Field-blank samples were collected using water that had undetectable concentrations of the analytes of interest. This "blank" water was processed through all sampling equipment, collected, and analyzed by the laboratory, in a similar manner to the processing of stream water. Data from blank samples were used to determine the extent of contamination (a positive bias) potentially introduced during sampling, sample processing and shipping, and analysis. Blank water for inorganic constituents was distilled, deionized water from the U.S. Geological Survey (USGS) Ocala, Florida laboratory. Blank water for organic constituents was Baker Analyzed HPLC Grade (J.T. Baker Company, Phillipsburg, New Jersey) water from lots purchased and assayed by the USGS National Water Quality Laboratory (NWQL), Arvada, Colorado.

Replicate samples are several samples (usually 2 or 3) collected in such a way that they are nearly identical in composition. In this study, replicates usually were collected as sample splits, where one stream-water sample was split into replicate samples. Some replicate samples were sequential, where the stream was sampled two or more times within a short time span. Data from the analysis of replicate samples are used to assess variability of the overall process, including sampling (sequential replicates only), sample processing, and analysis.

Replicate-sample data were reviewed by calculating a coefficient of variation (CV = (standard deviation/mean) X 100) for each analyte for each set of replicates. To summarize the variability of each analyte, pooled CVs were calculated as the square root of the weighted mean (weighted to degrees of freedom of each replicate set) of the squared CVs. Data less than the MDL were not included in this analysis.

For many analytes, CVs bore no relation to concentration, and a single, pooled CV was calculated for summarizing data variability. For some analytes, CVs were highly variable at low concentrations, but relatively low and constant at higher concentrations. For these analytes, replicate data were split into low-concentration (mean was less than 5 or 10 times the minimum detection limit, or MDL) and high-concentration (mean was greater than or equal to 5 or 10 times the MDL) groups. Separate pooled CVs were calculated for each group. The NWQL commonly rounds low-concentration data to one significant figure, which artificially increases or decreases the variability in a set of replicates.

A matrix spike is a stream-water sample to which known amounts of target analytes have been added. Matrix spiked samples were used to assess the recovery of pesticides in stream-water samples. Possible sources of bias are degradation of analytes, interference due to matrix effects (such as dissolved organic matter affecting the recovery of organic analytes), and bias inherent in the laboratory analysis.

Matrix spike data for each pesticide were analyzed in several steps. First, if the pesticide was detected in the paired, unspiked stream-water samples, the mean stream-water concentration was subtracted from the spiked-sample concentration. Next, the concentration was converted to mass of recovered pesticide, divided by mass of added pesticide, and multiplied by 100. Spike-recovery calculations are more accurate if the analyte is at low concentration (or less than MDL) in the ambient stream water. If the amount of analyte in the ambient sample approaches or exceeds the amount added to spiked stream-water samples, the spike-recovery result tends to be masked by uncertainty (imprecision) of the data.

Surrogates are chemicals that are added to each sample in a known amount to provide a means of assessing analytical recovery for each analysis. Surrogates should have similar chemical properties to the analytes of interest, but should not interfere with quantitation of the analytes of interest. In this study, surrogates were used only for the pesticide analytical schedules. Surrogates were added to all pesticide samples immediately before solid-phase extraction, as outlined by Zaugg and others (1995). Surrogate data are reported as percent recovery of added surrogate.

Summary of Quality-Control Data

Quality-control data were summarized to assess likelihood of contamination of samples and the accuracy and reproducibility of the data. The quality-control data indicate that data for most constituents were fairly accurate (low bias and variability). However, data for some pesticides were found to be either imprecise, or substantially biased, or both.

Nutrients and major ions

Infrequent, low-level (near or at MDLs) detection of nitrite plus nitrate, ammonia, and total phosphorus in blank samples indicated little potential for contamination of stream-water samples (table 3). Ammonia nitrogen was detected at low levels (0.02 mg/L as nitrogen) in two blank samples. Ammonia often is detected at low concentrations in laboratory blanks because it often is present as a vapor in laboratory air and readily dissolves in sample water.

There were between 5 and 15 sets of replicates for each nutrient species for which concentrations were greater than the reporting limits. Pooled coefficients of variation were less than 17 percent for most of the analytes. Nitrite concentrations, when detected, were always near the detection limit and were variable on a relative basis, although absolute differences in replicate-sample concentrations were small. Coefficients of variation for dissolved ammonia and ammonia plus organic nitrogen were substantially lower at concentrations greater than 5 times the MDL than at lower concentrations (table 3A).

For all major ions except fluoride, the maximum concentration detected in blank samples was less than the minimum concentration detected in ambient stream-water samples (table 3C). Thus, the sampling and analysis procedures did not impart significant levels of contamination of most major ions. Fluoride was detected (at its MDL, 0.1 mg/L) in one of seven blank samples. Thus, low-level (0.10 mg/L) fluoride detections in stream water are potentially influenced by infrequent, low-level contamination. Major ion data were highly reproducible, with pooled CVs of 0–2.9 percent for all analytes (table 3C). DOC contamination from cleaning the sampling equipment with detergent and methanol, was discovered early in this study. The sampling procedure was changed in mid-1993 to prevent contact of DOC-sample water with equipment that had contacted detergent and/or methanol. Subsequent to this change, only one DOC blank sample was collected, yielding a DOC concentration of 0.3 mg/L. Stream-water samples from this study always had DOC concentrations at least tenfold higher than this. However, more DOC blanks are needed to adequately assess data quality.

Suspended sediment

Sixteen sets of sequential, replicate suspended-sediment samples were collected during this study. Most of these samples were intended to determine how suspended-sediment concentrations differed between cone-split samples and samples collected using a separate, depth-integrating suspended-sediment sampler. The accuracy and reproducibility of samples split using the cone-splitter are described by Capel and Larson (1996). The pooled CV for replicate suspended-sediment samples was 15.7 and ranged from 0.3 to 31.4. Only three of the samples had CVs higher than 13. Excluding these high-CV replicate sets, the pooled CV was 7.9.

Pesticides analyzed by gas chromatography/mass spectroscopy

Only one of five equipment blank samples showed low-level contamination of atrazine (0.005 µg/L) and simazine (0.007 µg/L); thus, the potential for sample contamination was quite low.

Most pesticide concentrations were typically near or less than MDLs in replicate environmental samples. Pooled CVs for replicate pesticide analyses were typically in the range of 12 to 20 percent for the few samples and compounds that were detected.

Target concentrations of pesticides in stream-water matrix spike samples for the GC/MS method were about 0.1 µg/L. Mean recoveries of most analytes were in the range of 78 to 130 percent, with most mean recoveries fairly close to 100 percent (table 4). Exceptions were desethylatrazine, *p,p'*-DDE, disulfoton, *cis*-permethrin, and phorate, all of which had low recoveries. Also, azinphos-methyl, carbaryl, and carbofuran had high and variable recoveries.

The reproducibility of spike recoveries was good for most analytes (table 4). CVs were less than 10 percent for several analytes and less than 40 percent for most analytes. Exceptions were azinphos-methyl, carbaryl, *p,p'*-DDE, disulfoton, and *cis*-permethrin. In the report describing this method, Zaugg and others (1995, p. 35) reported highly variable recoveries for carbofuran, carbaryl, terbacil (which had good recoveries in spike data from this study), and azinphos-methyl. Reported concentrations of these compounds are "estimated" and are not suitable for quantitative purposes.

Pesticides analyzed by high-performance liquid chromatography

No pesticides from this analytical method were detected in blank samples.Thus, the potential for sample contamination was low. Because of low-level, infrequent detections in replicate samples, variability was assessed only with spike-recovery data.

Target concentrations for each analyte in stream-water matrix spikes were about 1 µg/L. Recoveries tended to be lower and more variable for this method than the GC/MS method. Because some data were deleted due to analytical problems, and some spike solutions did not contain all analytes for this method, spike-recovery data for this study were limited for some analytes. Mean recoveries were based on one to eight spiked stream-water samples for each analyte (table 5). Mean recoveries were greater than 50 percent, with CVs of less than 25 percent for fifteen of the pesticides. Mean recoveries were greater than 50 percent, with CVs of 25 to 50 percent, for seven pesticides. Pesticides having lower mean recoveries and/or higher CVs included aldicarb, aldicarb sulfone, aldicarb sulfoxide, bentazon, carbaryl, chlorothalonil, dacthal, 2,4-DB, dicamba, esfenvalerate, MCPA, methiocarb, 1-naphthol, neburon, oxamyl, picloram, and propoxur.

From analysis of a broader data set of laboratory-control spiked samples and field-submitted spiked samples, the NWQL found that recoveries usually were fairly good, but substantially more variable for the HPLC method than for the GC/MS method (Werner and others, 1996; U.S. Geological Survey NAWQA/NWQL Quality Assurance Committee for Schedule 2050/2051 Pesticide Method, written commun., Dec. 1, 1995). Method performance varied by analyte and by time period. During some time periods, recoveries of certain analytes were highly variable, including recoveries of zero percent for a small percentage (typically less than 5 percent) of spiked samples. The NWQL considers analytical data for compounds that had low and/or highly variable recoveries to be appropriate only for qualitative purposes. These compounds include 1-naphthol, chlorthalonil, dichlobenil, DNOC, and esfenvalerate. In addition, aldicarb sulfone, aldicarb sulfoxide, carbaryl, MCPB, methiocarb, and oxamyl had low and/or highly variable recoveries during some time periods during this study.

The main concern over low recoveries is that of low-biased data, including "false negatives" (compounds that are in a sample at concentrations greater than the detection limit, but which fail to be detected because of analytical problems). Concentration ranges and frequencies of detection are potentially low-biased for such compounds, although the extent to which this is a problem cannot be determined because "true" concentrations are unknown. The problem of "false negatives" is likely to be much more widespread than the opposite situation of "false positives" (a detection is reported when the "true" concentration is less than the MDL). The NWQL is confident that when a compound is detected at concentrations greater than the detection limit, the compound has been properly identified and quantified.

Streamflow and Major Ions

Streamflow (and runoff) was higher than normal during data collection for this study, particularly during the summers of 1993 and 1994 and could affect water-quality data collected for this study. Streamflow at the Red River at Emerson, Manitoba, represents most streams in the Red River Basin study unit, although it has much higher streamflow and encompasses streamflow from most of the study unit. During 1913–95 the annual mean streamflow was about 3,570 ft^3/s. During 1993 and 1994 the annual mean streamflow was 7,000 ft^3/s and 6,370 ft^3/s, respectively, making the annual mean streamflow for these years the 7th and 11th highest on record. Figure 4 shows the annual hydrographs from 1993 through 1995 compared to historical data for the Red River at Emerson, Manitoba. Snowmelt runoff in 1993 and 1994 that occurred during late March or early April was fairly typical. In 1995, snowmelt runoff was much higher than normal because soils were saturated from at least 2 years of above-normal precipitation and the melting and runoff of a deeper than normal winter snow pack, followed by spring rains falling on saturated ground. Following snowmelt runoff, it is typical for flows to be sustained or increase slightly during May and June as rains fall on soil that is still moist. In an average year, streamflow would continue to decline through the summer as rainfall amounts decrease and evapotranspiration reduces soil moisture and runoff potential. In 1993, persistent rainfall during June and into July caused streamflow to increase. Continued rainfall after mid-July and into August caused streamflow to increase substantially more and to greatly exceed the 1993 snowmelt runoff and historical monthly records for August and September. The monthly mean streamflow during August 1993 was 3.7 times the previous record and 12 times the average monthly mean streamflow. Monthly mean streamflow during September 1993 was 5.7 times the average monthly mean streamflow. An unusually wet summer also occurred in 1994, but the runoff was not as great as in 1993. Monthly mean streamflow during July 1994 was the third highest on record and was 3.3 times average. Streamflow also was above average during July 1995, but not as much as in the previous 2 years. These unusually high streamflows are particularly important because they occurred during the growing season after agricultural chemicals had been applied.

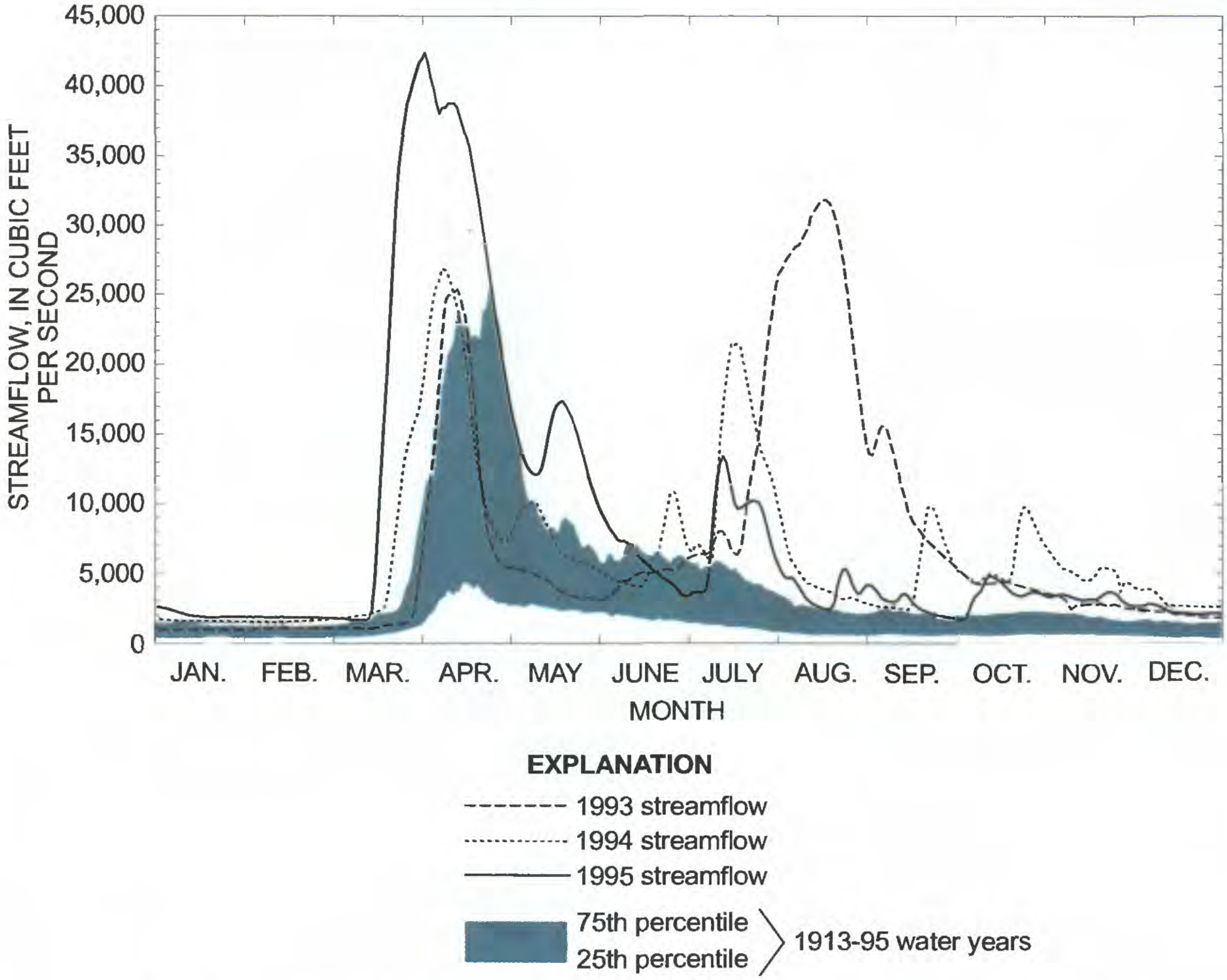


Figure 4. Historical and recent annual streamflow in the Red River of the North at Emerson, Manitoba.

Figure 5 shows how the mean annual streamflow for each of the 1993–95 calendar years compared to the distribution of historical mean annual streamflows for those sampling sites or nearby streamflow sites having historical data. At most sites, the streamflow during all 3-calendar years of data collection exceeded the 90th percentile of historical mean annual streamflows. This was particularly evident for southern and western streams, where runoff was especially large. Mean annual flows during 1993–95 in the northern streams, including the Red Lake, Roseau, Turtle, and Pembina Rivers, generally were well above the historical median, but exceeded the 90th percentile in no more than one of the 3 years. The Forest River is shown on figure 5 for comparison with the Turtle River site.

The ionic chemistry (major cations and anions) of streams in the Red River Basin study unit will not be discussed in detail in this report. However, an overview of ionic chemistry can help explain differences in physiographic areas. Figure 6 is a Piper diagram graphically showing the ionic composition of streams sampled for this study based on median ion concentrations. All the streams have relatively similar cationic compositions with calcium and magnesium being the predominant cations. Streams draining the Drift Prairie (sites 1–4) tend to have a larger proportion of sodium.

Although chloride comprised less that 10 percent of the anions in all streams in the Red River Basin study unit, the other anions showed marked differences. In streams draining the Lake-Washed Till Plain and Moraine (sites 5–9) more than 80 percent of the anions were bicarbonate (carbonate was usually negligible); in the Otter Tail (sites 7 and 8) and Roseau (site 5) Rivers nearly 90 percent or more of the anions

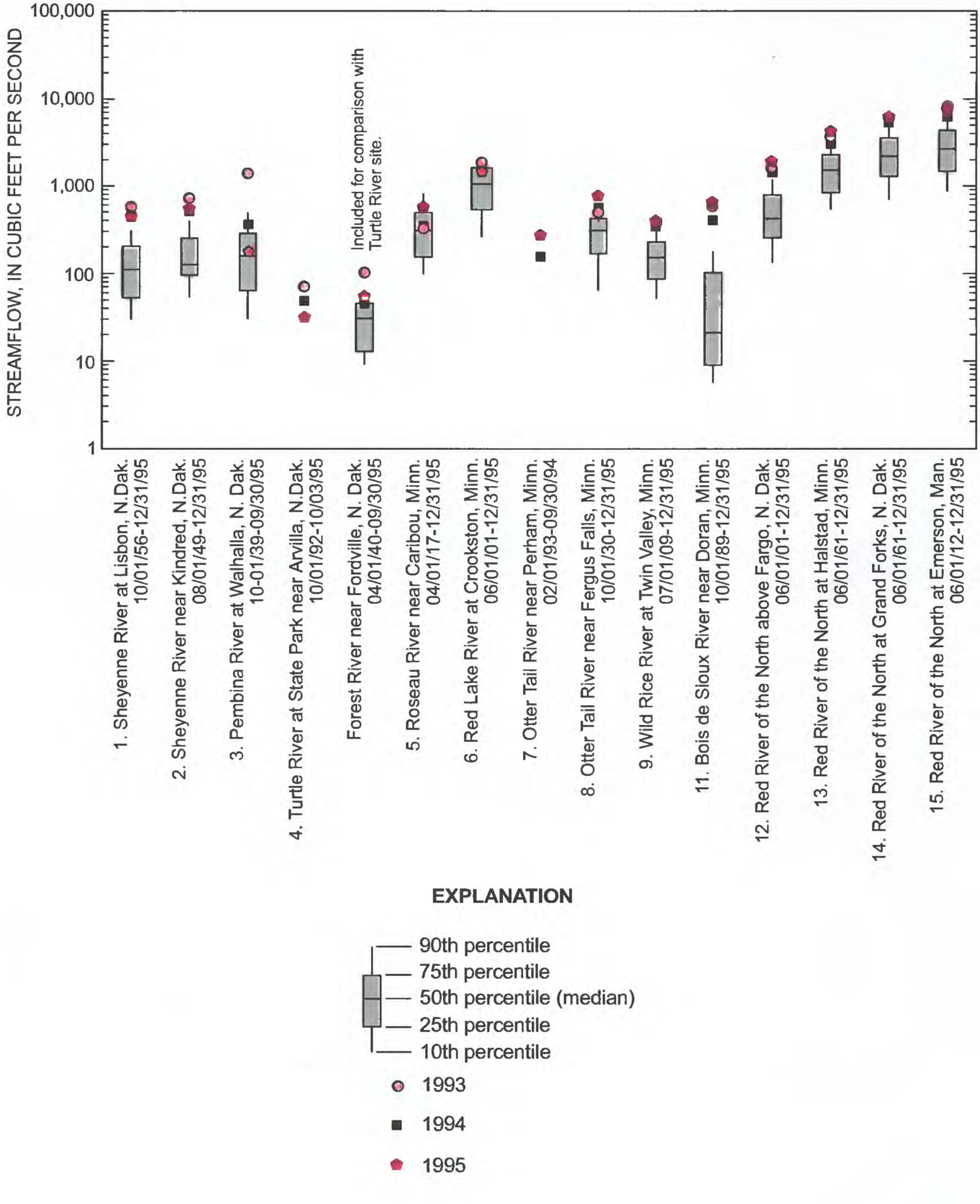


Figure 5. Distribution of mean annual streamflow in the Red River of the North Basin study unit. (Sites referenced on figure 2)

were bicarbonate. The Snake River (site 10), primarily draining the Red River Valley Lake Plain, had a considerably higher proportion of sulfate than other eastern streams. Sulfate comprised about 40 percent of the anions for streams draining the Drift Prairie. In the Bois de Sioux River (site 11) sulfate comprised more than 60 percent of the anions. The Red River (sites 12–15) exhibited a mixture of waters from various physiographic area and are grouped closely on the diagram relative to other streams (fig. 6).

The grouping of sites by physiographic area is evident when the cations and anions from the trilinear plots of the Piper diagram are projected onto the quadralinear plot (fig. 6). The waters from the two eastern physiographic areas are similar. The Bois de Sioux River (site 11) has the most distinct ionic composition. The Red River (sites 12–15) ionic composition reflects a mixture of all the tributaries. Although the Red River sites are closely grouped, the Red River at Grand Forks (site 14) shows the influence of the Red Lake River (site 6), which contributes a significant amount (about 1/3) of the streamflow at the Red River at Grand Forks.

The dissolved-solids concentrations for each of the sampling sites varied by physiographic area. The streams draining the Drift Prairie had the highest concentrations of dissolved solids, and the Bois de Sioux River had a mean of about 800 mg/L of dissolved solids. Lake-Washed Till Plain and Moraine streams had much lower concentrations; the upstream part of the Otter Tail River had a mean of about 200 mg/L dissolved solids. The Red River at Emerson, Manitoba, had a mean concentration of 419 mg/L, which was not substantially different from the historical mean of 406 mg/L reported by Stoner and others (1993).

Nutrients, Suspended Sediment, and Pesticides in Streams

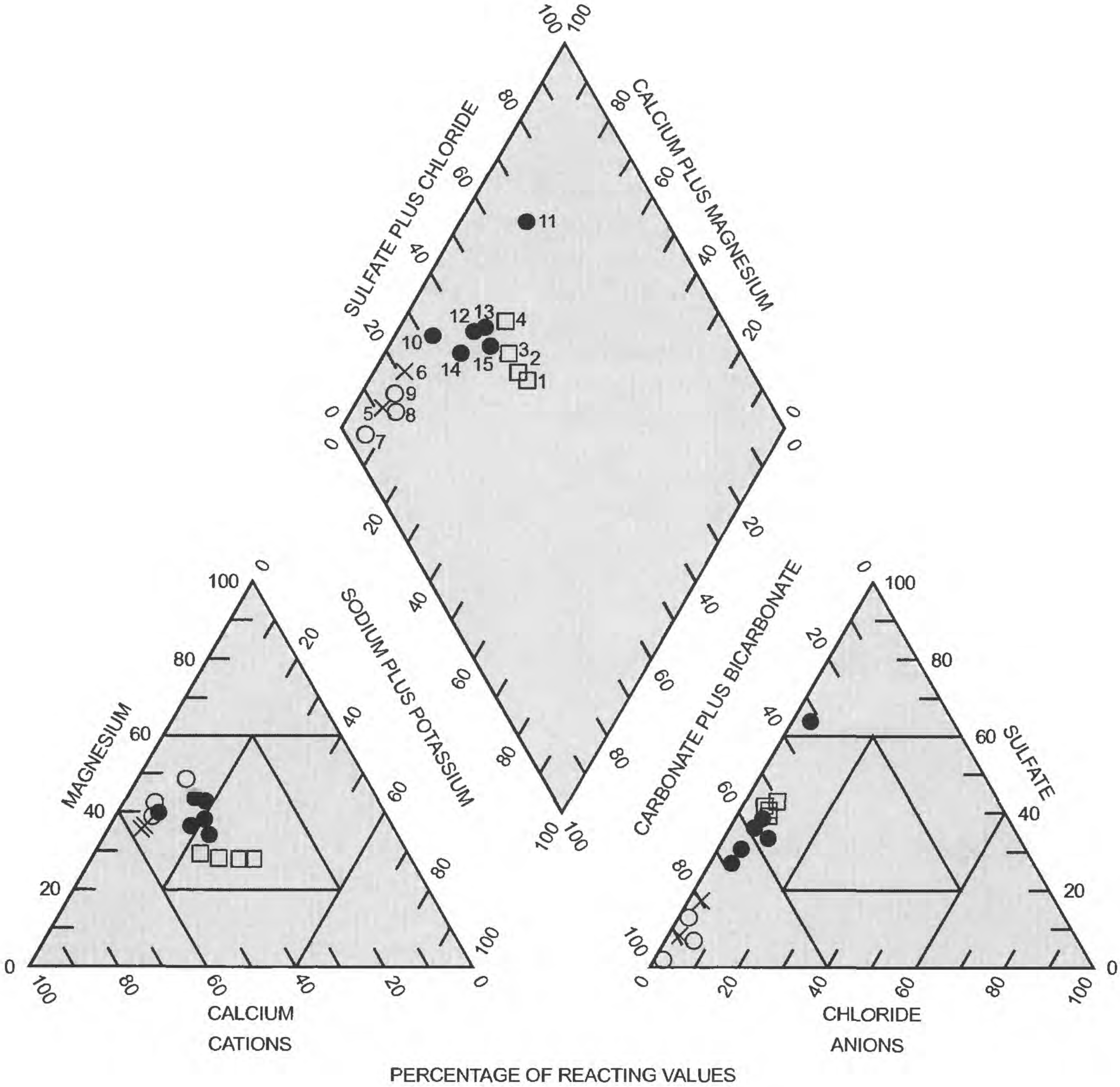
Nutrients, various forms of nitrogen and phosphorus, are potentially important contaminants in water because they can fertilize naturally-occurring aquatic plants, including algae and rooted plants. Excessive growth of these plants upsets the normal stream or lake ecosystem and often results in wide fluctuations of dissolved oxygen. Excessive algal growth can prevent sunlight from reaching aquatic plants in the bottom of the stream or lake.

Some forms of nitrogen (nitrite, nitrate, and ammonia) can be toxic when present in sufficient concentrations, although each is toxic at different levels and by different mechanisms. Common sources of nutrients in aquatic systems include wastewater treatment systems and runoff from lawns and cropland to which fertilizers have been applied; some nutrients are known to be deposited from atmospheric sources.

Organic carbon generally is not considered an essential plant nutrient, but it is related to plant growth and will be discussed in the "Nutrients" section of this report. It commonly is present as a result of decaying vegetation. It also may increase the transport or solubility of hydrophobic organic chemicals.

Suspended sediment can create several problems in riverine systems. Sediment can deposit on fish-spawning grounds and fill reservoirs and lakes; it also can prevent sunlight from reaching aquatic plants. Suspended sediment also can be a carrier of hydrophobic pollutants in stream systems. Sources of sediment to streams include runoff from exposed soil and erosion of stream banks, especially during periods of above-normal streamflow. Previously-deposited and windblown sediment also can be resuspended and transported downstream during above-normal streamflow events.

Pesticides are used to control a variety of undesirable or destructive insects, plants, and fungi. Several pesticides are inorganic toxins, but most are complex organic molecules that often are designed with a high degree of specificity for target species. Because pesticides characteristically interfere with various metabolic pathways, there is concern they may affect nontarget species. Because of this concern, pesticide use is highly regulated, and a variety of standards have been established to protect the health of humans and aquatic biota using water where pesticides might be found. Possible sources of pesticides include runoff from agricultural and urban applications, atmospheric transport, spills, and applications along roadways and in forested areas.



EXPLANATION

- □ Site 1-4, Drift Prairie
- × Site 5-6, Lake-Washed Till Plain
- ○ Site 7-9, Moraine
- ● Site 10-15, Red River Valley Lake Plain and mixed sites physiographic areas

Figure 6. Composition of ions in streams in the Red River of the North Basin study unit (see table 1 for site descriptions).

Nutrients

Several different forms of nitrogen were measured for this study. The forms of dissolved nitrogen measured include nitrite, nitrite plus nitrate, ammonia, and ammonia plus organic. In most aquatic systems nitrite is unstable, so the nitrite plus nitrate essentially is all nitrate. When streams are well-oxygenated, ammonia concentrations are negligible; and the organic nitrogen is the largest part of the ammonia plus organic nitrogen. Ammonia plus organic nitrogen also was measured in unfiltered samples and can be used to calculate the amount of suspended organic nitrogen.

Three different forms of phosphorus were measured for this study: dissolved phosphorus, orthophosphate, and total phosphorus (on unfiltered samples). Dissolved phosphorus includes the orthophosphate form, measured in mg/L as phosphorus, and other forms (hereinafter referred to as non-ortho phosphorus). Orthophosphate is important because it is readily available for uptake by aquatic plants. Suspended phosphorus (computed as total minus dissolved) includes phosphorus that is attached to or part of suspended sediment and phosphorus that is incorporated into algal cells. Although little of the attached phosphorus is available to plants, some could become available in time and contribute to possible eutrophication and nuisance plant growth.

Nitrogen concentration and distribution

Figure 7 shows the median concentration of all forms of dissolved nitrogen measured for this study at each of the sampling sites. The sum of each of the components of the bar chart approximates the total dissolved nitrogen. The lowest concentrations of dissolved nitrogen were in the Otter Tail River. Other streams draining the Moraine and streams draining the Lake-Washed Till Plain also had low concentrations. These streams had relatively low levels of nitrate (less than 0.1 mg/L) and ammonia (less than 0.05 mg/L) nitrogen, and almost no nitrite nitrogen. Most of the nitrogen, particularly in streams in the northern part of these areas, was organic.

Streams draining the Drift Prairie, including the Sheyenne, Pembina, and Turtle Rivers, had much higher concentrations of nitrate nitrogen (about 0.3–0.4 mg/L) than other streams. The Bois de Sioux River, which drains the Red River Valley Lake Plain and some of the Drift Prairie, had nitrogen species concentrations nearly identical to those of the Snake River, which has a large portion of its drainage in the Red River Valley Lake Plain. Both of these streams had relatively high organic nitrogen concentrations.

The four sites along the Red River had similar concentrations of dissolved nitrogen species. Small amounts of ammonia and nitrite were present, but nitrate and organic nitrogen predominated. The site at Halstad had a larger proportion of nitrate and more ammonia and nitrite than the other Red River sites. This probably is caused by municipal and industrial wastes from the Fargo-Moorhead area, because tributary inflows (especially the Wild Rice River) would dilute rather than augment nitrate, ammonia, and nitrite concentrations.

Concentrations of dissolved ammonia plus organic nitrogen generally were highest in the Bois de Sioux and Snake Rivers and were lowest in streams draining the Moraine and in the Turtle and Red Lake Rivers. Concentrations of total ammonia plus organic nitrogen had a similar distribution and were much more variable, suggesting that suspended organic nitrogen causes some of the variability.

The Sheyenne (at Kindred), Pembina, and Red (at Halstad) Rivers had the highest suspended organic nitrogen (the difference between the dissolved and suspended ammonia plus organic nitrogen) concentrations. Concentrations were highly variable. The Red River at Halstad had the most variability, and more than 10 percent of the samples had suspended organic nitrogen in excess of 1.4 mg/L. This may be related to urban effects from Fargo-Moorhead.

Hem (1985) states that nitrite is unstable in aerated waters and generally is considered an indicator of pollution. Median nitrite concentrations were highest (0.02 mg/L or higher) in the Sheyenne (at Kindred), Bois de Sioux, and Snake Rivers and in the Red River sites above Fargo and at Halstad. Twenty-five percent or more of the concentrations in the Bois de Sioux and Snake Rivers and the Red River at Halstad exceeded 0.05 mg/L. Ten percent of the samples in the Pembina, Bois de Sioux, and Snake Rivers, and in the Red River above Fargo, at Grand Forks, and at Emerson were at or above 0.10 mg/L.

Median ammonia nitrogen concentrations also were highest (0.8 mg/L or higher) in the Bois de Sioux and Snake Rivers and in the Red River at Halstad. Ammonia concentrations were variable at several sites

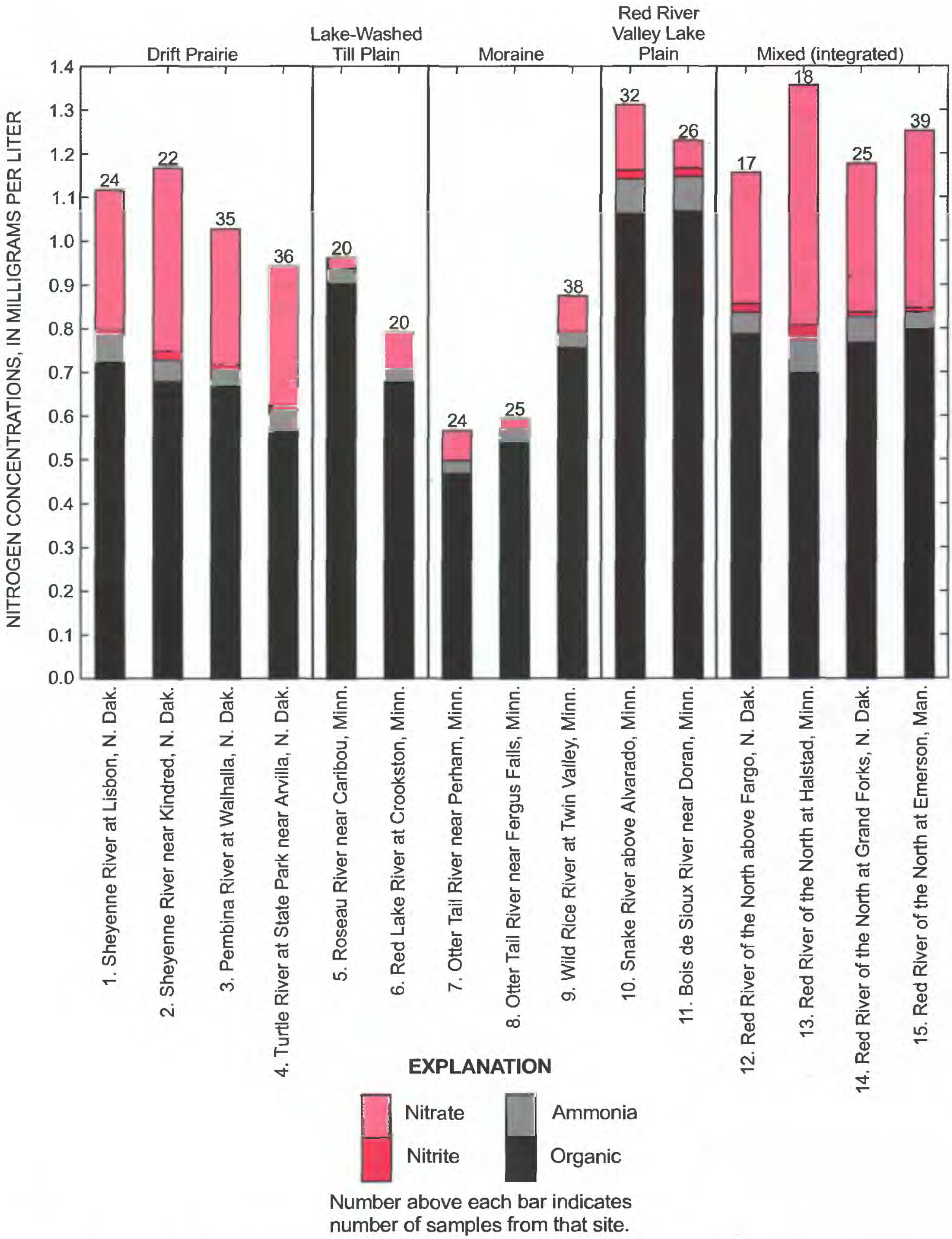


Figure 7. Median concentrations of all measured forms of dissolved nitrogen in streams in the Red River of the North Basin study unit. (Site number referenced on figure 2)

suggesting that the streams were affected by wastewater discharges or ammonia was generated in the stream under reducing (low oxygen) conditions.

Nitrate concentrations measured during this study were variable, but did not pose a threat to human health. The highest concentration, 5.8 mg/L measured at the Red River at Emerson, Manitoba, was well below the drinking water standard of 10 mg/L (U.S. Environmental Protection Agency, 1996). Drift Prairie streams and the Red River generally had the highest median nitrate concentrations, about 0.4 mg/L. Median concentrations from eastern streams, including Lake-Washed Till Plain, Moraine, and Red River Valley Lake Plain streams were about 0.1 mg/L or less. Many of the streams, including the Pembina, Bois de Sioux, and Snake Rivers and most of the Red River sites had nitrate concentrations that exceeded 2 mg/L in at least 10 percent of the samples.

The nitrogen results from basin-wide synoptic sampling were inconclusive because of several factors. The most important factor was the difficulty in sampling streams at the same flow regime. Another factor was dilution affecting concentrations. For example, dissolved and total ammonia plus organic nitrogen concentrations generally were lowest when the streamflow was high but stable (except in the Sheyenne, Forest, and Bois de Sioux Rivers). A third factor was the variability of concentrations within the same flow regime at each site. For example, the Goose River was sampled twice during a rising stage in 1994. During May, the nitrate nitrogen was below detection (0.05 mg/L), but during July, the concentration was 0.36 mg/L.

Within-stream synoptic samples collected following rainfall runoff, including samples from the intensive indicator sites, showed that nitrogen concentrations were reasonably consistent along the Turtle, Snake, and Wild Rice Rivers. The mean dissolved ammonia plus organic nitrogen along each of the streams was about 1.0 mg/L, and the standard deviation was less than 0.18. Total ammonia plus organic nitrogen was most variable in the Snake River with a mean of 1.4 mg/L and a standard deviation of about 0.4. However, the sample at the mouth of the Snake River was collected before flow from the runoff had reached that site. Nitrite plus nitrate nitrogen was the most variable in all of the streams with means that ranged from 0.42 to 1.5 mg/L and standard deviations that ranged from 0.25 to 1.1.

Phosphorus concentration and distribution

Figure 8 shows the median concentration of all forms of phosphorus measured for this study at each of the sampling sites. The sum of each of the components of the bar chart approximates the median total phosphorus concentration. The amount of phosphorus carried by streams varied considerably. In many streams, most of the phosphorus was dissolved, predominately orthophosphate with a small amount of non-ortho phosphorus. Hem (1985) suggests that other forms of dissolved phosphorus are unstable phosphates that eventually will revert to orthophosphate. Orthophosphate is readily available to aquatic algae and may result in algal blooms when present in excessive amounts. Water-quality criteria defining "excessive amounts" of phosphorus in streams generally are not available, but the Minnesota Pollution Control Agency proposes a goal of 0.10 mg/L average total phosphorus concentration for the Minnesota River (E.E. Van Nieuwenhuyse, Minnesota Pollution Control Agency, written commun., 1996). Lakes and reservoirs with total phosphorus concentrations of about 0.1–0.4 mg/L are considered eutrophic (Wetzel, 1983, p. 293).

The lowest concentrations of phosphorus occurred in streams draining the Moraine and Lake-Washed Till Plain areas. Although the phosphorus measured at the Otter Tail River near Perham, Minnesota, was entirely suspended, most streams in the Moraine and Lake-Washed Till Plain areas had some dissolved orthophosphate. Two streams, the Roseau and Wild Rice Rivers, also had some dissolved non-ortho phosphorus.

Streams draining the Drift Prairie had considerably higher concentrations of orthophosphate than eastern streams. The highest concentrations of orthophosphate were in the Pembina and Bois de Sioux Rivers. The Bois de Sioux River also had slightly more non-ortho phosphorus than the other Drift Prairie streams.

Phosphorus concentrations at sites along the Red River were comparable to those found in western streams and in the Snake River and generally increased downstream. The proportion of orthophosphate to suspended phosphorus also increased downstream, except at Grand Forks where water from the Red Lake River probably diluted concentrations in the Red River.

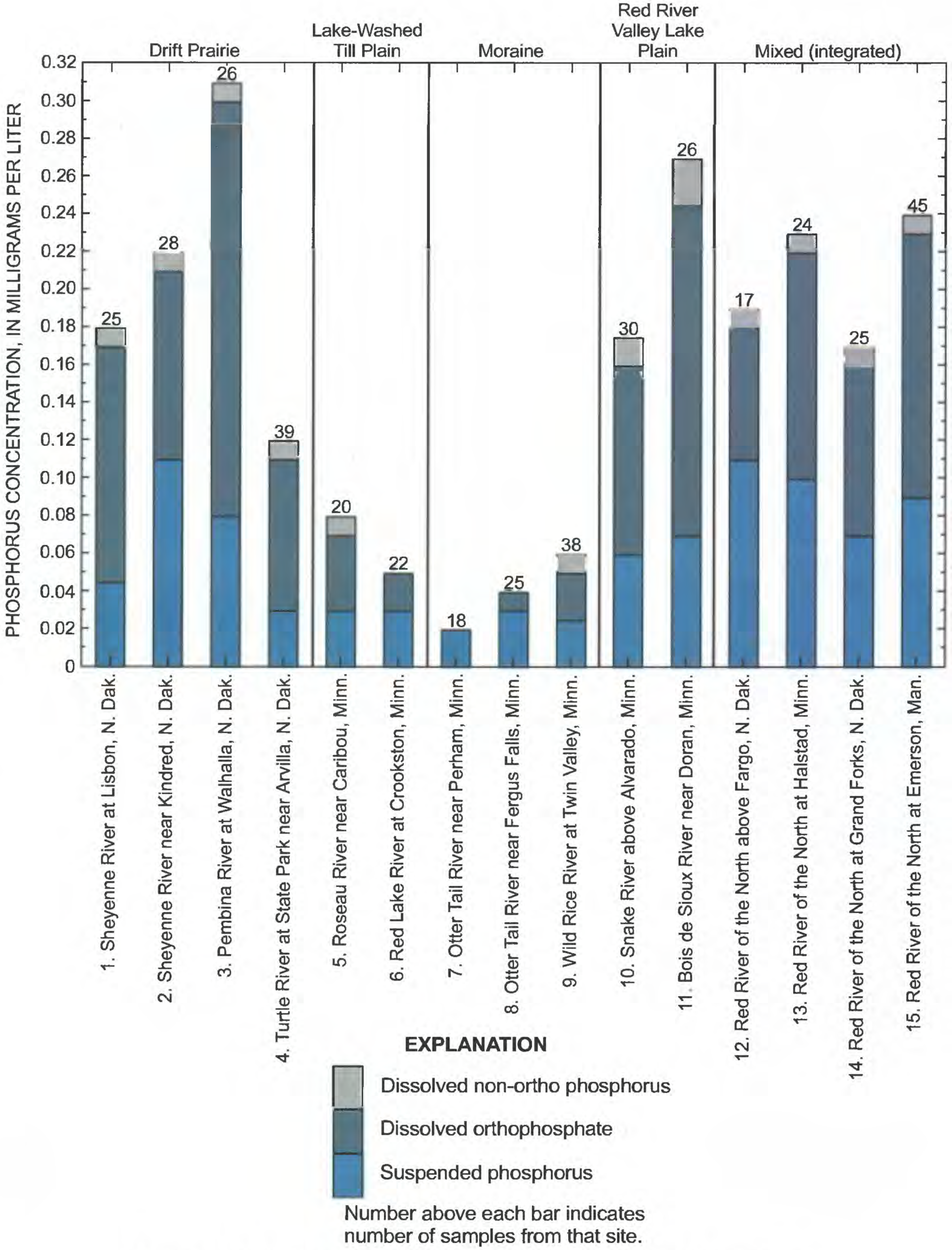


Figure 8. Median concentrations of all measured forms of phosphorus in streams in the Red River of the North Basin study unit. (Site number referenced on figure 2)

Dissolved phosphorus, most of which is orthophosphate, was most variable in streams draining the Drift Prairie and Red River Valley Lake Plain. The Bois de Sioux and Turtle Rivers drain both of these areas and had a particularly large range between the 25th and 75th percentiles (the interquartile range). The cause of this high variability is not known, but could result from point or nonpoint inputs to the stream or phosphorus periodically released from bottom sediments deposited in shallow reservoirs upstream of the sampling sites.

Suspended phosphorus was highest and most variable in streams draining the Drift Prairie and along the Red River. Suspended phosphorus was highly variable in the Pembina River. This stream has extensive grazing near the river and drains some of the steepest topography in the Red River Basin study unit, so it has more energy to carry suspended particles that might contain phosphorus. An increase in the concentration of suspended phosphorus and decrease in orthophosphate concentration between Lisbon and Kindred, North Dakota on the Sheyenne River could relate to an increase in algae between the two sites.

Total phosphorus concentrations in basin-wide synoptic samples were variable, but provided more consistent results than did the nitrogen concentrations. Although most of these sites are influenced by the Red River Valley Lake Plain, they have concentrations that are typical of the physiographic area of their headwaters. Streams draining the Drift Prairie had median total phosphorus concentrations of 0.26 mg/L, with 0.16 mg/L dissolved, of which 0.14 mg/L was orthophosphate. Red River Valley Lake Plain streams had median total phosphorus concentrations of 0.20 mg/L, with 0.13 mg/L dissolved, all of which was orthophosphate. Streams draining the Lake-Washed Till Plain had median total phosphorus concentrations of 0.10 mg/L, with 0.04 mg/L dissolved and nearly all of which was orthophosphate.

Within-stream synoptic samples collected following rainfall runoff, including samples at the intensive indicator sites, were analyzed for phosphorus concentrations. Total phosphorus concentrations increased along the Wild Rice River, especially as the stream flowed through the Red River Valley Lake Plain. Dissolved orthophosphate concentrations measured along the Wild Rice River were virtually constant. Both constituents had a mean of 0.07 mg/L and standard deviation of 0.01. Phosphorus concentrations were higher, more variable, and followed no discernible pattern along the Turtle and Snake Rivers.

Organic carbon concentration and distribution

Dissolved organic carbon (DOC) concentrations, shown in figure 9, were highest in the Roseau, Snake, and Red Lake Rivers where median concentrations exceeded 15 mg/L. These streams primarily drain two different physiographic areas, the Lake-Washed Till Plain and the Red River Valley Lake Plain. As other streams in the Red River Valley Lake Plain did not have these high DOC concentrations, the source of DOC in these streams is concluded to be extensive peatlands near the headwaters. DOC concentrations were highest near the headwaters of the Snake River during synoptic sampling. The Bois de Sioux and Wild Rice Rivers had DOC concentrations that were nearly 15 mg/L. It is uncertain why the Bois de Sioux River had elevated DOC, but the Wild Rice River has considerable wetlands in its headwaters. DOC was not measured in samples collected along the Wild Rice River to verify that the source was in the headwaters.

Suspended organic carbon (SOC) had a different distribution than DOC (fig. 9). SOC concentrations were highly variable and generally were highest during runoff. The highest and most variable concentrations of SOC were measured at the Sheyenne River at Kindred, and the Pembina River, and there is considerable increase in the SOC on the Sheyenne River between Lisbon and Kindred. The variable streamflow and sediment concentration of the Pembina River could be expected to result in variable transport of suspended material including SOC. However, the Sheyenne River at Kindred has relatively stable flow because of relatively flat topography with dams and reservoirs upstream. This could favor algal growth, which would convert DOC to SOC. DOC concentrations decline between the two sites, but some of this may result from dilution by ground water that enters the stream between Lisbon and Kindred. The increase in SOC is consistent with the increase in suspended phosphorus observed between Lisbon and Kindred. Samples of algae or chlorophyll could help determine whether uptake of nutrients is occurring.

Regional patterns of DOC from synoptic samples generally relate to the physiographic areas.

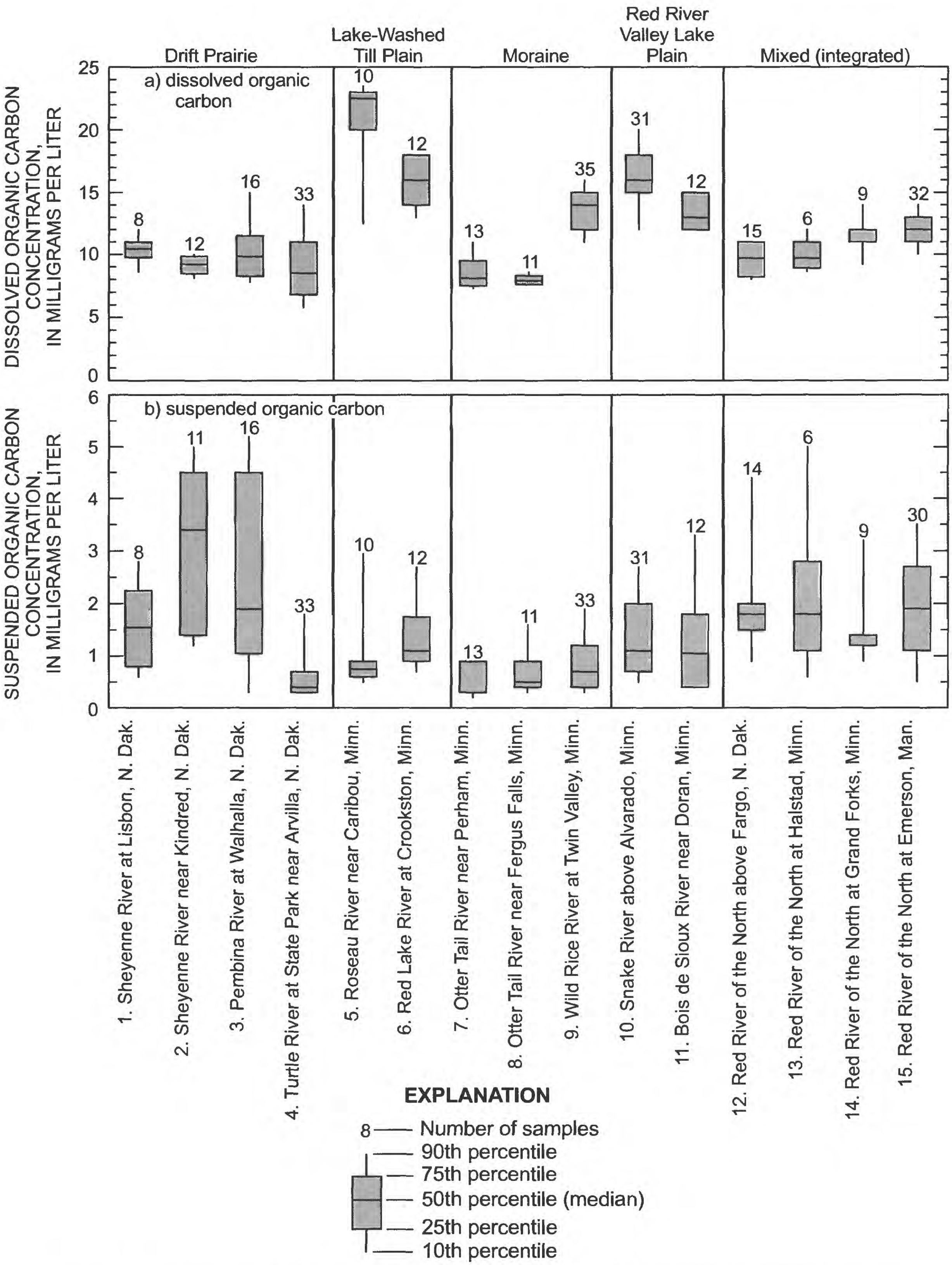


Figure 9. Distribution of a) dissolved organic carbon, and b) suspended organic carbon concentrations in streams in the Red River of the North Basin study unit. (Site number referenced on figure 2)

Streams associated with the Lake-Washed Till Plain tended to have the highest DOC concentrations, followed by streams draining the Red River Valley Lake Plain. Moraine streams grouped as the third highest and Drift Prairie streams generally had the lowest DOC concentrations.

SOC concentrations in synoptic samples were generally low and variable. No regional patterns were evident.

Seasonality

Concentrations of many of the nutrients varied considerably over time, often related to variations in flow, seasons, and application of fertilizer. Figure 10 shows a plot of total nitrogen concentrations and streamflow during the 3 years of sampling at the Wild Rice River at Twin Valley, Minn. Total nitrogen concentrations were about 1 mg/L or less during much of the year, but substantially exceeded that value during runoff. Nitrogen concentrations were highest during snowmelt runoff, but also were elevated during rainfall runoff. This seasonal pattern is evident in all streams in the Red River Basin study unit, although measured concentrations may be different. At sites on the Red River, nitrogen peaks resulting from rainfall runoff were much less evident probably because these sites receive runoff from several sources.

The several species of nitrogen have seasonal variations in concentration. Figure 11 shows the variation throughout the year in the species that comprise the dissolved nitrogen in the Turtle, Snake, and Wild Rice Rivers. The figure is based on 3 years of data overlaid and plotted by the date in the year the samples were collected.

Nitrate-nitrogen concentrations were highest during mid to late March because of snowmelt runoff. Additional nitrate often was flushed into streams with rainfall runoff, but concentrations did not approach those observed during snowmelt runoff. Nitrite followed a pattern similar to nitrate, but at much lower concentrations.

Ammonia nitrogen concentration often was highest under ice cover and with the first flush of snowmelt runoff. Elevated ammonia also was associated with rainfall runoff, but concentrations were not as high as in the late winter. Ammonia levels were negligible the rest of the year. Tornes and Brigham (1994) noted elevated ammonia concentrations during winter months for selected streams in the basin. We speculate that the winter build up of ammonia is because streams under ice and snow cover cannot replenish oxygen via photosynthesis and reaeration.

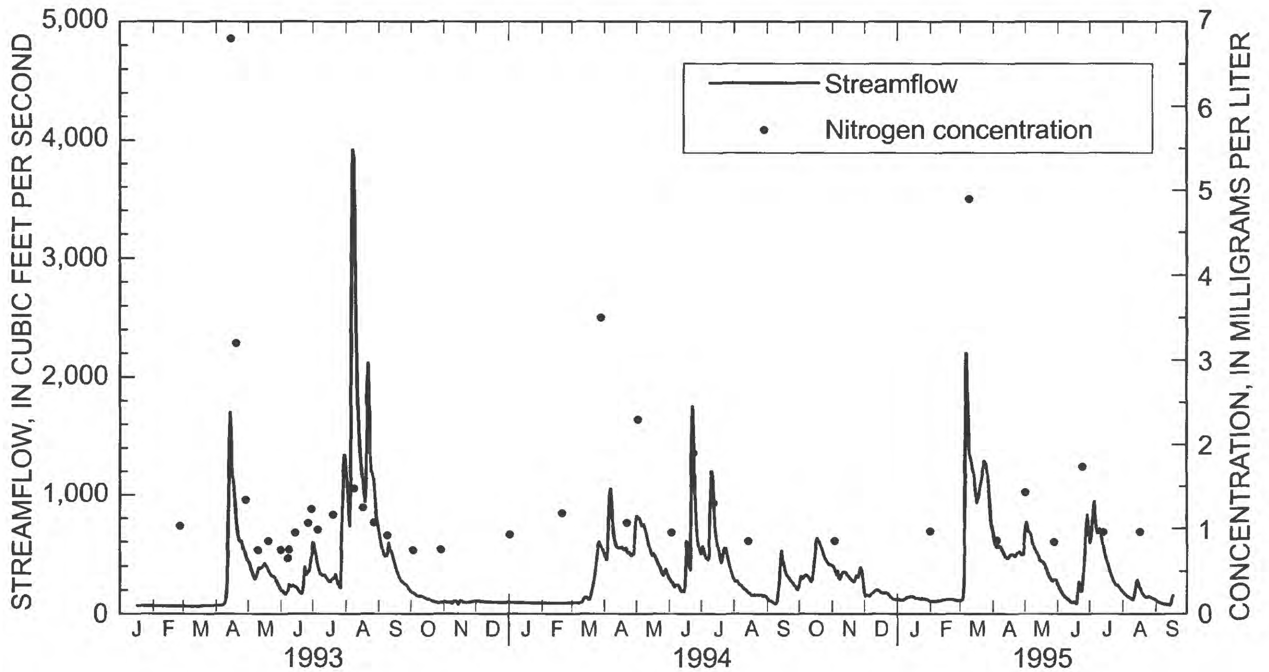


Figure 10. Total nitrogen concentrations and streamflow in the Wild Rice River at Twin Valley, Minn.

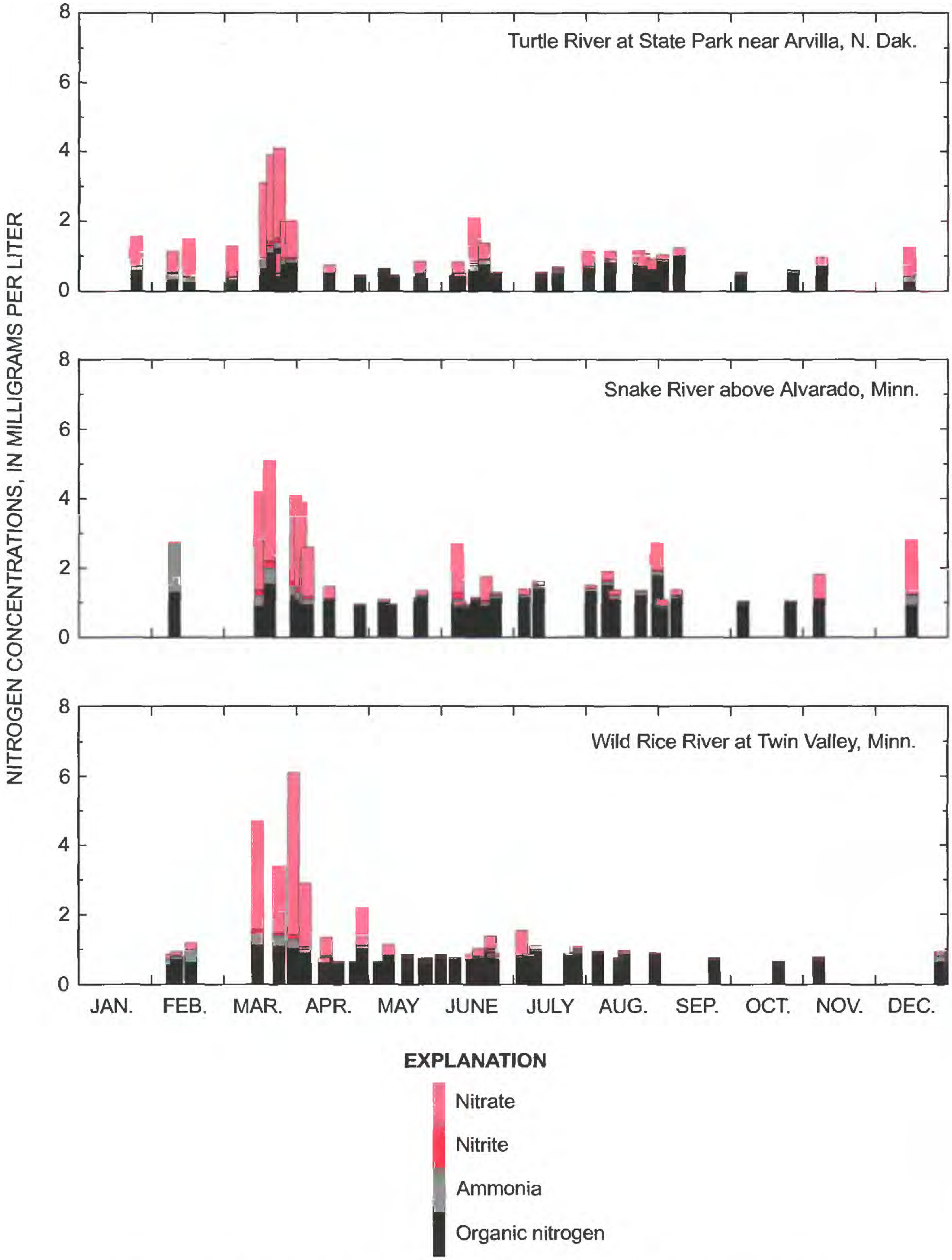


Figure 11. Variations of forms of dissolved nitrogen for three sites in the Red River of the North Basin study unit (1993-95 combined).

Another factor may be that cold temperatures reduce the rate of uptake of ammonia by organisms or the rate of conversion to other forms of nitrogen such as nitrate. Low oxygen may account for a few of the high ammonia observations. One of the highest ammonia concentrations, 1.4 mg/L, was measured under ice in the Snake River and the dissolved oxygen concentration was 0.6 mg/L. The dissolved oxygen would have been nearly 14 mg/L if the stream water were in equilibrium with the atmosphere. However, very few samples from this study had low (<1 mg/L) oxygen, and several high-ammonia samples also had high levels of oxygen.

Organic nitrogen concentrations did not vary as much as other dissolved nitrogen species. This relative stability suggests organic nitrogen concentrations are little affected by streamflow conditions in the basin.

The high concentrations of nitrite, nitrate, and sometimes other forms of dissolved nitrogen during snowmelt runoff occurred annually in virtually every stream sampled in the Red River Basin study unit, and probably are not related to point-source inputs.

Nitrogen released from thawing soils is a likely source of dissolved nitrogen to streams during snowmelt runoff. Honeycutt (1995) reviewed many studies that tested the effects of freezing and thawing on soils. As soil temperatures drop below 5 degrees Fahrenheit, a large percentage of the soil organisms (including bacteria and nematodes) are killed. Honeycutt (1995) also noted that freezing causes water to migrate from deeper, unfrozen areas to more shallow frozen soils. As the soil thaws, nutrients released from organism carcasses readily dissolve into soil pore water. Soils in the Red River Basin study unit can freeze several feet deep, and air temperatures often reach −10 degrees Fahrenheit during winter. Peak snowmelt runoff in the study unit typically coincides with partially thawed, saturated soils that could release nutrients to adjacent streams.

In addition to mineralization of soil nitrogen, snowpack may contain substantial amounts of nitrogen. Melting of snowpack is known to contribute significant nitrogen loads to streams (Murdoch and Stoddard, 1992, and references therein).

As streamflows decrease after snowmelt runoff, dissolved nitrogen concentrations return to 'normal'. The excess probably has been flushed from the system or assimilated by aquatic plants. Because suspended nitrogen concentrations generally did not or only moderately increased, phytoplankton probably are not a significant sink for the nitrogen observed during snowmelt runoff.

Orthophosphate, which comprised most of the dissolved phosphorus, tended to be highest during snowmelt runoff and often during rainfall runoff events. Figure 12a shows a typical example of this variation for the Turtle River. The Snake River (fig. 12b) also shows this pattern, but had at least one high value (0.38 mg/L), during low flow (0.20 ft^3/s), in winter. This high concentration of orthophosphate coincided with low (0.6 mg/L) dissolved oxygen and probably was released from anoxic sediments.

Concentrations of suspended phosphorus also increased during runoff events, but especially during rainfall runoff when soils were not frozen. Figure 13 shows the variability of suspended phosphorus for the Red River at Grand Forks. Although suspended phosphorus can be elevated during snowmelt runoff, many of the highest concentrations occurred during runoff events in the summer.

Figure 14 shows the variation throughout the year of each component of the total phosphorus for the most intensively sampled tributaries. In most streams the phosphorus concentration was lowest during late autumn and winter. Exceptions to this general trend can occur infrequently during winter low flows. Orthophosphate may be released from anoxic bottom sediments under low-oxygen conditions. Concentrations of phosphorus increased during snowmelt runoff and were mostly orthophosphate. During the summer, phosphorus concentrations were quite high, and a relatively large proportion of it was in the suspended phase, particularly when sediment concentrations were high.

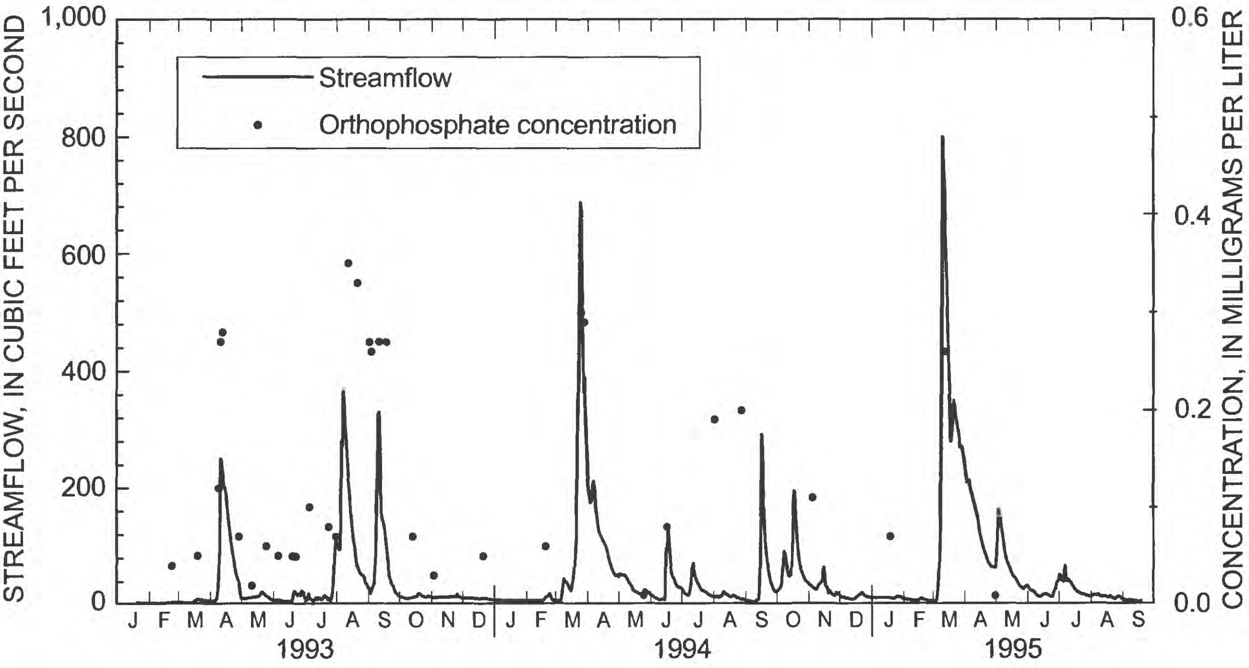
Comparison to historical data

Historical data and data for this study generally are comparable. Historical data (U.S. Geological Survey data from 1970 to 1991; see Tornes and Brigham, 1994) typically were collected on a regular schedule without regard to streamflow conditions.

Data collected for this study were collected to present the full range of streamflows for each season. Streamflow conditions were above the historical average during this study.

The comparison between historical and this study's nitrite plus nitrate nitrogen concentrations is shown on figure 15. Streams draining the Moraine and

a) Turtle River at State Park near Arvilla, N. Dak.



b) Snake River above Alvarado, Minn.

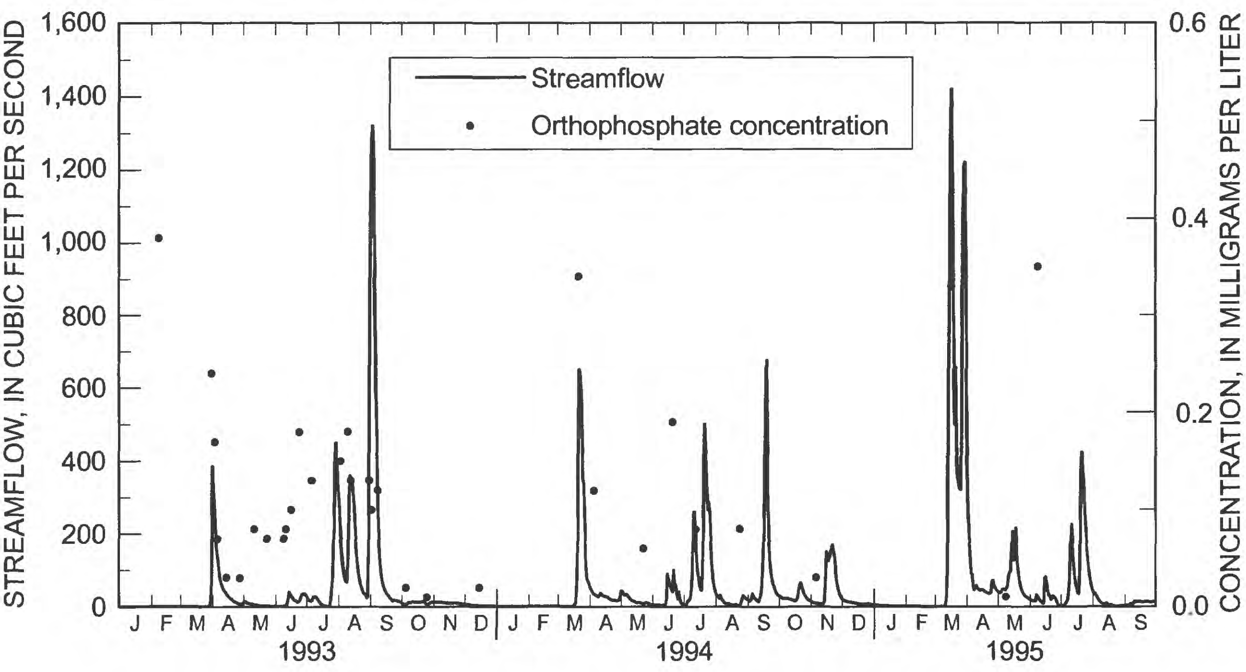


Figure 12. Concentrations of dissolved orthophosphate and streamflow in the a) Turtle River, and b) Snake River in the Red River of the North Basin study unit.

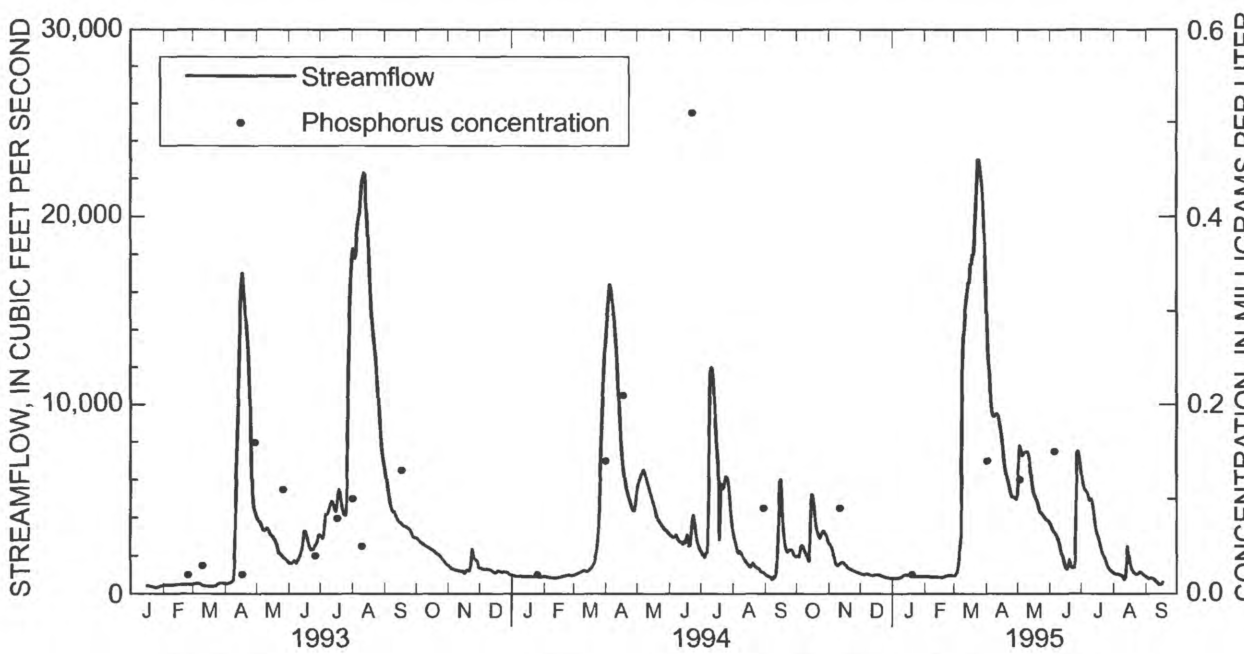


Figure 13. Concentrations of suspended phosphorus and streamflow in the Red River of the North at Grand Forks, North Dakota.

Lake-Washed Till Plain had low concentrations in both data sets. Nitrite plus nitrate nitrogen concentrations in streams draining the Drift Prairie generally were much higher in samples collected for this study than they were in historical samples. Above normal precipitation and runoff during this study provided a better definition of concentrations at higher streamflows.

Nitrite plus nitrate nitrogen concentrations also tended to be slightly higher than historical concentrations at sites along the Red River, although flow-adjusted nitrite plus nitrate concentrations show no statistically significant trends at the 5 percent level of significance (seasonal Kendall test; Hirsch and others, 1991) at either Red River site. Median ammonia concentrations for the Red River at Halstad, downstream from the Fargo-Moorhead urban area, were about 0.16 mg/L in historical samples, but only 0.08 mg/L in samples collected for this study. The decrease in flow-adjusted ammonia concentrations is significant ($p<0.01$; seasonal Kendall test). Increases in nitrate and decreases in ammonia have been identified in several streams nationwide, particularly downstream of urban areas; these trends likely reflect improved aeration of wastewater effluent, whereby ammonia is nitrified to nitrate (Mueller and others, 1995). It also is possible that reduced loading of oxygen-demanding materials is allowing streams to remain aerated, decreasing the instream production of ammonia.

Figure 16 compares the distribution of historical total phosphorus concentrations to those measured for this study. Total phosphorus concentrations in Moraine and Lake-Washed Till Plain streams (Wild Rice, Roseau, and Red Lake Rivers) were low, and the distribution of concentrations were quite similar. Total phosphorus concentrations in Drift Prairie streams sampled for this study were considerably higher than in historical samples. Because this part of the study unit tends to be relatively dry during the summer growing season, runoff of nutrients normally is much less than from eastern streams. Abnormally high rainfall and runoff during this study probably resulted in increased nutrient runoff.

The phosphorus data collected for this study show a greater concentration range than did historical data. This is related to the emphasis on sampling more high-flow events during this study. The comparison between historical and recent dissolved phosphorus

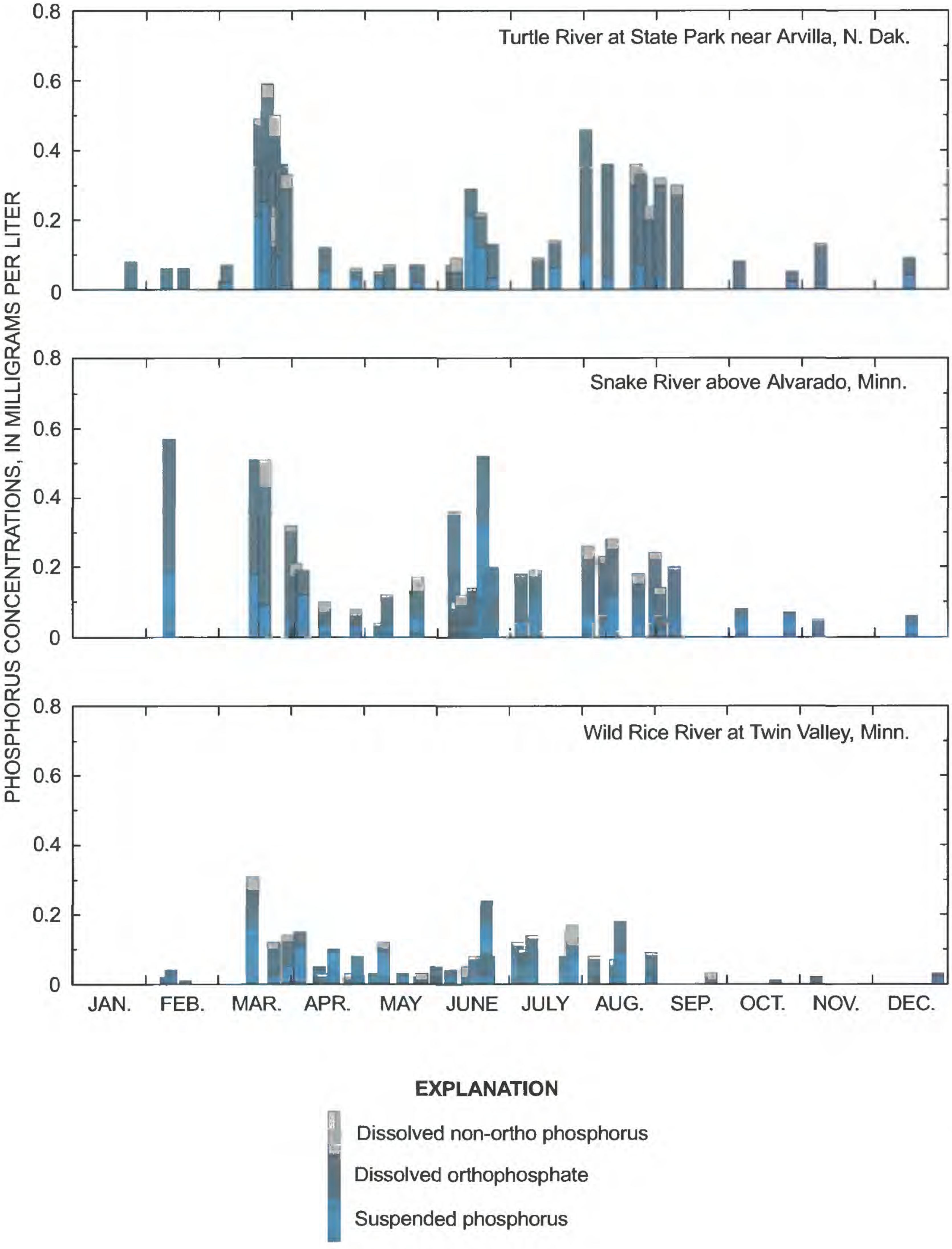


Figure 14. Variations of forms of phosphorus for three sites in the Red River of the North Basin study unit (1993-95 combined).

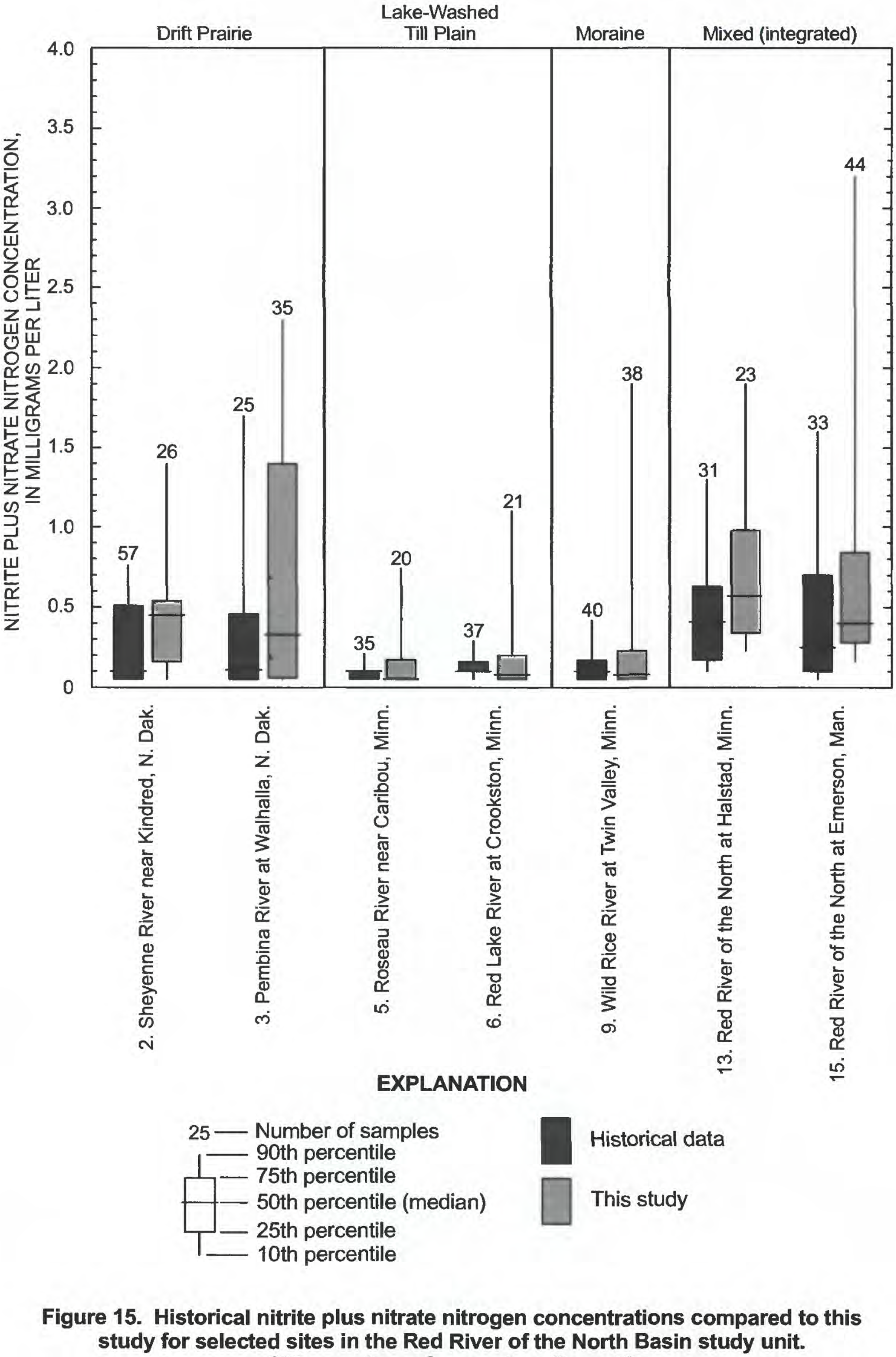


Figure 15. Historical nitrite plus nitrate nitrogen concentrations compared to this study for selected sites in the Red River of the North Basin study unit. (Site number referenced on figure 2)

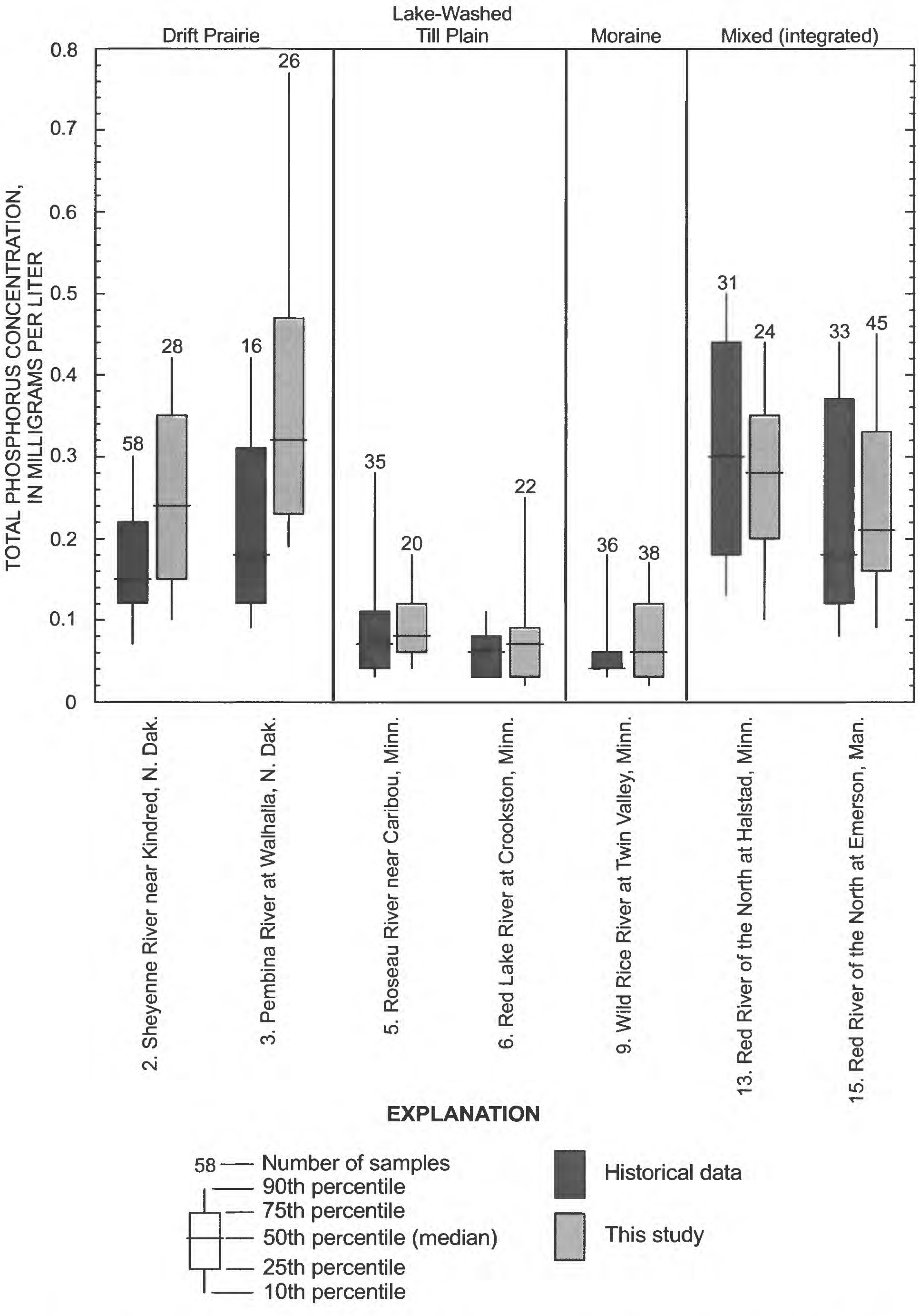


Figure 16. Historical total phosphorus concentrations compared to this study for selected sites in the Red River of the North Basin study unit. (Site number referenced on figure 2)

concentrations (not shown) is nearly the same, although the ranges in values were smaller.

Historical and recent total phosphorus concentrations in the Red River (at Halstad, Minnesota and Emerson, Manitoba) also were similar, but the ranges of values for this study were smaller. The large ranges in historical values may have been caused by anoxic releases and/or point source inputs during low flows; high phosphorus concentrations during low flows were noted by Tornes and Brigham (1994). These point-source inputs probably are less evident during recent sampling because low streamflows did not occur or because of reduced point-source releases.

Loads and yields

Table 6 shows the parameters and coefficients for the regression model Estimator used for each of the

Table 6.—Model parameters and coefficients used to calculate nitrogen and phosphorus loads for streams in the Red River of the North Basin study unit

[ln, natural logarithm; Q, streamflow in cubic feet per second; a, b, c, and d are model coefficients; T, julian sample date expressed as fraction of a year; q, center value for logarithm of streamflow, R^2, coefficient of determination; π, 3.1416]

Map number	Site	a	b	c	d	q	R^2
	Nitrogen (N) model $\ln(N) = a+b*[\ln(Q)-q]+c*\text{sine}(2\pi T)+d*\text{cosine}(2\pi T)$						
1	Sheyenne River at Lisbon, N. Dak.	7.66	1.26	0.15	0.15	6.351	94.0
2	Sheyenne River at Kindred, N. Dak.	7.47	1.27	.22	.18	6.225	92.5
3	Pembina River at Walhalla, N. Dak.	7.80	1.21	.12	.35	6.403	96.3
4	Turtle River at Turtle River State Park near Arvilla, N. Dak.	5.34	1.29	.047	.33	4.105	94.7
5	Roseau River near Caribou, Minn.	6.24	1.05	.15	.21	5.111	97.3
6	Red Lake River at Crookston, Minn.	8.98	1.42	.19	.11	7.778	94.5
7	Otter Tail River near Perham, Minn.	6.11	1.07	.14	.26	5.424	83.0
8	Otter Tail River below Orwell Dam near Fergus Falls, Minn.	6.98	.761	.14	.06	6.237	63.1
9	Wild Rice River at Twin Valley, Minn.	7.24	1.45	.21	.39	6.041	93.0
10	Snake River above Alvarado, Minn.	5.20	1.06	.25	.42	3.557	98.3
11	Bois de Sioux River at Doran, Minn.	6.17	1.04	.36	.36	4.562	97.0
12	Red River of the North above Fargo, N. Dak.	8.82	1.31	.089	.12	7.330	92.6
13	Red River of the North at Halstad, Minn.	9.48	1.17	.37	.13	7.992	94.7
14	Red River of the North at Grand Forks, N. Dak.	10.18	1.45	.35	.31	8.771	97.0
15	Red River of the North at Emerson, Minn.	10.25	1.33	.23	.31	8.776	94.9

sites to compute nutrient loads. Once a regression model that worked well for a majority of sites was chosen, the same model parameters were used for every site. Additional explanatory parameters might have produced a better model at a given stream site, but would have made the models less comparable. These constituent transport models are different than those used in Tornes and Brigham (1994) because the explanatory variable "square of the logarithm of the streamflow" was not used for nutrient data collected for this study.

Parameter coefficients for the sites shown in table 6 do not seem to be related to physiographic area. Generally the models do a good job explaining the variations in nutrient loads for most streams in the study unit, with coefficients of determination greater

Table 6.—Model parameters and coefficients used to calculate nitrogen and phosphorus loads for streams in the Red River of the North Basin study unit—continued

Map number	Site	a	b	c	d	q	R^2
	Phosphorus (P) model $\ln(P) = a+b*[\ln(Q)-q]+c*\text{sine}(2\pi T)+d*\text{cosine}(2\pi T)$						
1	Sheyenne River at Lisbon, N. Dak.	5.97	1.34	-.027	0.24	6.351	85.3
2	Sheyenne River at Kindred, N. Dak.	5.55	1.27	.0039	-.17	6.225	88.6
3	Pembina River at Walhalla, N. Dak.	6.32	1.20	-.097	.080	6.403	97.1
4	Turtle River at Turtle River State Park near Arvilla, N. Dak.	3.26	1.47	-.26	-.13	4.105	94.8
5	Roseau River near Caribou, Minn.	3.43	1.20	.22	.43	5.111	88.2
6	Red Lake River at Crookston, Minn.	6.14	1.83	-.012	-.38	7.778	86.5
7	Otter Tail River near Perham, Minn.	2.74	1.13	.17	.093	5.424	57.4
8	Otter Tail River below Orwell Dam near Fergus Falls, Minn.	3.92	.70	.013	-.21	6.237	28.7
9	Wild Rice River at Twin Valley, Minn.	4.06	1.71	-.027	-.15	6.041	89.1
10	Snake River above Alvarado, Minn.	2.51	1.18	.22	-.36	3.557	96.8
11	Bois de Sioux River at Doran, Minn.	4.22	1.00	-.069	.018	4.562	90.3
12	Red River of the North above Fargo, N. Dak.	6.48	1.78	-.82	-.23	7.330	95.8
13	Red River of the North at Halstad, Minn.	7.48	1.22	-.26	-.22	7.992	94.6
14	Red River of the North at Grand Forks, N. Dak.	7.92	1.49	-.021	-.11	8.771	91.8
15	Red River of the North at Emerson, Minn.	8.10	1.39	-.28	-.03	8.776	94.3

than 90 for nitrogen and greater than 85 for phosphorus. The exceptions are the Otter Tail River at both sampling sites, which are largely affected by numerous lakes and reservoirs along the river, so that streamflow is poorly related to constituent transport. It is difficult to develop a reliable constituent-transport model for the Otter Tail River.

Figure 17 shows the plots of estimated (model calculated) daily loads compared to the instantaneous-measured loads for total nitrogen and phosphorus at the Red River at Emerson, Manitoba. The model closely approximates the measured instantaneous load for most samples. The estimated loads averaged over the 3-year sampling period should be reasonably close to actual nutrient transport for those years.

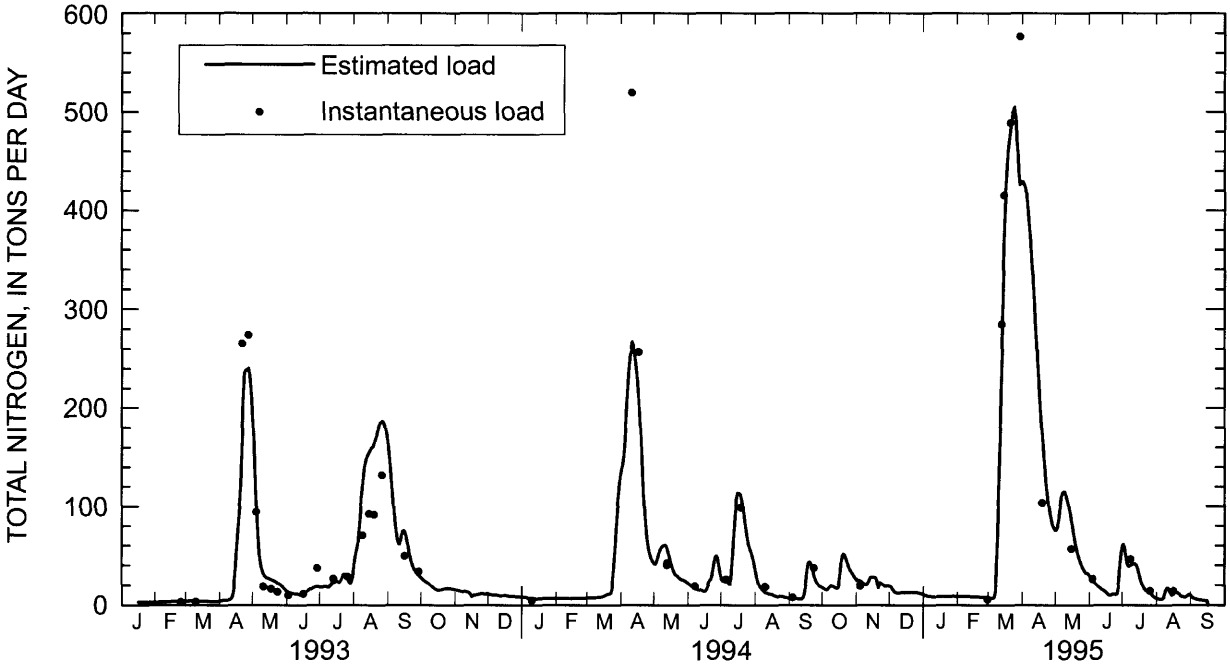
Loads of total nitrogen and total phosphorus (table 7) generally were proportional to the size of the stream and its watershed. The Red Lake River contributes the most nitrogen, over 10,000 lb/d, followed by the Pembina and Bois de Sioux Rivers, which each contribute more than 6,000 lb/d. The smallest load of nitrogen came from the Turtle and Snake Rivers. The Red River carried the largest amount of nitrogen, and the amount increased by a factor of four from Fargo, North Dakota, downstream to Emerson, Manitoba.

Phosphorus loads in tributaries were highest for the Pembina River, carrying nearly 1,800 lb/d, followed by the Bois de Sioux, Sheyenne, and Red Lake Rivers. The smallest loads were in the Snake and Turtle Rivers. Although the Otter Tail River near Perham, Minnesota, carried the smallest load of phosphorus, that load was substantially higher where the river was sampled near Fergus Falls. The Red River carried the largest load of phosphorus, and that amount also increased fivefold from Fargo downstream to the Canadian border.

Although loads are useful for understanding the contribution of nutrients from various streams in the Red River Basin study unit, they are heavily weighted by the streamflow which depends on the size of the watershed and runoff. The yield, however, describes how much material is being carried per unit area of the watershed and can be used to determine relative sources of nutrients.

Nitrogen yields (table 7; fig. 18) varied considerably throughout the study unit. The Bois de Sioux River contributed about 4.8 lb/mi^2/d, substantially more than any other stream in the study unit. The Bois de Sioux River drains an area where corn and soybeans are the major crops; corn requires substantial nitrogen application and growing soybeans add nitrogen to the soil through the action of nitrogen-fixing bacteria. The counties drained by the Bois de Sioux River have some of the highest rates of nitrogen application in the study unit (Tornes and Brigham, 1994). Yields from the Red River Valley Lake Plain, including primarily the Snake and Bois de Sioux Rivers, were 3.5 lb/mi^2/d or greater. Counties having some of the highest nitrogen application rates in the study unit are located primarily in the Red River Valley Lake Plain (Tornes and Brigham, 1994). Streams draining the Drift Prairie had yields ranging from about 1.2 to 2.6 lb/mi^2/d, and yields appear to be higher in the smaller, more northern streams, such as the Turtle River, where most of the drainage is from counties where nitrogen application rates are relatively high. The highest yields from the Drift Prairie were from the Pembina River and may be related to rapid runoff to the streams caused by the steep slopes in the watershed and extensive grazing near the river and its tributaries. Yields of nitrogen from the Lake-Washed Till Plain were about 2 lb/mi^2/d, whereas yields from the Moraine ranged from about 1.6 to more than 3 lb/mi^2/d. Yields for sites along the Red River ranged from about 2.7 to nearly 3.5 lb/mi^2/d and appear to be influenced by the adjacent Red River Valley Lake Plain. The highest yield along the Red River was upstream from Fargo where the Bois de Sioux River watershed, and possibly other unsampled watersheds, exhibit a large influence on stream-water quality.

Phosphorus yields were highest from the Pembina and Bois de Sioux watersheds, about 0.56 and 0.69 lb/mi^2/d, respectively. Although the watersheds for each of these streams are partially in the Drift Prairie, they probably are not typical of streams draining that physiographic area, but are influenced more by local factors. The counties drained by the Bois de Sioux River have some of the highest rates of phosphorus application in the Red River Basin study unit (Tornes and Brigham, 1994). Other streams draining the Drift Prairie yielded only about 0.2 to 0.3 lb/mi^2/d. The Snake River watershed, which drains the Red River Valley Lake Plain almost exclusively, yielded about 0.39 lb/mi^2/d phosphorus. Counties in the Red River Valley Lake Plain had some of the highest phosphorus application rates in the study unit (Tornes and Brigham, 1994). Yields from Moraine streams ranged from about 0.09 lb/mi^2/d in the Otter Tail watershed to about 0.21 lb/mi^2/d in the Wild Rice River watershed. Streams draining the Lake-Washed



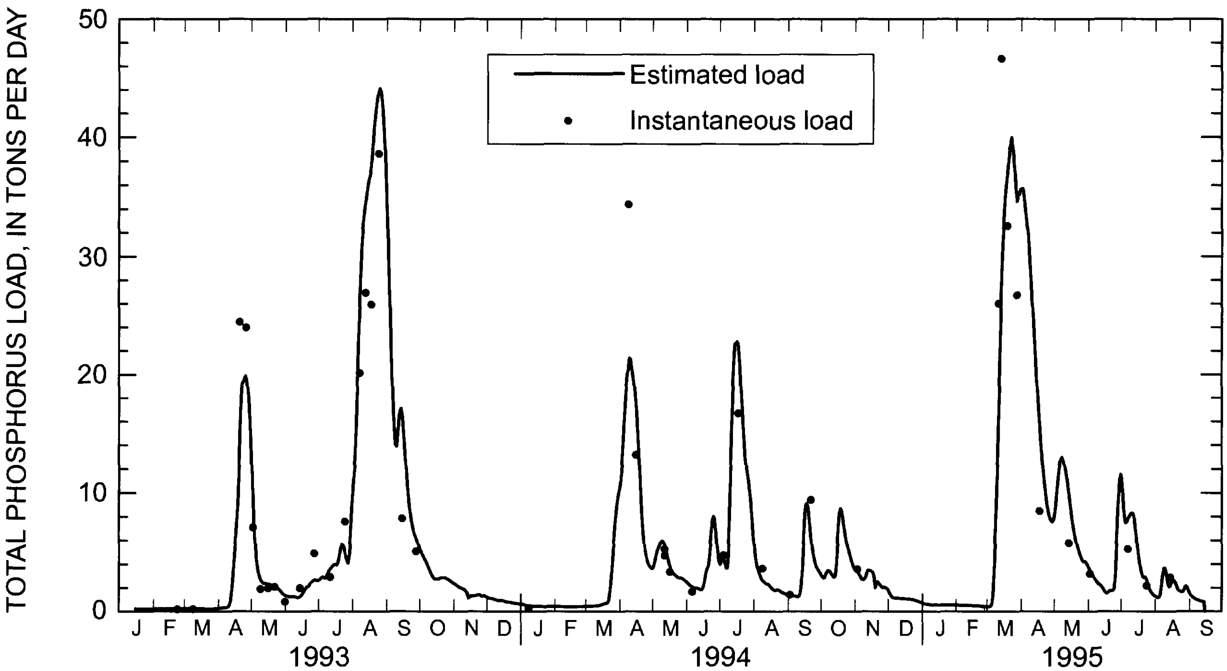


Figure 17. Estimated mean daily and instantaneous loads of total nitrogen and phosphorus in the Red River of the North at Emerson, Manitoba.

Table 7.—Mean load and yield of total nitrogen and phosphorus at streams in the Red River of the North Basin study unit (October 1992–September 1995)

[lb, pound; mi^2, square mile; S.E. pred. (percent), standard error of prediction, expressed as a percentage of the mean load.]

		Nitrogen			Phosphorus		
Map number	Site	Mean load (lb/day)	S.E. pred. (percent)	Mean yield ($lb/mi^2/day$)	Mean load (lb/day)	S.E. pred. (percent)	Mean yield ($lb/mi^2/day$)
1	Sheyenne River at Lisbon, N. Dak.	4,970	13	1.20	959	23	0.232
2	Sheyenne River at Kindred, N. Dak.	5,690	13	1.23	903	16	.196
3	Pembina River at Walhalla, N. Dak.	8,500	14	[1]2.65	1,790	11	[1].558
4	Turtle River at Turtle River State Park near Arvilla, N. Dak.	480	14	2.04	69.4	15	.295
5	Roseau River near Caribou, Minn.	2,940	8	2.01	245	22	.168
6	Red Lake River at Crookston, Minn.	10,800	9	2.20	925	24	.189
7	Otter Tail River near Perham, Minn.	770	6	[2]2.73	28.5	13	[2].107
8	Otter Tail River below Orwell Dam near Fergus Falls, Minn.	2,690	7	1.63	147	15	.0891
9	Wild Rice River at Twin Valley, Minn.	2,780	9	3.22	179	19	.207
10	Snake River above Alvarado, Minn.	707	15	3.50	78.4	20	.388
11	Bois de Sioux River at Doran, Minn.	6,810	13	4.76	984	24	.688
12	Red River of the North above Fargo, N. Dak.	22,100	17	[1]3.46	2,160	13	[1].436
13	Red River of the North at Halstad, Minn.	45,500	11	2.84	6,280	12	.392
14	Red River of the North at Grand Forks, N. Dak.	68,900	8	2.91	7,910	14	.333
15	Red River of the North at Emerson, Minn.	88,800	9	2.71	10,800	8	.329

[1]Based on data from October 1993 through September 1995.

[2]Based on data from October 1994 through September 1995.

Till Plain averaged about 0.18 $lb/mi^2/d$. The Otter Tail watershed phosphorus yields may be low because numerous lakes and reservoirs upstream of the sampling site act as sinks for phosphorus in the system. Yields determined for the Red River at the Canadian border were about the same as the average yield of the tributaries sampled. Yields along the Red River decreased downstream.

Mass balance

A rigorous mass balance of nutrients accounts for all inputs of nutrients including fertilizer, human and animal waste, atmospheric inputs, and nitrogen fixation; and outputs including crop harvesting, denitrification, and transport by rivers. The mass balance also must include settling of particle-bound

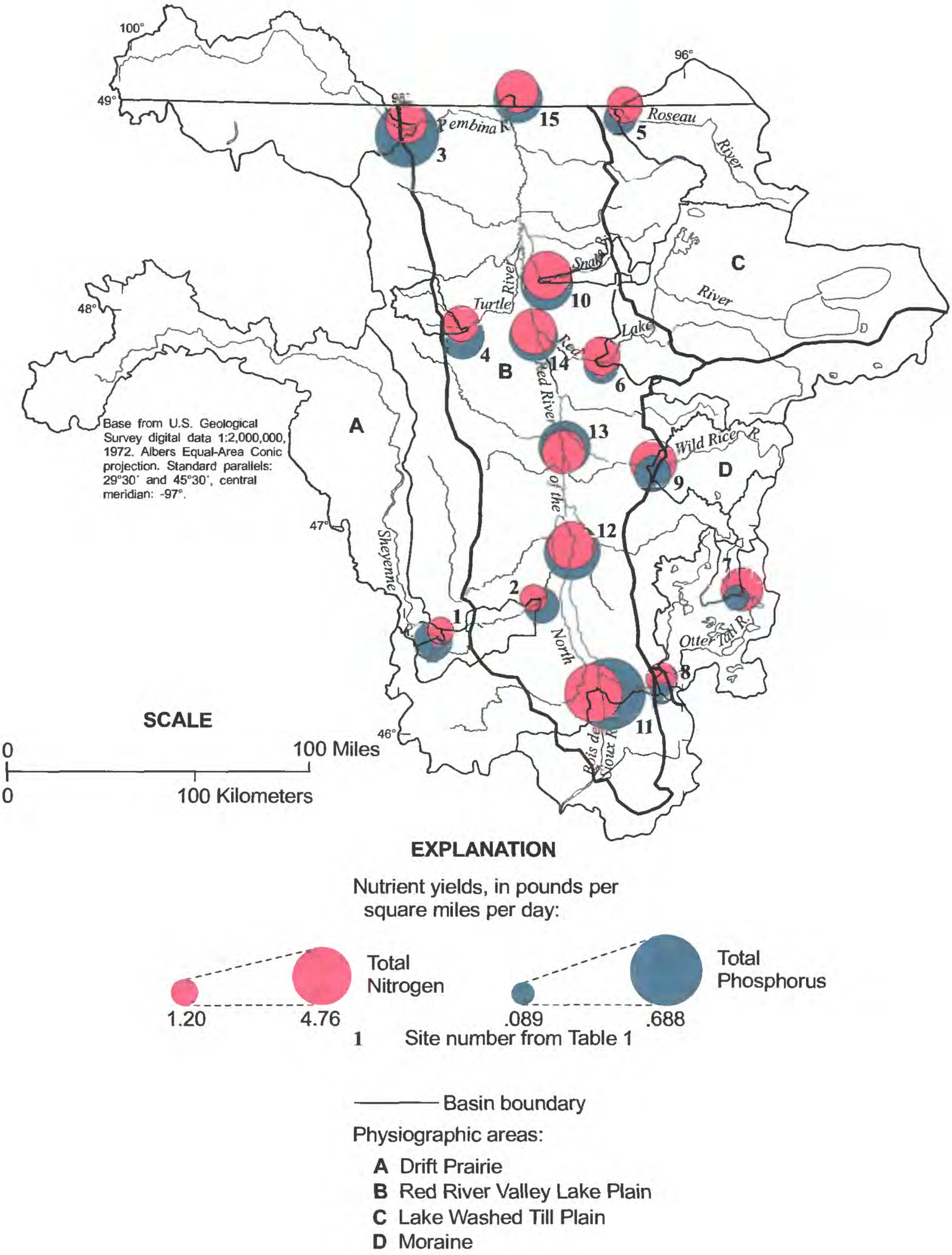


Figure 18. Average yield of total nitrogen and total phosphorus in streams in the Red River of the North Basin study unit.

nutrients to the bottom of streams, lakes, reservoirs, and wetlands. It is beyond the scope of this report to do a complete mass-balance analysis. Only an estimate of the percentage of inputs leaving the basin in the Red River at Emerson, Manitoba, will be made.

The fertilizer application rates reported in Tornes and Brigham (1994) were checked against application rate data available from other sources and determined to be as reliable or more reliable than other sources of data. The county statistics reported were modified to account for the proportion of that county actually within the Red River Basin study unit. Nitrogen from atmospheric sources reported in Tornes and Brigham (1994) also was added to account for that additional source of nitrogen. Nitrogen and phosphorus inputs from sewage treatment plants were determined from average permitted flows for each of the 11 major communities in the study unit, and assuming that all sewage effluent had an average concentration of 11.2 mg/L nitrogen and 7.0 mg/L phosphorus (Larry Puckett, U.S. Geological Survey, written commun., 1993). Nitrogen added to the soil by nitrogen-fixing bacteria was not included.

The loads determined for the Red River at Emerson, Manitoba (shown in table 8), were assumed to encompass essentially all of nutrient transport in streams out of the Red River Basin study unit, excluding loads from the Roseau River Basin, which flows into the Red River downstream from Emerson. The loads determined for this study are considerably higher than reported in Tornes and Brigham (1994) because of increased runoff during this study. Based on data from Tornes and Brigham , 1994), the output of nitrogen and phosphorus at Red River at Emerson, Manitoba, typically is less than 2 percent of the total input to the drainage basin (table 8).

Suspended Sediment

Suspended sediment is composed of clay-sized to sand-sized particles. For this report, suspended sediment was divided into two classes, finer than sand or coarser than sand (63 µm).

Concentration and distribution

Figure 19 shows the distribution of suspended-sediment concentrations at each of the sites sampled for this study. The Pembina River had the highest concentrations of suspended sediment with about one-half the values greater than 400 mg/L and the largest range in values; more than 10 percent of the values were greater than 1,200 mg/L. The lowest concentrations and ranges were measured in streams largely affected by lakes, reservoirs, and wetlands where sediment in water can be deposited. These streams include the Otter Tail, Roseau, Turtle, Red Lake and Bois de Sioux Rivers.

Streams draining or flowing through the Red River Valley Lake Plain, including the Snake River and the four sites on the Red River, had relatively high and variable sediment concentrations. The median sediment concentration increased downstream along the Red River, except at Grand Forks where concentrations probably are diluted by the Red Lake River.

Table 8.—Nutrient mass balance for the Red River of the North Basin study unit
[units in millions of pounds per year]

	Inputs				Load at Emerson, Manitoba	Percent output
	Application	Atmospheric	Wastewater	Total		
Nitrogen						
1979-88[1]	765	30.4	2.12	798	15.0	1.88
1993-95	765	30.4	2.12	798	32.4	4.06
Phosphorus						
1975-88[1]	161	0	1.33	162	2.76	1.07
1993-95	161	0	1.33	162	3.94	2.43

[1]From Tornes and Brigham, 1994.

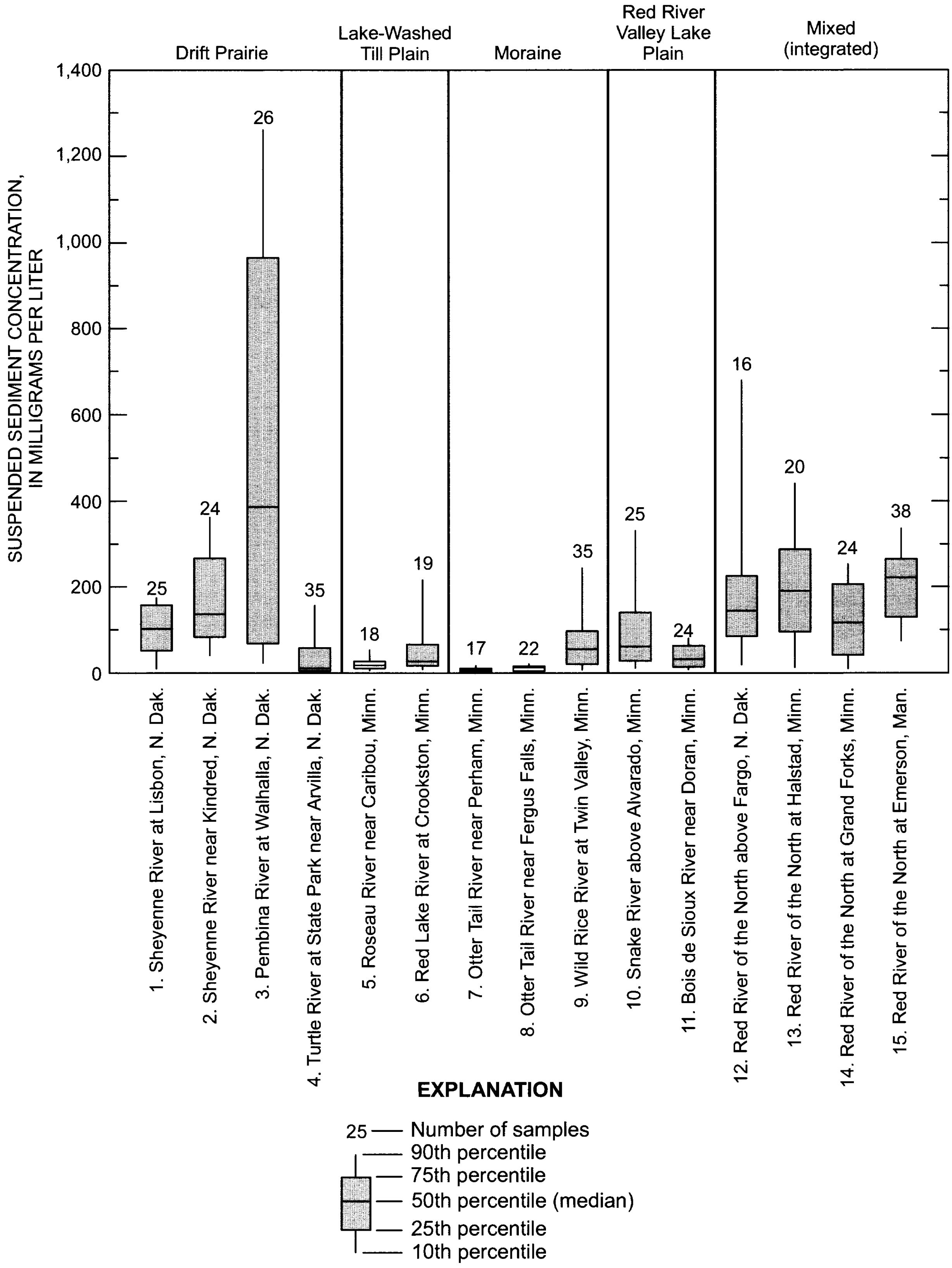


Figure 19. Distribution of suspended-sediment concentrations in streams in the Red River of the North Basin study unit. (Site number referenced on figure 2)

Although stream and land-surface slopes are relatively flat in the Red River Valley Lake Plain, the soil and streambank material is predominantly clays and silts. These erodible, fine-sized sediments do not require high-streamflow velocities to remain in suspension. A large amount of the sediment carried by these streams may be eroded from streambanks as the streams meander in their channels. However, the relative contributions of upland erosion versus channel erosion to the suspended-sediment load in Red River Basin streams is not known.

Consistent with the findings in Tornes and Brigham (1994), most of the suspended sediment carried by streams in the Red River Basin study unit is finer than sand (63 μm). The distribution of fine sediment looks very similar to what is shown in figure 19, although the values are slightly less. More than 95 percent of the sediment was finer than sand in most samples from most streams. Exceptions were the Otter Tail River near Perham, Minnesota, and the Wild Rice and Turtle Rivers where the median percentages of fine material were 90, 88, and 91, respectively. More than 99 percent of the sediment was finer than sand in at least one-half of the samples from the Red River, the Sheyenne River at Lisbon, and the Snake River.

Another factor affecting sediment concentrations in streams can be the soil upstream of the sampling site. Tributaries to the Red River become visibly more turbid after flowing through the lowest part of the Red River Valley Lake Plain. Lorenz and Stoner (1996) show that the soil texture changes from a mixture of sand and loam in the upper parts of the Red River Valley Lake Plain to a mixture of clay and loam in the lowest parts.

This tendency toward increased sediment concentration as streams cross soils having a high clay content and very poor to moderate drainage (Lorenz and Stoner, 1996) was observed in within-stream, high-flow synoptic samples. After the Turtle River crossed areas having these poorly-drained, clay-rich soils, the sediment concentration increased substantially. Sediment concentration decreased as the stream passed through areas where the soils had a low clay content, then increased again near the mouth of the stream in the Red River Valley Lake Plain. Similar relations were determined in the Snake and Wild Rice Rivers, except at the mouth of the Snake River, which was sampled before the runoff reached that most downstream sampling site.

The Pembina River flows down steep slopes that increase sediment-carrying capacity and also flows through soils that are poorly drained and have a high clay content. These combined factors probably result in the high concentrations measured.

Loads and yields

The regression model Estimator was used to compute sediment loads. However, different parameters were found to be important for modeling suspended sediment than for modeling nutrients. The same model parameters are used for all sites in the study unit, rather than developing a separate model for each site, to simplify comparison between sites. Table 9 shows the model used and the coefficients for the parameters at each of the sites sampled for this study. The sediment-load regression models explain substantially less variation than the nutrient-load models, as indicated by the lower coefficient of determination.

Figure 20 shows the estimated mean daily sediment load compared to the instantaneous suspended-sediment loads measured at the Red River at Emerson, Manitoba. Although some estimated values are substantially different than individual measurements, the average loads for the period of data collection are reasonably accurate (standard error of prediction = 12 percent).

The loads and yields of suspended sediment computed from data collected for this study are shown in table 10. As would be expected, the highest loads generally were carried by the Red River, and the loads increase downstream with increasing streamflow. The Sheyenne and Red Lake Rivers, having a relatively high streamflow during 1993–95, also carried a relatively high load of suspended sediment.

The 1,010 $lb/mi^2/d$ sediment yield from the Pembina River watershed was more than twice the yield determined for any other sampling site in the study unit. The steep slopes that increase sediment-carrying capacity and the erodible clayey soils are the primary cause of this high sediment yield. The next highest yields were at sites along the Red River where erodible streambank material is available for transport. It is uncertain why sediment yields measured at the Red River above Fargo, North Dakota, were so high compared to other sites, including most tributaries, but this site was sampled only during 1994–95, and snowmelt runoff (when soils are likely to be exposed to erosive forces) was unusually high during 1995

Table 9.—Model parameters and coefficients used to calculate suspended-sediment loads for streams in the Red River of the North Basin study unit (1993-95)

[ln, natural logarithm; S, suspended sediment load; Q, streamflow in cubic feet per second; a, b, and c are model coefficients; q, center value for logarithm of streamflowl; R^2, coefficient of determination]

Site number (figure 2)	Site	a	b	c	q	R^2
	$\ln(S) = a+b*[\ln(Q)-q]+c*[\ln(Q)-q]^2$					
1	Sheyenne River at Lisbon, N. Dak.	11.89	1.54	-0.057	6.351	76.5
2	Sheyenne River at Kindred, N. Dak.	12.44	1.56	-.054	6.475	81.2
3	Pembina River at Walhalla, N. Dak.	13.05	1.84	-.14	6.403	95.8
4	Turtle River at Turtle River State Park near Arvilla, N. Dak.	7.86	1.81	.20	4.144	86.7
5	Roseau River near Caribou, Minn.	9.00	1.13	-.059	5.166	85.4
6	Red Lake River at Crookston, Minn.	12.61	2.17	.099	7.829	89.8
7	Otter Tail River near Perham, Minn.	8.41	1.23	.29	5.466	32.7
8	Otter Tail River below Orwell Dam near Fergus Falls, Minn.	8.86	1.28	1.3	6.237	30.4
9	Wild Rice River at Twin Valley, Minn.	11.31	2.08	-.32	6.198	84.0
10	Snake River above Alvarado, Minn.	8.64	1.36	-.010	3.651	92.9
11	Bois de Sioux River at Doran, Minn.	8.76	1.04	.010	4.581	89.5
12	Red River of the North above Fargo, N. Dak.	13.32	1.59	-.20	8.415	78.3
13	Red River of the North at Halstad, Minn.	15.10	1.36	-.85	8.415	87.0
14	Red River of the North at Grand Forks, N. Dak.	15.05	1.76	-.95	8.874	87.1
15	Red River of the North at Emerson, Minn.	15.67	1.34	-.66	9.108	85.3

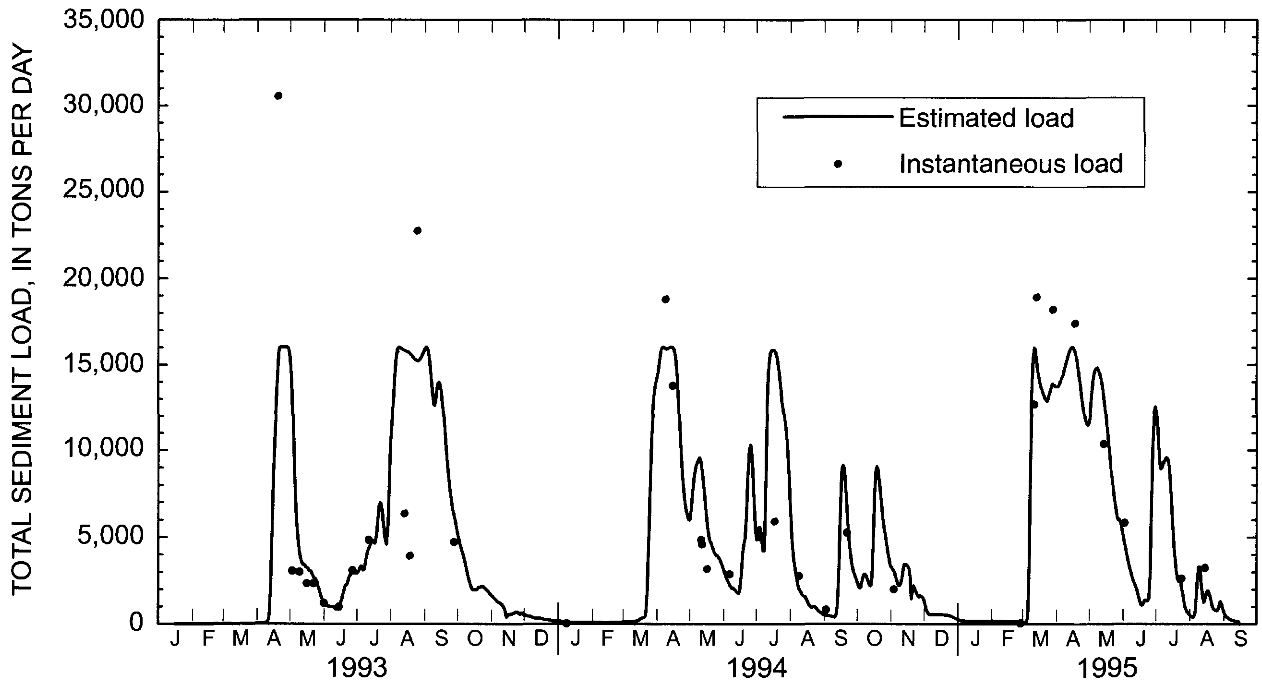


Figure 20. Estimated mean daily and instantaneous loads of suspended sediment in the Red River of the North at Emerson, Manitoba.

Table 10.—Mean annual load and yield of suspended sediment for streams in the Red River of the North Basin study unit (October 1992–September 1995)

[lb, pound; mi^2, square mile; S.E. pred., standard error of prediction, expressed as a percentage of the mean load]

Site number (figure 2)	Site	Mean load (lb/day)	S.E. pred. (percent)	Yield ($lb/mi^2/day$)
1	Sheyenne River at Lisbon, N. Dak.	527,000	39	117
2	Sheyenne River at Kindred, N. Dak.	795,000	29	159
3	Pembina River at Walhalla, N. Dak.	323,000	27	[1]1,010
4	Turtle River at Turtle River State Park near Arvilla, N. Dak.	30,600	61	120
5	Bois de Sioux River at Doran, Minn.	124,000	21	65.1
6	Snake River above Alvarado, Minn.	49,300	36	226
7	Roseau River near Caribou, Minn.	51,300	25	33.0
8	Red Lake River at Crookston, Minn.	576,000	27	109
9	Otter Tail River near Perham, Minn.	11,200	28	[2]33.4
10	Otter Tail River below Orwell Dam near Fergus Falls, Minn.	45,400	31	26.1
11	Wild Rice River at Twin Valley, Minn.	189,000	24	203
12	Red River of the North above Fargo, N. Dak.	2,560,000	37	[1]387
13	Red River of the North at Halstad, Minn.	4,400,000	19	254
14	Red River of the North at Grand Forks, N. Dak.	5,150,000	20	200
15	Red River of the North at Emerson, Man.	8,500,000	12	239

[1]Based on data from October 1993 through September 1995.

[2]Based on data from October 1994 through September 1995.

(fig. 4). Also, the load estimates for this site are based only on 16 observations, and the standard error is relatively large. Yields generally decrease along the Red River because some portion of the sediment is dropped from suspension. The Snake River, which like the Red River, flows through the Red River Valley Lake Plain, had relatively high sediment yields. Streams draining watersheds having considerable numbers of lakes, reservoirs, or wetlands (the Otter Tail and Roseau Rivers) had the lowest sediment yields. Reservoirs probably also reduced sediment yields for the Bois de Sioux River watershed. Other streams in the study unit had sediment yields ranging from more than 109 $lb/mi^2/d$ in the Red Lake River drainage basin to 203 $lb/mi^2/d$ in the Wild Rice River drainage basin.

Pesticides

Of the pesticides listed in tables 4 and 5, only a few were routinely used throughout the study unit. Many pesticides were used only on certain crops and/or in certain parts of the study unit. Table 11 shows commonly used pesticides on selected crops in the study unit determined by consulting state publications on reported pesticide application rates (Minnesota Department of Agriculture, 1992; North Dakota State University, 1992). Only one, relatively infrequently used fungicide was analyzed for this study. Because of the wet conditions that occurred during this study, fungicide use was probably above normal.

Concentration and distribution

Forty-two pesticides and two pesticide metabolites analyzed for this study were detected in one or more stream samples from the study unit. Although usage of some pesticides detected in this study is not documented in most publications, it is possible that they are used in small quantities on certain specialty crops. The pesticides and related compounds that were

Table 11.—Herbicides and insecticides commonly used in the Red River of the North Basin study unit and the crops on which they are applied

Compound	Crop
Herbicides	
2,4-D	Barley, field corn, oats, timothy, wheat
Acifluorfen	Soybeans
Alachlor	Field corn
Atrazine	Field corn
Bentazon	Edible beans, soybeans
Bromoxynil	Barley, field corn, wheat
Clopyralid	Sugar beets
Cyanazine	Field corn
Cycloate	Sugar beets
Desmedipham	Sugar beets
Dicamba	Field corn, timothy, wheat
Diclofop	Wheat
EPTC	Field corn, potatoes, sugar beets
Ethalfluralin	Edible beans, soybeans, sunflowers
Imazethapyr	Soybeans
MCPA	Barley, oats, timothy, wheat
Nicosulfuron	Field corn
Pendimethalin	Potatoes
Phemedipham	Sugar beets
Sethoxydim	Soybeans, sugar beets
Thifensulfuron	Wheat
Tribenuron	Barley, wheat
Trifluralin	Barley, edible beans, potatoes, soybeans, sunflowers, wheat
Insecticides	
Azinphos-methyl	Potatoes
Carbofuran	Potatoes
Chlopyrifos	Sugar beets
Endosulfan	Potatoes
Esfenvalerate	Potatoes, sunflowers
Ethyl Parathion	Sunflowers
Methamidophos	Potatoes
Phorate	Potatoes
Terbufos	Sugar beets

detected in more than one-half of the samples from the study unit include: (in decreasing frequency of detection) atrazine, desethyl atrazine (an atrazine metabolite), metolachlor, and cyanazine. Table 16 (at the back of the report) lists the compounds detected at intensive sites and for all remaining sampled sites.

Detection of pesticides in the streams sampled was highly seasonal and related to runoff events. The highest concentrations of pesticides were detected during runoff events following application (Tornes and Brigham, 1995).

Atrazine was the most commonly detected pesticide at all five of the intensive (pesticide) sampling sites. Atrazine is the most heavily applied organic pesticide in the United States (Majewski and Capel, 1995). It was detected in every sample from both sites on the Red River—in 90 percent of the samples from the Wild Rice and Snake Rivers and in 74 percent of samples in the Turtle River. Atrazine is commonly applied to corn. Because this crop was grown in the watersheds upstream from all sites sampled for pesticides, the occurrence of atrazine at all sampling sites was not surprising. However, its occurrence in all samples from the Red River indicates that it is persistent in stream water throughout the year, as it also was detected in several samples that were collected in the winter when runoff did not occur. This year-round persistence of atrazine probably results from the release of reservoir or lake water containing pesticides from previous applications. Battaglin and Goolsby (1996) reported persistence of herbicides in outflow from reservoirs in the midwestern United States. It is likely that other herbicides persist to a certain extent, but atrazine has relatively higher concentrations and a very low MDL (0.001 µg/L), making it more likely to be detected throughout the winter.

The maximum atrazine concentration, 4.5 µg/L, was measured in the Turtle River during an early summer runoff event; this unusually high concentration was corroborated by a sample collected at a site downstream of our routine sampling site. The concentration is greater than the U.S. Environmental Protection Agency's (1996) drinking water standard of 3 µg/L. Figure 21 shows the distribution of atrazine concentrations at the five intensive sites. Although the Turtle River had the highest measured atrazine concentration, it usually had relatively low concentrations. The highest concentrations generally occurred in the Red River, especially at the site upstream of Fargo.

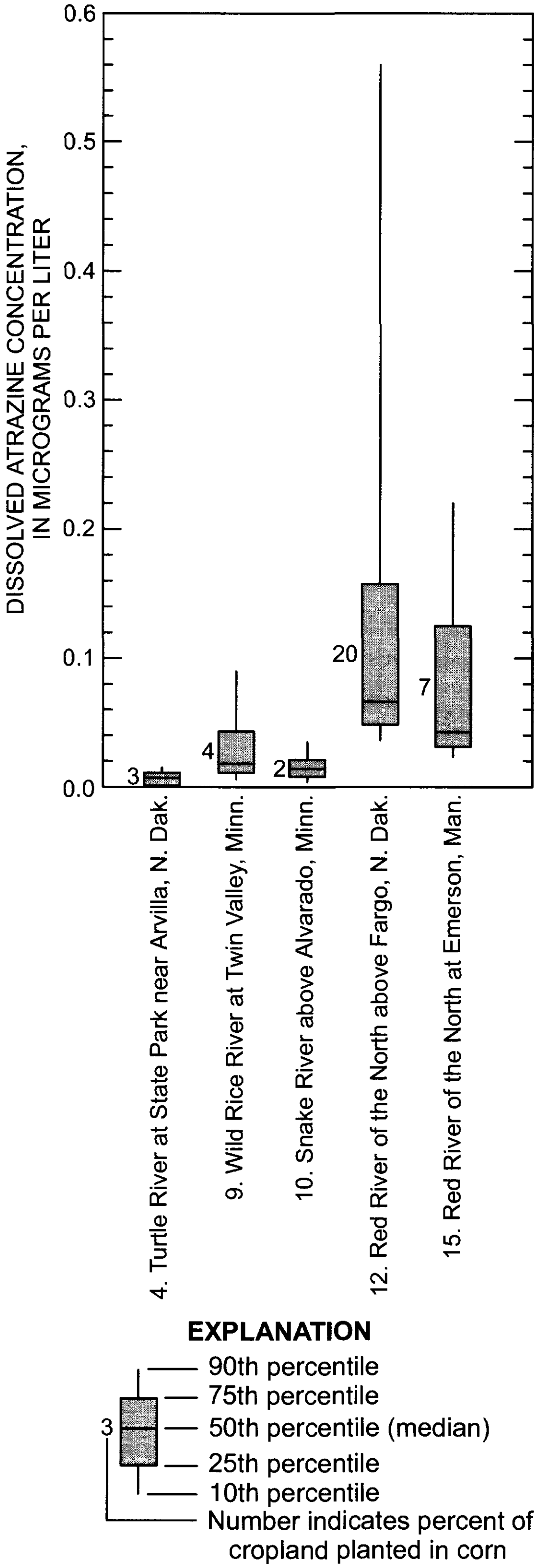


Figure 21. Distribution of atrazine concentrations at pesticide sampling sites in the Red River of the North Basin study unit.(Site number referenced on figure 2)

Corn is a common crop in the watershed upstream from Fargo, but is grown less commonly in other parts of the study unit. The distribution of atrazine concentrations shown in figure 21 generally reflects the percent of cropland in the basin planted in corn upstream of the sampling sites.

Another potential source of atrazine and other pesticides, particularly in watersheds where the pesticide is not used, is from transport through the atmosphere. Majewski and Capel (1995) report that precipitation-weighted atrazine concentrations in rainfall over the Red River Basin study unit during mid-April through mid-July ranged from below detection (less than 0.05 µg/L) to nearly 0.30 µg/L in samples collected during 1990 and 1991.

The second most commonly detected pesticide compound was a metabolite of atrazine, desethylatrazine. It was detected in 66 percent of the samples collected throughout the study unit. Desethylatrazine had a mean spiked-sample recovery of 43 percent, so these data are biased low. The rate of detection and concentrations at each of the sampling sites were proportional to, but less than, those found for atrazine. Another principal metabolite of atrazine, desisopropylatrazine, was not analyzed for this study.

Metolachlor, used on a variety of crops including corn, beans, and potatoes, was detected in 61 percent of the pesticide samples. Although it was the second most commonly detected pesticide in the Turtle River, the concentrations of metolachlor were highest in the Red River, especially at the site upstream of Fargo. This probably results from extensive use on corn, which is grown primarily in the southern part of the study unit.

Cyanazine, which is used only on corn, was detected in 57 percent of samples from the study unit and was the second most commonly detected pesticide at both sites on the Red River. It was detected much less frequently in the Snake (36 percent) and Turtle (26 percent) Rivers.

Triallate was the fourth most commonly detected pesticide and occurred in 46 percent of the samples from the study unit. Unlike the top three detected pesticides, triallate is not used on corn, but is used on a variety of other crops including small grains, beans, and sunflowers. It was detected in less than 20 percent of the samples collected in the Red River upstream from Fargo, but was detected in more than 80 percent of the samples from the Snake River and more than 65 percent of the samples from the Wild Rice River. Figure 22 shows the distribution of triallate concentrations at each of the intensive pesticide-sampling sites. Although the Snake River had the highest average triallate concentrations, a few high concentrations also were measured in the Wild Rice River. The Red River at Emerson, Manitoba, had higher concentrations than the site upstream of Fargo, because of inputs from tributaries downstream of Fargo. One sample from the Snake River had a triallate concentration of 0.28 µg/L, which exceeds the interim Canadian guidelines for the protection of freshwater aquatic life (Canadian Council of Ministers of the Environment, 1992).

EPTC is used on a variety of crops including corn, potatoes, sugar beets, and edible beans and was found in about one-fourth to one-half of the samples from each of the sampling sites. The highest concentrations occurred in the Red River upstream of Fargo and the lowest in the Wild Rice River, but differences in concentrations between sites were much less than for other pesticides.

Simazine was the sixth most commonly detected pesticide in the study unit. This was unexpected because it generally is not used for agricultural purposes although it occasionally is applied to pasture. Application records (Minnesota Department of Agriculture, 1992; and North Dakota State University, 1992) suggest that simazine had very limited agricultural use in the study unit during this study. Majewski and Capel (1995) indicate that simazine is detected in rain samples much more frequently than would be expected from normal agricultural use, and that significant nonagricultural use, such as right-of-way application, probably accounts for that increased occurrence. Simazine also is relatively persistent compared to other pesticides (Barbash and Resek, 1996). The distributions of simazine concentrations were virtually identical at each of the sampling sites suggesting that simazine inputs were relatively uniform across the study unit. This relative conformity is consistent with an atmospheric source of simazine.

Prometon also was detected frequently in Red River Basin streams, but like simazine, generally was not applied to crops in the study unit. Majewski and Capel (1995) indicated that prometon rarely was used in agriculture and that it was detected in rainwater. Barbash and Resek (1996) reported that prometon often was used to control plant growth along powerlines, roadways, and other rights-of-way.

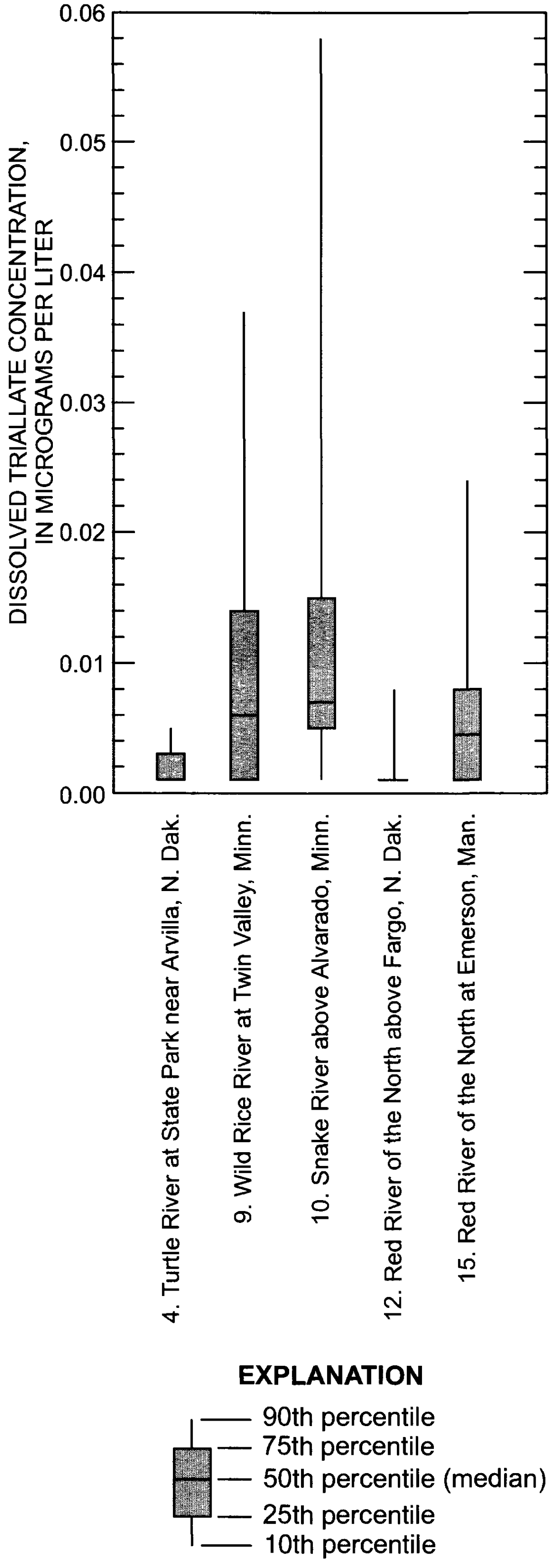


Figure 22. Distribution of triallate concentrations at pesticide sampling sites in the Red River of the North Basin study unit. (Site number referenced on figure 2)

Therefore, prometon could be carried into the study unit from external sources by atmospheric processes or distributed throughout the study unit by widespread application to rights-of-way.

Two other commonly detected herbicides, trifluralin and bentazon, were used on a variety of crops grown throughout the study unit.

2,4-D and MCPA are the most heavily used herbicides in the study unit, but were not the most frequently detected. These closely-related compounds are used to control broadleaf weeds in a variety of crops, including most small grains and corn, and often are used on fallow acres and for domestic purposes. 2,4-D was detected in 12 percent of samples and was most frequently detected in the Snake River (21 percent). MCPA was most frequently detected in the Turtle River where it was found in 11 percent of the samples. Although results for these compounds are variable, more frequent detection might be expected solely based on usage rates. Because both of these herbicides are directly applied to vegetation, they probably are rapidly taken up and metabolized by the target plants. Many pre-emergent herbicides, on the other hand, are applied to the soil where they may be washed into adjacent surface water. If 2,4-D and MCPA reach the soil, Montgomery (1993) suggested that both can degrade quickly (several days) under optimum conditions of sunlight, soil moisture, and the presence of certain soil bacteria. It is likely that most 2,4-D and MCPA degraded before reaching the sampled streams.

Acetochlor is an herbicide that was licensed for use exclusively on corn starting in 1994 in Minnesota. It is used as a substitute herbicide for atrazine, and its use is partly intended to help reduce the concentrations of atrazine and related compounds detected in water supplies in some parts of the United States. We began analyzing for acetochlor in 1994. Acetochlor was not detected in any of the samples from the three tributary streams, but was detected in 38 percent of the samples collected upstream of Fargo with a maximum concentration of 0.11 μg/L. Acetochlor use probably is greatest in this part of the study unit. There are insufficient data to conclusively show that atrazine load was lower in 1994 and 1995 than in 1993.

All of the pesticides discussed above are herbicides. Insecticides were infrequently detected in samples from the study unit. This infrequent detection probably is because they are effective at controlling target biota at much lower concentrations than herbicides, so residual concentrations in the environment would be proportionately lower—probably lower than our ability to detect them.

Carbofuran was the most frequently detected insecticide and was found in about 16 percent of the samples. The highest concentration found was about 0.4 µg/L, well below the 40 µg/L drinking water standard (U.S. Environmental Protection Agency, 1996). Carbofuran concentrations generally were below 0.015 µg/L. Carbofuran is used mostly on potatoes (table 11), but also is applied to a variety of crops including small grains. Carbofuran was detected most frequently (25 percent of samples) in the Red River at Emerson, Manitoba, which is downstream of all the other sampling sites. Many of the highest concentrations were measured in the Snake River. High carbofuran concentrations with fewer detections show the effects of this compound being flushed into the stream with subsequent dilution and/or degradation to levels below detection limits.

Other insecticides that were analyzed were detected in less than 5 percent of samples from the study unit. Some of the more commonly applied insecticides that were analyzed but not, or rarely, detected include esfenvalerate, chlorpyrifos, malathion, parathion, and turbufos.

Pesticides in synoptic samplings followed the regional patterns seen at the intensive-sampling sites. The triazine herbicides (including atrazine and cyanazine) often were found in samples from throughout the basin, but concentrations were highest where corn is a major crop and lowest or not found in areas where corn is a minor crop. Simazine and prometon were rarely detected in basin-wide or within-stream synoptic samples. Detections followed no particular pattern, but concentrations were quite low. Triallate was rarely detected in synoptic samples from southern streams where small grains production is less, but it was frequently detected in synoptic samples from more northern streams. 2,4-D, MCPA, and the insecticide carbofuran were rarely detected, or found at very low concentrations, in synoptic samples.

Pesticide samples collected during synoptic sampling in each of the drainage basins of intensive sites showed some common characteristics. The number of pesticides detected generally increased downstream. Concentrations of several pesticides increased downstream; these included atrazine in the Wild Rice River, EPTC in the Turtle and Snake Rivers, and triallate in the Wild Rice and Snake Rivers.

The above summary uses raw data without accounting for analytical differences among the pesticides. Differences in method detection limits and analytical recovery affect frequencies of detection. To account for such differences, we chose a censoring level of 0.1 µg/L for all pesticides and multiplied this value by the mean spike-sample recovery for each pesticide. Based on these recovery-corrected censoring levels, the most frequently detected pesticides at concentrations greater than or equal to 0.1 µg/L (last column in table 16, at the back of the report), ordered by decreasing frequency, were bentazon, atrazine, 2,4-D, acifluorfen, and MCPA; all other compounds were detected at this level in less than 5 percent of the samples considering results from all sites.

The relation between pesticide occurrence in streams and its application to fields is very complicated, affected by the physical properties of the pesticide, the method and timing of application, weather, soil properties, and the physical setting of the field. Table 12 is a listing of crops grown on each of three basins in the Red River Basin, and table 13 is a listing of relative application rates of selected pesticides in each of those basins. Figure 23 shows the percent of each pesticide detected at greater than or equal to 0.1 µg/L. Table 14 is a listing of the physical properties of selected pesticides. It is difficult to infer any relation between application rates, physical properties, and frequency of detection as presented in tables 12–14 and figure 23.

Loads and mass balance

Based on relative rates of application and detection, atrazine, triallate, and 2,4-D were considered important herbicides in the study unit in terms of calculating loads and mass balance for the Red River at Emerson, Manitoba. Loads and mass balances were not computed for other sites because of the uncertainty of application rates of pesticides. Estimator was used to calculate atrazine and triallate loads, but 2,4-D had such a high proportion of censored (below the MDL) values that Estimator could not be used. Therefore, 2,4-D loads were estimated from instantaneous measured values of concentration and streamflow. When 2,4-D values were censored, the concentration was assumed to be one-half the MDL. This can

Table 12.—Average percentage of cropland planted (1993–95) in selected crops in each of three selected basins within the Red River of the North Basinstudy unit

Crop	Wild Rice River at Twin Valley	Turtle River at Turtle River State Park	Snake River near Alvarado
Small grains	49	56	66
All beans	11	14	12
Sunflowers	11	10	5
Corn	4	3	2
Oats	2	1	1
Sugar beets	1	0	5
Potatoes	0	3	2

Table 13.—Approximate relative pesticide application rates on selected basins in the Red River of the North Basin study unit

[The number is based the sum of the percent of crop treated multiplied by the percent of crop grown in the basin for each crop (Minnesota Department of Agriculture, 1992; and North Dakota State University, 1992). A value of 2 is used arbitrarily as the low value, based on the uncertainty of information for any pesticide/crop combination, and is assumed to apply to pesticides approved for use in Minnesota or North Dakota, but not listed in this table.]

Compound	Wild Rice River at Twin Valley	Turtle River at Turtle River State Park	Snake River near Alvarado
Trifluralin	48	56	58
2,4-D	31	34	39
MCPA	29	33	39
Dicamba	26	29	33
Bromoxynil	15	17	20
Ethalfluralin	12	13	9
Tribenuron	11	12	15
Sethoxydim	9	11	8
Bentazon	6	7	3
Imazethapyr	2	3	2
Esfenvalerate	2	2	2
Desmedipham	2	2	9
Terbufos	2	2	3
Phemedipham	2	2	5
Pendimethalin	2	3	2
Methamidophos	2	5	2
Ethyl parathion	2	2	3
Carbofuran	2	3	2

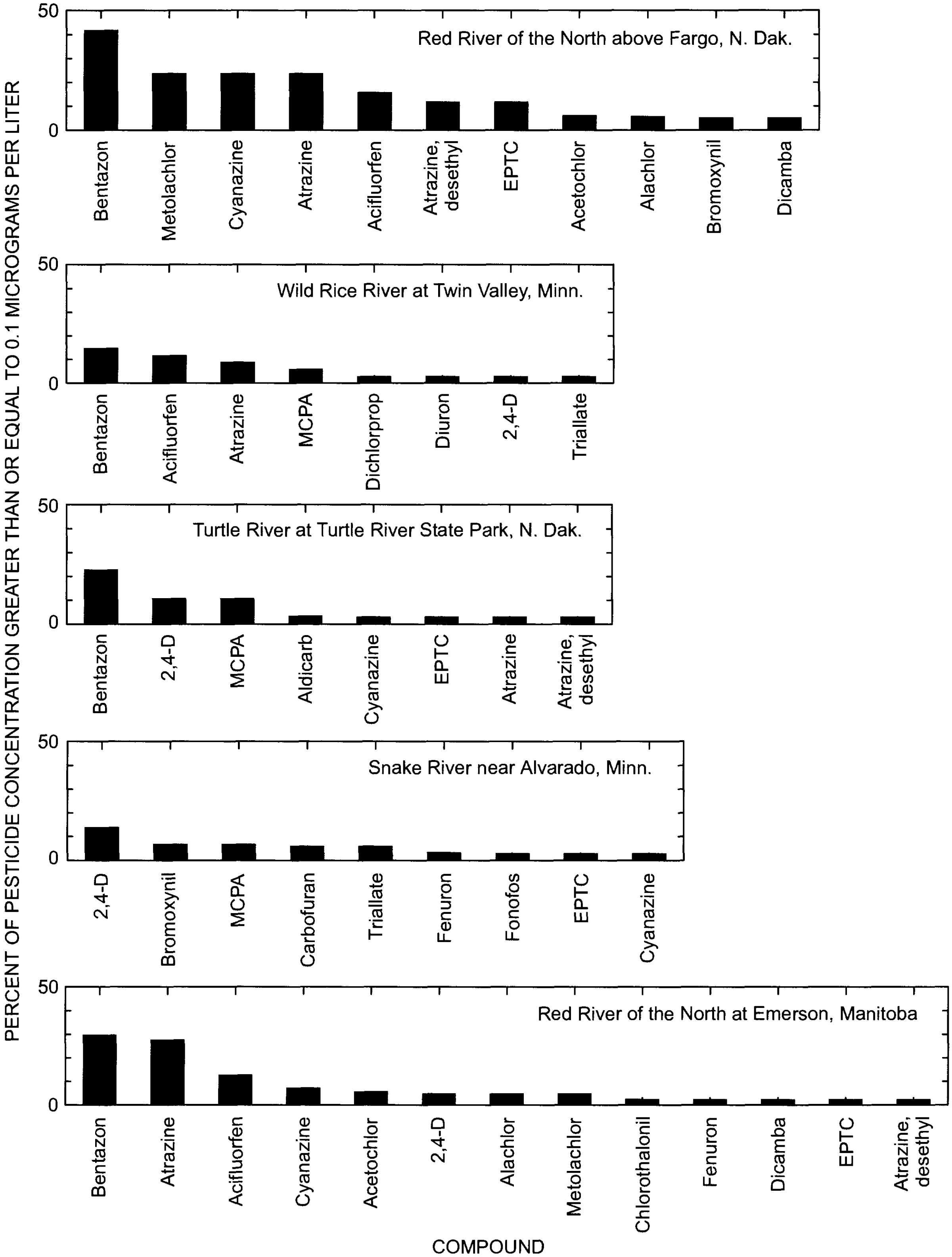


Figure 23. Percent of pesticides detected at concentrations greater than or equal to 0.1 micrograms per liter with recovery correction at selected sites in the Red River of the North Basin study unit.

Table 14.—Physical properties of selected pesticides

[Preferred values from the Agricultural Research Service Pesticide Properties data base (URL: http://www.arsusda.gov/rsml/ppdb.html); --, no data]

Compound	Solubility in water (parts per million)	Field dissipation rate (days)	Vapor pressure (millipascals)	Base 10 logarithm of the octanol/water partitioning coefficient
2,4-D-acid	23,180	14	0.019	-0.75
Acifluorfen	129	31	.0013	--
Alachlor	240	27	2.9	2.90
Aldicarb	5,900	50	.387	1.13
Atrazine	33	173	.038	2.68
Azinphos-methyl	29	10	.213	2.8
Bentazon	500	27	.001	--
Bromoxynil	14	10	9	4.46
Carbofuran	350	41	.082	1.41
Chlopyrifos	1.18	43	2.5	5.0
Chlorothalonil	.6	48	.076	2.88
Clopyralid	9,000	13	1.7	2.55
Cyanazine	170	30	.000213	2.1
Cycloate	95	27	210	--
Desmidipham	9	30	.0004	3.52
Dicamba	8,310	16	1.66	.54
Dichlorprop	350	10	.013	3.0
Diuron	42	90	.0092	2.8
Endosulfan	.32	60	.023	3.3
EPTC	375	18	3,200	3.13
Esfenvalerate	.002	42	.0002	4.0
Ethalfluralin	.3	41	12	5.11
Ethyl parathion	11	14	.89	3.83
Fenuron	850	60	5	--
Fonofos	16.9	37	45	3.9
Imazethapyr	1,400	95	.013	1.5
MCPA	825	25	.2	2.8
Methamidophos	miscible	3.5	4.27	-.79
Metolachlor	488	141	4.2	2.6
Nicosulfuron	2,000	21	.161	-1.70
Pendimethalin	.275	174	1.2	5.2
Phenmedipham	22	37	84.7	3.92
Sethoxydim	4,700	5	.02	1.38
Terbufos	4.5	12	42.0	4.7
Triallate	4	74	14.6	4.29
Tribenuron	2,040	10	.000053	-.44
Trifluralin	.32	81	14.6	5.07

overestimate actual 2,4-D concentrations. However, the variable and occasionally low analytical recoveries of this compound tend to low-bias 2,4-D data from this study. The load estimates for 2,4-D are considered gross estimates.

Table 15 shows the estimate of average annual application in the study unit of the three selected herbicides and the estimated annual load of those herbicides carried, during 1993–95, by the Red River at Emerson, Manitoba. The annual application was estimated from acreage planted (Minnesota Agricultural Statistics Service, 1991; and North Dakota Agricultural Statistics Service, 1992), acreage treated (Minnesota Department of Agriculture, 1992; and North Dakota State University, 1992), and application rates (Minnesota Extension Service, 1991) for each crop treated with atrazine, triallate, or 2,4-D. Desethylatrazine, a metabolite of atrazine, was not added to the atrazine load shown. A variety of 2,4-D formulations are applied to crops, but in aquatic systems they are rapidly converted to the acid form that was analyzed for this study.

Typically less than 1 percent of the atrazine applied in the study unit was carried out of the study unit. Because this does not account for the primary atrazine metabolites, the total amount carried out probably is larger. Although triallate is more widely used, only 0.06 percent of this compound was carried out of the study unit. 2,4-D is the most extensively applied pesticide used in the study unit, but only 0.02 percent of it is found in the streams.

Implications for Water Quality

Although streamflow during this sampling period was considerably above normal, the data collected help define constituent transport at higher, rarely-sampled flow regimes. Load models developed from this data set should be reasonably accurate for a variety of flow conditions, except during extreme low flows when processes other than runoff control constituent transport.

Most stream quality generally can be related to physiographic areas in the Red River Basin, which represent relatively homogenous areas of land use, land cover, and other factors affecting water quality. This is particularly true for major ions, especially sulfate, but also is applicable for nutrients, pesticides, and organic carbon.

Some streams are affected by local conditions and stand out as potential locations where changes in water and land management might better protect water resources of the study unit. One of these is the Bois de Sioux River where sulfate, probably from geologic sources, makes the stream chemistry very different from other streams that were sampled for this study. Sulfate affects potability, which has implications for municipal supply for Fargo. In addition to having high sulfate and low dissolved-oxygen concentrations, the Bois de Sioux River also has relatively high concentrations of nitrogen and phosphorus. It is likely that farming practices are a major source of these nutrients.

Figure 24 shows the relation between annual application rates and yields for both nitrogen and phosphorus for 14 stations in the basin based on 1993–95 data. Site 3 (the Pembina River) was not included because about 60 percent of the basin lies in Canada, for which we had no application data. A regression analysis indicated that the average annual yield was about 4 percent of the applied nitrogen and 2.8 percent of the applied phosphorus. In both regression analyses, the intercept was not appreciably different from

Table 15.—Estimated average annual application and stream load at Emerson, Manitoba, of three selected pesticides used in the Red River of the North Basin study unit

[units in pounds per year]

Pesticide	Annual rate of application (1990)	Load at Emerson (1993–95)	Percent output
Atrazine	120,000	1,100	0.9
Triallate	450,000	270	.06
2,4-D	1,700,000	370	.02

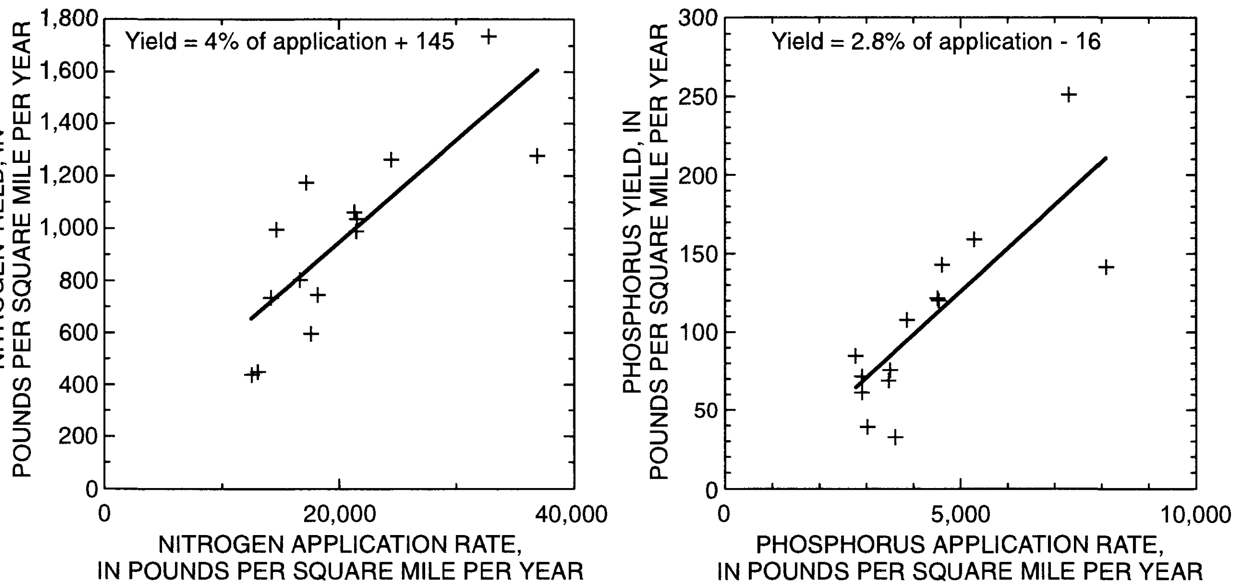


Figure 24. Relation between average annual application rates and yields for nitrogen and phosphorus in the Red River of the North Basin, 1993-95 study unit.

zero,and the relation/regression was highly significant (at the 0.001 significance level). The application rates were computed from Alexander and Smith (1990) and are assumed to be approximately valid for the 1993–95 period. Although other factors may account for some of the nitrogen and phosphorus in streams, it appears that application of fertilizers affects stream-water quality.

The effect of municipal wastewater discharges on the total nitrogen concentration can be estimated by assuming that the total nitrogen concentration is 11.2 mg/L (Larry Puckett, U.S. Geological Survey, written commun., 1993) in sewage treatment outflow and weighting the total nitrogen concentration by the average daily outflow and streamflow at the time of measurement. Adding the inputs from Fargo and Moorhead increases the median total nitrogen concentration from 1.41 mg/L upstream of Fargo to 1.68 mg/L downstream of Fargo. The effect on the Red River is difficult to assess farther downstream, because the streamflow nearly doubles between Fargo and Halstad.

Several factors that can increase the load of nitrogen and phosphorus carried by streams in spring runoff are release of nutrients from soils as they thaw, biological or freeze-thaw degradation of plant materials, nutrient accumulation near the surface of minimum-or no-till fields, and flushing of animal wastes that accumulate in wintering areas. More detailed investigation would be required to understand which processes are major sources of nutrients to streams and what management practices can be implemented to reduce the amount of nutrients that flow into adjacent waters.

The Red River and its tributaries in the Red River Valley Lake Plain and Drift Prairie typically carry phosphorus concentrations that exceed 0.1 mg/L, a proposed goal for the Minnesota River (E.E. Van Nieuwenhuyse, Minnesota Pollution Control Agency, written commun., 1996) and are considered eutrophic for lakes and reservoirs (Wetzel, 1983, p. 293). During the drier summers of 1989–90, phosphorus concentrations commonly exceeded 0.5 mg/L in the Red River downstream of the Fargo-Moorhead area (Wesolowski, 1994).

Eutrophication due to high concentrations of phosphorus (which is commonly the limiting nutrient in freshwaters; Wetzel, 1983) may be of concern in streams and in receiving waters (reservoirs and lakes). Noxious algal blooms have occurred frequently in Lake Winnipeg (Nielsen and others, 1996), the outlet of the Red River about 100 miles north of the study unit. From 1969 to 1974, the Red River contributed about 58 percent of the total phosphorus and 9 percent of the flow to Lake Winnipeg (Brunskill and others, 1980). More recently, from 1975 to 1988 the Red River contributed, on average, twice the phosphorus load and one-fifth the flow of the Winnipeg River (the other major tributary to the southern part of Lake Winnipeg); furthermore, about 60 percent of the phosphorus load at the outflow of the Red River comes from the United States portion of the Red River Basin (Brigham and others, 1996).

The Pembina River contributes much more sediment per unit area to the Red River than any other stream sampled for this study. It also contributes a large amount of nitrogen and phosphorus. The naturally steep slopes that result in high stream energy, with a high sediment-carrying capacity, cannot be changed. However, practices that reduce the rate of runoff and careful management of agricultural practices in riparian areas could reduce streambank erosion and reduce the amount of nutrients from fertilizer and animal waste that flow into the stream.

Most of the suspended sediment in streams was clay and silt. This relates to the relatively flat slopes and low energies of most streams in the study unit and to sediment sources. The soil and streambank material in the Red River Valley Lake Plain is silts and clays and probably is the source of fine suspended sediment measured in streams draining that area. Some of the suspended sediment could be eroded wind-blown soils that have been deposited in streams and ditches.

The apparent relation between soil texture (and possibly soil drainage) and the sediment concentration of streams may help focus sediment control efforts to those parts of stream reaches that contribute most to the sediment in the streams. Field observations and synoptic samples suggested that streams carry more sediment as they pass through soil areas having fine texture and poor drainage as defined by Lorenz and Stoner (1996). Controlling sediment transport from these areas would be more effective than basin-wide erosion-control efforts.

Pesticides are extensively used in this heavily agricultural area, but are not found in streams at levels of concern. The largest portion of herbicides found in stream water was the triazine group (including atrazine). Triazines are most heavily used in the southern part of the study unit upstream of Fargo.

The most heavily used agricultural herbicides, including 2,4-D and MCPA, were not detected in stream- water samples at levels commensurate with their use. Various conditions present in the study unit, including natural organic carbon and beneficial soil bacteria in the relatively widespread clay soils, contribute to the degradation of these herbicides.

Figure 25 shows the distribution of selected constituents relative to the physiographic areas of this study. The ranges in concentration depicted in this illustration are categorized relative to each of the other sites sampled for this study; they do not indicate that a problem exists. For example, the 'high' range of nitrate concentration includes median values greater than 0.40. The highest median nitrate concentrations, 0.55 mg/L, is very low compared to the 10 mg/L drinking water standard (U.S. Environmental Protection Agency, 1996).

Streams draining the Drift Prairie had the highest concentrations of sulfate and sodium ions, followed by streams draining or associated with the Red River Valley Lake Plain. At streams where these ion concentrations were in the high or medium range, it was common for total phosphorus and/or orthophosphate to be in the high or medium range also. Exceptions to the correlation between phosphorus, sulfate, and sodium are the Red River at Halstad, Minnesota, and at Emerson, Manitoba, where urban areas input phosphorus.

Streams draining the Lake-Washed Till Plain have the highest DOC concentrations. In the Snake and Roseau Rivers, high DOC coincides with high organic nitrogen concentrations. It is probable that the decomposition of the organic-rich sediments that release organic carbon also could release organic nitrogen. Nitrate nitrogen, on the other hand, is elevated mostly in streams affected by urban inputs.

There is broad interest to identify and reduce nonpoint effects on Red River Basin streams. Based on results reported here, additional work focused on a few critical tributary basins, such as the Bois de Sioux and Pembina River Basins that contribute disproportionate amounts of nutrients and sediment to the Red River system, could provide valuable data for developing mitigating measures for water-quality improvement.

Continued monitoring of pesticide concentrations in streams should verify whether efforts to reduce chemical inputs to aquatic systems are successful. Decreased concentrations of atrazine in stream water would be expected to result from reduced use of this pesticide. Monitoring also should indicate

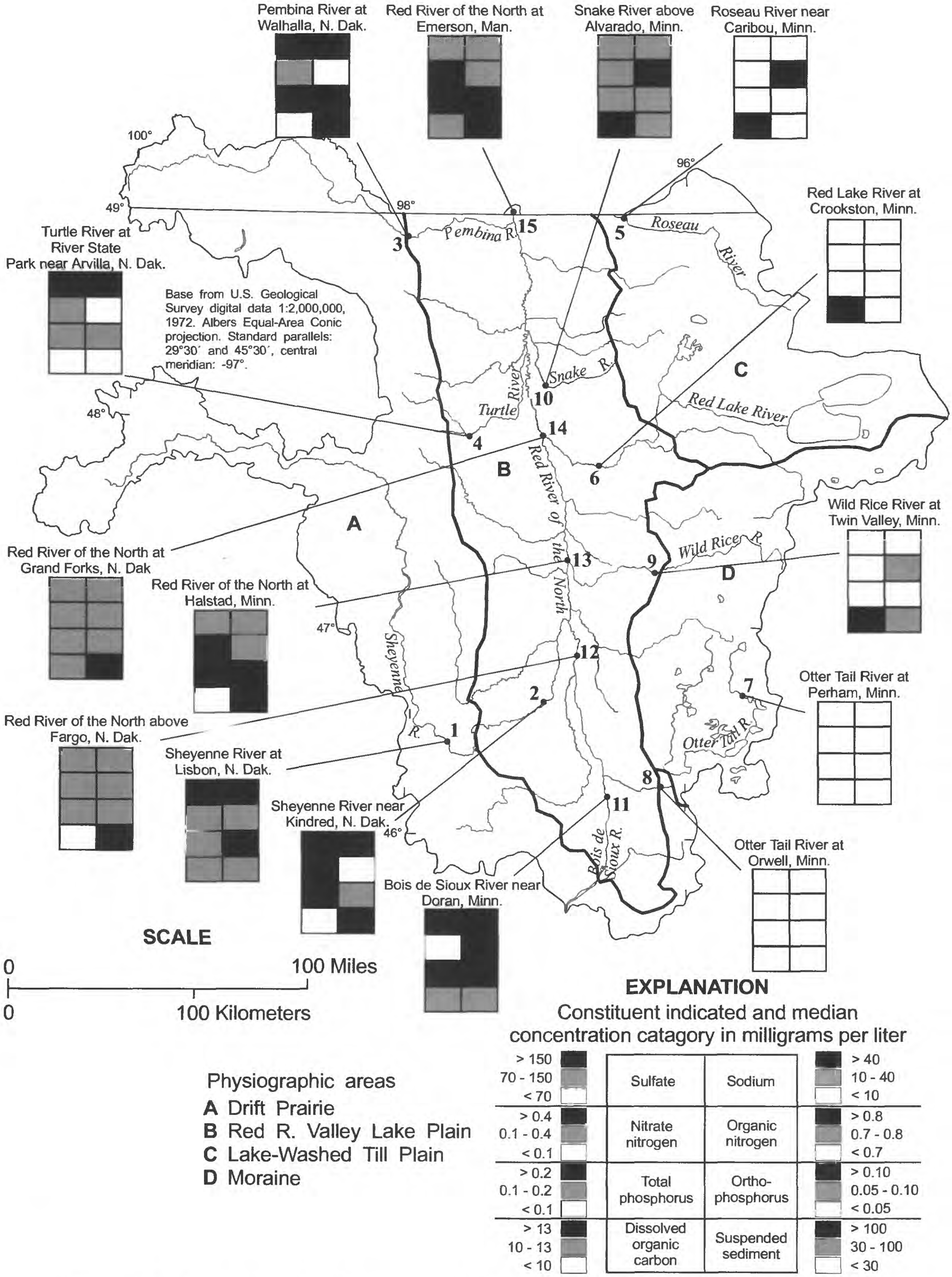


Figure 25. Groupings of median concentrations of selected constituents for streams in the Red River of the North Basin study unit.

whether new pesticides, such as acetochlor, affect water quality.

In several streams suspended-sediment concentrations can be quite high, but the actual source of that sediment cannot reliably be inferred from the data collected for this study. Additional studies would help to determine whether bank erosion or erosion from exposed fields are the major source of the sediment. This information would help managers to better focus efforts to control sediment at its source.

Several findings may warrant further evaluation by basin managers. The Bois de Sioux and Pembina Rivers contributed disproportionately high amounts of nutrients to the basin. Sediment concentrations appeared to increase as streams pass through areas having fine textured soil. Snowmelt runoff contained elevated concentrations of nutrients. Concentrations and yields of several constituents measured for this study were strongly related to the physiographic area of the watershed sampled.

Summary and Conclusions

Fifteen sites in the highly agricultural Red River Basin study unit were sampled during 1993–95 for nutrients, organic carbon, and suspended sediment, and five sites were sampled for pesticides. Precipitation and runoff during this sampling were considerably higher than normal. Concentrations varied seasonally and were related to periods of application and runoff. Nutrient concentrations generally were related to the physiographic area the stream drains, but other factors such as land use frequently complicated that relation.

The ionic composition of streams was closely related to the physiographic area the streams drained. Moraine and Lake-Washed Till Plain streams generally had low concentrations of dissolved solids and a predominance of calcium bicarbonate; Drift Prairie streams had relatively more sodium and sulfate with higher concentrations of dissolved solids. Sulfate comprised more than 60 percent of the anions in the Bois de Sioux River.

Median dissolved nitrogen concentrations were lowest in the Otter Tail River and highest in streams draining or associated with the Red River Valley Lake Plain, including the Red, Bois de Sioux, and Snake Rivers. Nitrite concentrations were negligible, and ammonia concentrations were low except in mid winter. Organic nitrogen comprised the largest part of the dissolved nitrogen in most streams. Nitrate concentrations in streams did not exceed the U.S. Environmental Protection Agency (1996) drinking water standard. Comparison of nitrogen concentrations in the Red River upstream and downstream of Fargo-Moorhead suggests that municipal and industrial wastes have some effect on stream-water quality.

Phosphorus in most streams was largely in dissolved forms and most of that was orthophosphate, which is readily available to biota. Streams draining the Moraine and Lake-Washed Till Plain physiographic areas typically had a large proportion of their phophorus in the suspended phase, sometimes exceeding the amount of dissolved phosphorus. Moraine and Lake-Washed Till Plain streams had the lowest concentrations of total phosphorus, whereas Drift Prairie and Red River Valley Lake Plain streams had the highest concentrations. The Pembina and Bois de Sioux Rivers had the highest median total phosphorus concentrations and the Pembina concentrations were highly variable, suggesting that these streams are influenced by other factors such as crop type or basin slope and probably are not typical of other streams in their physiographic area.

Dissolved organic carbon concentrations were highest, typically more than 15 mg/L, in streams having extensive peatlands in their headwaters areas. Suspended organic carbon concentrations were highly variable and generally were highest during runoff.

Most forms of nutrients had strongly seasonal patterns; those patterns were not consistent between different forms of nutrients. Organic nitrogen concentrations were relatively constant most of the year. Ammonia typically accumulated under ice in late winter, but was negligible the rest of the year. Nitrate concentrations generally were highest during snowmelt runoff and occasionally were high during rainfall runoff. Concentrations of both dissolved and suspended phophorus increased substantially during runoff of snowmelt and rainfall. Dissolved phosphorus (mostly orthophosphate) concentrations often were elevated during snowmelt and rainfall runoff events, and occasionally, under anoxic, ice-covered conditions.

Loads of total nitrogen and total phosphorus generally were proportional to the size of the stream and its watershed. Yields provide some insight to the source of nutrients in the stream system. The highest nitrogen yields were from the Bois de Sioux River Basin and probably are related to agricultural practices. The highest phosphorus yields were from the Pembina and Bois de Sioux River Basins. Phosphorus from the Bois de Sioux Basin probably is related to agricultural practices, whereas phosphorus from the Pembina River Basin probably is related to agricultural practices and is exacerbated by steep terrain.

Some trends in nutrient concentrations and loads were evident. Ammonia concentrations have declined downstream of the Fargo-Moorhead urban area. This probably is related to increased aeration of treated wastewater that causes ammonia to be nitrified to nitrate. The total load of nitrogen and phosphorus carried out of the study unit by the Red River, about 4.1 and 2.4 percent, respectively, of the amounts introduced to the study unit, was about twice as high during this study than had previously been reported. The increased load probably is related to the increased rainfall and runoff during this study.

The suspended sediment carried by streams measured for this study tended to be finer than sand (63 μm). In more than one-half the samples at most stream sites, more than 95 percent of the sediment was clay and silt. The Pembina River had the highest concentrations and yield of suspended sediment, probably the result of erosive forces caused by steep slopes in the watershed. The lowest concentrations and yields were carried by streams draining areas with an abundance of lakes, reservoirs, and wetlands; these typically were streams draining the Moraine and Lake-Washed Till Plain physiographic areas.

Some pesticides were frequently detected. Atrazine and other triazine herbicides were the most commonly detected pesticides in streams of the Red River Basin study unit. Concentrations of triazines were highest in the southern parts of the study unit, where most of the corn is grown, but were detected in streams throughout the study unit. Triallate, which usually is applied to small grains, beans, and sunflowers, was more commonly detected in more northern streams where small grains and sunflowers are the predominant crops. Simazine and prometon were commonly detected. These pesticides primarily are used for nonagricultural purposes in the study unit, but may also be transported into the study unit by atmospheric processes.

The most heavily used herbicides, 2,4-D and MPCA, were infrequently detected in samples of stream water. It is likely that broadleaf weeds, to which these compounds are applied, metabolize these compounds and that soil conditions and microbial populations are effective at degrading these compounds before they reach the streams.

Few insecticides were detected in stream-water samples. Carbofuran, an insecticide used mostly on potatoes and occasionally small grains, was the most commonly detected insecticide. It was found in 16 percent of the samples collected. Other insecticides that were analyzed were detected in less than 5 percent of the samples.

Detection of pesticides in the streams was highly seasonal and related to runoff events. The highest concentrations of pesticides were detected during runoff events following application.

Although the study unit has a large amount of agriculture and pesticides are widely used, the relative amount of pesticides carried out of the study unit is quite small. Of the estimated applications of atrazine, triallate, and 2,4-D, it was estimated that about 0.9, 0.06, and 0.02 percent of each of these compounds, respectively, was carried out of the study unit by the Red River of the North during 1993–95.

References

Alexander, R.B., and Smith, R.A., 1990, County-level estimates of nitrogen and phosphorus fertilizer use in the United States, 1945 to 1985: U.S. Geological Survey Open-File Report 90–130, 12 p.

Battaglin, W.A., and Goolsby, D.A., 1996, Using GIS and regression to estimate annual herbicide concentrations in outflow from reservoirs in the Midwestern USA, 1992–93, *in* Hallam, C.A., Salisbury, J.M., Lanfear, K.J., and W.A. Battaglin, eds., GIS and Water Resources: American Water Resources Association, TPS–96–3, p. 89–98.

Barbash, J.E., and Resek, E.A., 1996, Pesticides in ground water—Distribution, trends and governing factors, *in* Gilliom, R.J., ed., Pesticides in the hydrologic system, v. II: Ann Arbor Press, Inc., Chelsea, Michigan, 588 p.

Brigham, M.E., Mayer, Tatiana, McCullough, G.K., and Tornes, L.H., 1996, Transport and speciation of nutrients in tributaries to southern Lake Winnipeg, Canada: North American Lake Management Society, 16th Annual International Symposium—Final Program, November 13–16, 1996, p. 64.

Brunskill, G.J., Elliot, S.E.M., and Campbell, P., 1980, Morphometry, hydrology, and watershed data pertinent to the limnology of Lake Winnipeg: Canadian Manuscript Report of Fisheries and Aquatic Sciences 1556, Department of Fisheries and Oceans, Winnipeg, Manitoba, 32 p.

Canadian Council of Ministers of the Environment, 1992, Canadian water quality guidelines, Appendix XI—updates (April 1992): Task Force on Water Quality Guidelines of the Canadian Council of Ministers of the Environment, Ottawa Ontario, variously paged.

Capel, P.D., and Larson, S.J., 1996, Evaluation of selected information on splitting devices for water samples: U.S. Geological Survey Water-Resources Investigations Report 95–4141, 103 p.

Cohn, T., Caulder, D.L., Gilroy, E.J., Zynjuk, L.D., and Summers, R.M., 1992a, The validity of a simple statistical model for estimating fluvial constituent loads—An empirical study involving nutrient loads entering Chesapeake Bay: Water Resources Research, v. 28, no. 9, p. 2353–2364.

Cohn, T., Gilroy, E.J., and Baier, W.G., 1992b, Estimating fluvial transport of trace constituents using a regression model with data subject to censoring, *in* Proceedings of the Section on Statistics and the Environment: American Statistical Association: Boston, Mass., August 9–13, 1992, p. 142–151.

Fishman, M.J., 1993, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory— Determination of inorganic and organic constituents in water and fluvial sediments: U.S. Geological Survey Open-File Report 93–125, 217 p.

Guy, H.P., 1969, Laboratory theory and methods for sediment analysis: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. C1, 58 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., Alexander, R.B., and Smith, R.A., 1991, Selection of methods for the detection of trends in water quality: Water Resources Research, v. 27, p. 803–813.

Honeycutt, C.W., 1995, Soil freeze-thaw process—Implications for nutrient cycling: Journal of the Minnesota Academy of Sciences, v. 59, no. 2, p. 9–14.

Lindley, C.E., Stewart, J.T., and Sandstrom, M.W., 1996, Determination of low concentrations of acetochlor in water by automated solid-phase extraction and gas chromatography with mass-selective detection: Journal of AOAC International, v. 79, p. 962–966.

Lorenz, D.L., and Stoner, J.D., 1996, Sampling design for assessing water quality of the Red River of the North Basin, Minnesota, North Dakota, and South Dakota, 1993–95: U.S. Geological Survey Water-Resources Investigations Report 96–4129, 2 plates.

Majewski, M.S., and Capel, P.D., 1995, Pesticides in the atmosphere—Distribution, trends, and governing factors, *in* R.J. Gilliom, ed., Pesticides in the hydrologic system, v. 1: Ann Arbor Press, Inc., Chelsea, Michigan, 214 p.

Minnesota Agricultural Statistics Service, 1991, Minnesota agricultural statistics 1991, St. Paul, Minn., 99 p.

Minnesota Department of Agriculture, 1992, 1990 pesticide use in rural Minnesota: Minnesota Department of Agriculture, St. Paul, Minnesota, 157 p.

Minnesota Extension Service, 1991, Cultural & chemical weed control in field crops, 1991: University of Minnesota Agricultural Bulletin AG–BU–3157–S, 64 p.

Montgomery, J.H., 1993, Agrochemicals desk reference—Environmental data: Lewis Publishers, Boca Raton, Fla., 625 p.

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.

Murdoch, P.S., and Stoddard, J.C., 1992, The role of nitrate in the acidification of streams in the Catskill mountains of New York: Water Resources Research, v. 28, p. 2707–2720.

Nielsen, E., McLeod, K.D., Pip, E., and Doering, J.C., 1996, Late Holocene environmental changes in southern Manitoba—Field trip guidebook A2: Geological Association of Canada/Mineralogical Association of Canada Annual Meeting, Winnipeg, Manitoba, May 27–29, 1996, 33 p.

North Dakota Agricultural Statistics Service, 1992, North Dakota agricultural statistics 1992, Fargo, North Dakota, 112 p.

North Dakota State University, 1992, Pesticide use and pest management practices for major crops in North Dakota, 1992: North Dakota State University, Fargo, 67 p.

Patton, C.J. and Truitt, E.P., 1992, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of total phosphorus by a Kjeldahl digestion method and an automated colorimetric finish that includes dialysis: U.S. Geological Survey Open-File Report 92–146, 36 p.

Pritt, J.W., and Raese, J.W., 1995, Quality assurance/quality control manual—National Water Quality Laboratory: U.S. Geological Survey Open-File Report 95–443, 35 p.

Sandstrom, M.W., 1995, Filtration of water-sediment samples for the determination of organic compounds:

U.S. Geological Survey Water-Resources Investigations Report 95–4105, 13 p.

Shelton, L.R., 1994, Field guide for collecting and processing stream-water samples for the National Water-Quality Assessment Program: U.S. Geological Survey Open-File Report 94–455, 42 p.

Stoner, J.D., Lorenz, D.L., Wiche, G.J., and Goldstein, R.M., 1993, Red River of the North Basin, Minnesota, North Dakota, and South Dakota: Water Resources Bulletin, v. 29, no. 4, p. 575–615.

Tornes, L.H., and Brigham, M.E., 1994, Nutrients, suspended sediment, and pesticides in waters of the Red River of the North Basin, Minnesota, North Dakota, and South Dakota, 1970–1990: U.S. Geological Survey Water-Resources Investigations Report 93–4231, 62 p.

———1995, Pesticide amounts are small in streams in the Red River of the North Basin, 1993–94: U.S. Geological Survey Open-File Report 95–283, 2 p.

U.S. Bureau of Census, 1991, Census of population and housing, 1990, Public law (P.L.) 94–171, data from compact disk ROM (Minnesota, North Dakota, and South Dakota), Washington, D.C.

U.S. Environmental Protection Agency, Office of Water, 1996, Drinking water regulations and health advisories: U.S. Environmental Protection Agency [variously paged].

U.S. Geological Survey, 1986, Land use and land cover digital data from 1:250,000- and 1:100,000-scale maps: National Mapping Program Technical Instructions Data User's Guide 4, 36 p.

Ward, J.R., and Harr, C.A., 1990, Methods for collection and processing of surface-water and bed-material samples for physical and chemical analyses: U.S. Geological Survey Open-File Report 90–140, 71 p.

Werner, S.L, Burkhart, M.R., and DeRusseau, S.N., 1996, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of pesticides in water by Carbopak-B solid-phase extraction and high-performance liquid chromatography: U.S. Geological Survey Open File Report 96–216, 42 p.

Wershaw, R.L., Fishman, M.J., Grabbe, R.R., and Lowe, L.E., eds., 1987, Methods for the determination of organic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A3, 80 p.

Wesolowski, E.A., 1994, Calibration, verification, and use of a water-quality model to simulate effects of discharging treated wastewater to the Red River of the North at Fargo, North Dakota: U.S. Geological Survey Water-Resources Investigations Report 94–4058, 143 p.

Wetzel, R.G., 1983, Limnology, 2nd ed.: Saunders College Publishing, Philadelphia, 767 p.

Zaugg, S.D., Sandstorm, M.W., Smith, S.G., and Fehlberg, K.M., 1995, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of pesticides in water by C-18 solid-phase extraction and capillary-column gas chromatography/mass spectrometry with selected-ion monitoring: U.S. Geological Survey Open-File Report 95–181, 60 p.

Appendix

Table 16.—Summary of pesticides detected at stream sites in the Red River of the North Basin study unit , by site, and all sites combined

[µg/L, micrograms per liter; N, number of samples; ≥, greater than or equal to; MDL, method detection limit, site number referenced on figure 2]

Pesticide	Concentrations: Median (µg/L)	Concentrations: Maximum (µg/L)	N	N≥MDL	Percent ≥MDL	Percent ≥0.1 µg/L with recovery correction[1]
4. Turtle River at Turtle River State Park, North Dakota						
Atrazine	0.007	4.5	31	23	74	3.2
Metolachlor	<.002	.013	31	15	48	0
Triallate	<.001	.016	31	11	35	0
Simazine	<.005	.034	31	10	32	0
EPTC	<.002	.16	31	9	29	3.2
Bentazon	<.014	.88	26	7	27	23
Cyanazine	<.004	.90	31	8	26	3.2
Desethylatrazine	<.002	.13	31	7	23	3.2
Trifluralin	<.002	.009	31	6	19	0
Tebuthiuron	<.010	.01	31	4	13	0
Carbofuran	<.003	.068	31	4	13	0
MCPA	<.050	.92	28	3	11	11
2,4-D	<.035	.38	28	3	11	11
Prometon	<.018	.018	31	3	9.7	0
Alachlor	<.002	.01	31	3	9.7	0
Propachlor	<.007	.007	31	2	6.5	0
Dacthal (DCPA)	<.002	.003	31	2	6.5	0
Aldicarb	<.016	.51	28	1	3.6	3.6
Terbacil	<.007	.01	30	1	3.3	0
p,p'-DDE	<.006	.006	31	1	3.2	0
Metribuzin	<.004	.006	31	1	3.2	0
Ethalfluralin	<.004	.033	31	1	3.2	0
Propanil	<.004	.005	31	1	3.2	0
10. Snake River near Alvarado, Minnesota						
Atrazine	.014	.084	33	30	91	0
Triallate	.007	.28	33	27	82	6.1
Metolachlor	.004	.037	33	20	61	0
Desethylatrazine	<.02	.09	33	14	42	0
Prometon	<.18	.37	33	13	39	0
Cyanazine	<.04	.25	33	12	36	3.0
Simazine	<.05	.7	33	11	33	0
EPTC	<.002	.12	33	11	33	3.0
Trifluralin	<.002	.028	33	10	30	0
2,4-D	<.035	.58	29	6	21	14
Carbofuran	<.003	.26	33	6	18	6.1
Dacthal (DCPA)	<.002	.003	33	4	12	0
MCPA	<.050	.23	29	3	10	6.9

Table 16.—Summary of pesticides detected at stream sites in the Red River of the North Basin study unit, by site, and all sites combined—continued

Pesticide	Concentrations: Median (µg/L)	Concentrations: Maximum (µg/L)	N	N≥MDL	Percent ≥MDL	Percent ≥0.1 µg/L with recovery correction
p,p′-DDE	<0.006	0.006	33	3	9.1	0
Chlorpyrifos	<.004	.031	33	3	9.1	0
γ-HCH	<.004	.038	33	3	9.1	0
Alachlor	<.002	.045	33	3	9.1	0
Bromoxynil	<.035	.12	29	2	6.9	6.9
Metribuzin	<.004	.012	33	2	6.1	0
Fenuron	<.013	.10	29	1	3.4	3.4
Terbacil	<.007	.007	32	1	3.1	0
Fonofos	<.003	.16	33	1	3.0	3.0
Malathion	<.005	.008	33	1	3.0	0
Ethalfluralin	<.004	.032	33	1	3.0	0
Carbaryl	<.003	.005	33	1	3.0	0
9. Wild Rice River at Twin Valley, Minnesota						
Atrazine	.018	.37	33	30	91	9.1
Desethylatrazine	.004	.025	33	23	70	0
Triallate	.006	.21	33	22	67	3.0
Metolachlor	.002	.075	33	17	52	0
Cyanazine	<.004	.11	33	16	48	0
Trifluralin	<.002	.018	33	15	45	0
Simazine	<.005	.008	33	9	27	0
EPTC	<.002	.013	33	8	24	0
Bentazon	<.014	.65	33	6	18	15
Alachlor	<.002	.021	33	6	18	0
Acifluorfen	<.035	.81	33	4	12	12
Propanil	<.004	.011	33	4	12	0
Prometon	<.018	.018	33	2	6.1	0
MCPA	<.050	.25	33	2	6.1	6.1
Metribuzin	<.004	.017	33	2	6.1	0
p,p′-DDE	<.006	.006	33	1	3.0	0
Propoxur	<.035	.035	33	1	3.0	0
2,4-D	<.035	.22	33	1	3.0	3.0
Diuron	<.020	.13	33	1	3.0	3.0
Dichlorprop	<.032	.09	33	1	3.0	3.0
Ethalfluralin	<.004	.015	33	1	3.0	0
Molinate	<.004	.019	33	1	3.0	0
Carbofuran	<.003	.01	33	1	3.0	0
Dacthal (DCPA)	<.002	.002	33	1	3.0	0

Table 16.—Summary of pesticides detected at stream sites in the Red River of the North Basin study unit, by site, and all sites combined—continued

Pesticide	Concentrations Median (µg/L)	Concentrations Maximum (µg/L)	N	N≥MDL	Percent ≥MDL	Percent ≥0.1 µg/L with recovery correction
12. Red River of the North above Fargo, North Dakota						
Atrazine	0.064	0.63	17	17	100	24
Desethylatrazine	.014	.066	17	16	94	12
Cyanazine	.031	.65	17	16	94	24
Metolachlor	.013	.17	17	14	82	24
Simazine	.005	.016	17	11	65	0
Prometon	.008	.018	17	10	59	0
Bentazon	<.014	2.8	19	9	47	42
EPTC	<.002	.55	17	8	47	12
Alachlor	<.002	.24	17	7	41	5.9
Trifluralin	<.002	.066	17	7	41	0
Acetochlor	<.002	.11	16	6	38	6.3
Acifluorfen	<.035	.44	19	4	21	16
Triallate	<.001	.038	17	3	18	0
Metribuzin	<.004	.026	17	2	12	0
Carbofuran	<.003	.082	17	2	12	0
Fonofos	<.003	.003	17	1	5.9	0
Chlorpyrifos	<.004	.004	17	1	5.9	0
Dicamba	<.035	.12	19	1	5.3	5.3
2,4-D	<.035	.05	19	1	5.3	0
Fenuron	<.013	.026	19	1	5.3	0
Bromoxynil	<.035	.25	19	1	5.3	5.3
15. Red River of the North at Emerson, Manitoba						
Atrazine	.040	.51	40	40	100	28
Cyanazine	.020	.18	40	38	95	7.5
Metolachlor	.012	.20	40	37	93	5.0
Desethylatrazine	.007	.065	40	36	90	2.5
Triallate	.004	.067	40	23	58	0
Prometon	.018	.034	40	22	55	0
Simazine	.005	.06	40	21	53	0
Alachlor	.003	.17	40	20	50	5.0
EPTC	<.002	.24	40	18	45	2.5
Trifluralin	<.002	.011	40	14	35	0
Bentazon	<.014	2.0	40	13	33	30
Acetochlor	<.002	.093	17	5	29	5.9
Carbofuran	<.003	.15	40	10	25	0
Acifluorfen	<.035	.58	40	5	13	13
Metribuzin	<.004	.016	40	5	13	0

Table 16.—Summary of pesticides detected at stream sites in the Red River of the North Basin study unit, by site, and all sites combined—continued

Pesticide	Concentrations: Median (μg/L)	Concentrations: Maximum (μg/L)	N	N≥MDL	Percent ≥MDL	Percent ≥0.1 μg/L with recovery correction
Chlorpyrifos	<0.004	0.034	40	4	10	0
Dacthal (DCPA)	<.002	.002	40	3	7.5	0
p,p'-DDE	<.006	.006	40	2	5.0	0
Malathion	<.005	.01	40	2	5.0	0
Diazinon	<.002	.004	40	2	5.0	0
2,4-D	<.035	.11	40	2	5.0	5.0
Chlorothalonil	<.035	.035	39	1	2.6	2.6
Dicamba	<.035	.05	40	1	2.5	2.5
Fenuron	<.013	.08	40	1	2.5	2.5
Diuron	<.020	.04	40	1	2.5	0
Tebuthiuron	<.010	.056	40	1	2.5	0
All stream sites (including synoptic-sampling sites, which are not listed above)						
Atrazine	.024	4.5	218	201	92	13
Desethylatrazine	.004	.13	218	144	66	1.8
Metolachlor	.004	.39	218	133	61	3.7
Cyanazine	.011	.90	218	125	57	4.6
Triallate	<.001	.28	218	102	47	1.4
EPTC	<.002	.55	218	76	35	3.2
Simazine	<.005	.11	218	73	33	.5
Trifluralin	<.002	.066	218	60	28	0
Prometon	<.018	.041	218	59	27	0
Alachlor	<.002	.24	218	46	21	2.8
Bentazon	<.014	2.8	211	42	20	17
Acetochlor	<.002	.11	71	12	17	2.8
Carbofuran	<.003	.43	218	34	16	2.3
2,4-D	<.035	.80	213	25	12	8.9
Acifluorfen	<.035	.81	213	18	8.5	7.0
Metribuzin	<.004	.033	218	17	7.8	0
MCPA	<.05	.92	213	13	6.1	5.6
Dacthal (DCPA)	<.002	.003	218	10	4.6	0
Chlorpyrifos	<.004	.034	218	9	4.1	0
p,p'-DDE	<.006	.006	218	8	3.7	0
Bromoxynil	<.035	.25	213	7	3.3	2.8
Tebuthiuron	<.01	.056	218	6	2.8	0
Ethalfluralin	<.004	.06	218	5	2.3	0
Propanil	<.004	.011	218	5	2.3	0
Fonofos	<.003	.16	218	4	1.8	.5
γ-HCH	<.004	.038	218	4	1.8	0

Table 16.—Summary of pesticides detected at stream sites in the Red River of the North Basin study unit, by site, and all sites combined—continued

Pesticide	Concentrations: Median (µg/L)	Concentrations: Maximum (µg/L)	N	N≥MDL	Percent ≥MDL	Percent ≥0.1 µg/L with recovery correction
Malathion	<.0.005	0.01	218	4	1.8	0
Fenuron	<.013	.10	212	3	1.4	.9
Diuron	<.02	.13	213	3	1.4	.5
Dicamba	<.035	.12	213	2	.9	.9
Carbofuran	<.028	.40	213	2	.9	.9
Terbacil	<.007	.01	215	2	.9	0
Propachlor	<.007	.007	218	2	.9	0
Diazinon	<.002	.005	218	2	.9	0
Carbaryl	<.003	.037	218	2	.9	0
Chlorothalonil	<.035	.035	210	1	.5	.5
Propoxur	<.035	.035	212	1	.5	0
Aldicarb	<.016	.51	212	1	.5	.5
Dichlorprop	<.032	.09	213	1	.5	.5
Parathion, methyl	<.006	.032	218	1	.5	0
Molinate	<.004	.019	218	1	.5	0
Disulfoton	<.017	.025	218	1	.5	0
Pendimethalin	<.004	.01	218	1	.5	0
Azinphos-methyl	<.001	.01	218	1	.5	0

[1] Censoring level chosen to account for differences in method detection limits and analytical recovery differences among the pesticides.

Table 17. Summary of nutrient concentration at stream sites in the Red River of the North Basin study unit, by site

[Note: concentrations given in milligrams per liter; site number referenced on figure 2]

Constituent	Concentrations					Number of samples
	Minimum	25th percentile	Median	50th percentile	Maximum	
1. Sheyenne River at Lisbon, North Dakota:						
Ammonia, dissolved	0.010	0.0450	0.0650	0.1900	0.30	24
Nitrite, dissolved	<.100	<.0100	..0100	.0300	.05	24
Ammonia plus organic nitrogen, dissolved	.600	.7000	.8000	1.0000	1.90	24
Ammonia plus organic nitrogen, total	.500	.9000	1.0000	1.2000	3.10	25
Nitrite plus nitrate nitrogen, dissolved	<.050	.0125	.3400	.4450	1.40	24
Phosphorus, total	.060	.1300	.2400	.3100	1.20	25
Phosphorus, dissolved	.030	.0750	.1250	.2100	.38	24
Orthophosphate, as phosphorus	.030	.0500	.1250	.1950	.34	24
2. Sheyenne River near Kindred, North Dakota:						
Ammonia, dissolved	<.015	.0200	.0450	.1800	.38	26
Nitrite, dissolved	<.010	<.0100	.0150	.0300	.15	26
Ammonia plus organic nitrogen, dissolved	.500	.7000	.7000	1.0000	1.10	22
Ammonia plus organic nitrogen, total	.600	.8000	1.0500	1.2000	2.10	28
Nitrite plus nitrate nitrogen, dissolved	<.050	<.0500	.4350	.5400	3.60	28
Phosphorus, total	.080	.1350	.2400	.3300	.63	28
Phosphorus, dissolved	.040	.0600	.1050	.1700	.30	26
Orthophosphate, as phosphorus	.030	.0600	.1000	.1400	.31	26
3. Pembina River at Wallhalla, North Dakota:						
Ammonia, dissolved	<.015	.0200	.0400	.1300	.23	35
Nitrite, dissolved	<.010	<.0100	.0100	.0400	.14	35
Ammonia plus organic nitrogen, dissolved	.300	.6000	.7000	.8000	1.30	35
Ammonia plus organic nitrogen, total	<.200	.7000	1.0000	1.4000	2.40	35
Nitrite plus nitrate nitrogen, dissolved	<.050	.0630	.3300	1.4000	2.70	35
Phosphorus, total	.040	.2300	.3300	.4700	1.00	35
Phosphorus, dissolved	.030	.1800	.2200	.2800	.60	35
Orthophosphate, as phosphorus	.030	.1700	.2200	.2800	.54	35
4. Turtle River at Turtle River State Park near Arvilla, North Dakota:						
Ammonia, dissolved	<.010	.0200	.0500	.1250	.26	36
Nitrite, dissolved	<.010	<.0100	.0100	.0250	.13	36
Ammonia plus organic nitrogen, dissolved	.300	.5000	.6000	.9000	1.40	36
Ammonia plus organic nitrogen, total	.300	.6000	.8000	1.1000	1.80	39
Nitrite plus nitrate nitrogen, dissolved	<.050	.0950	.3200	.8550	2.70	36
Phosphorus, total	.050	.0700	.1400	.3200	.59	39
Phosphorus, dissolved	<.010	.0550	.0850	.2750	.36	36
Orthophosphate, as phosphorus	<.010	.0500	.0800	.2650	.35	36

Table 17. Summary of nutrient concentration at stream sites in the Red River of the North Basin study unit, by site

[Note: concentrations given in milligrams per liter; site number referenced on figure 2]

Constituent	Concentrations					Number of samples
	Minimum	25th percentile	Median	50th percentile	Maximum	
5. Roseau River near Caribou, Manitoba:						
Ammonia, dissolved	<0.015	0.0250	0.0350	0.1800	0.69	20
Nitrite, dissolved	<.010	<.0100	<.0100	.0200	.07	20
Ammonia plus organic nitrogen, dissolved	.700	.9000	1.0000	1.1000	1.60	20
Ammonia plus organic nitrogen, total	.800	1.0000	1.1500	1.2500	1.90	20
Nitrite plus nitrate nitrogen, dissolved	<.050	<.0500	<.0500	.1700	.99	20
Phosphorus, total	.030	.0600	.0800	.1200	.42	20
Phosphorus, dissolved	<.010	.0200	.0450	.0750	.40	20
Orthophosphate, as phosphorus	<.010	.0200	.0400	.0600	.37	20
6. Red Lake River at Crookston, Minnesota:						
Ammonia, dissolved	<.015	.0200	.0300	.0700	.36	21
Nitrite, dissolved	<.010	<.0100	<.0100	.0200	.09	21
Ammonia plus organic nitrogen, dissolved	.500	.7000	.7000	.9000	1.60	21
Ammonia plus organic nitrogen, total	.700	.8000	.8500	1.2000	2.00	21
Nitrite plus nitrate nitrogen, dissolved	<.050	<.0500	.0900	.2600	2.40	21
Phosphorus, total	<.010	.0300	.0700	.1100	.56	21
Phosphorus, dissolved	<.010	<.0100	.0200	.0600	.24	21
Orthophosphate, as phosphorus	<.010	<.0100	.0200	.0500	.20	21
7. Otter Tail River near Perham, Minnesota:						
Ammonia, dissolved	<.015	.0200	.0300	.0650	.21	24
Nitrite, dissolved	<.010	<.0100	<.0100	<.0100	.02	24
Ammonia plus organic nitrogen, dissolved	.400	.5000	.5000	.6000	.80	24
Ammonia plus organic nitrogen, total	.400	.6000	.6500	.7500	.90	24
Nitrite plus nitrate nitrogen, dissolved	<.050	<.0500	.0710	.1950	.65	24
Phosphorus, total	<.010	.0200	.0300	.0400	.06	24
Phosphorus, dissolved	<.010	<.0100	<.0100	.0200	.06	24
Orthophosphate, as phosphorus	<.010	<.0100	<.0100	.0100	.04	24
8. Otter Tail River below Orwell Dam near Fergus Falls, Minnesota:						
Ammonia, dissolved	<.015	.0200	.0300	.0800	.19	25
Nitrite, dissolved	<.010	<.0100	<.0100	.0100	.03	25
Ammonia plus organic nitrogen, dissolved	.400	.5000	.6000	.7000	1.20	25
Ammonia plus organic nitrogen, total	.500	.6000	.7000	.8000	1.50	25
Nitrite plus nitrate nitrogen, dissolved	<.050	<.0500	<.0500	.1600	.50	25
Phosphorus, total	.020	.0300	.0300	.0600	.29	25
Phosphorus, dissolved	<.010	<.0100	.0200	.0200	.04	25
Orthophosphate, as phosphorus	<.010	<.0100	.0100	.0200	.04	25

Table 17. Summary of nutrient concentration at stream sites in the Red River of the North Basin study unit, by site

[Note: concentrations given in milligrams per liter; site number referenced on figure 2]

	Concentrations					
Constituent	Minimum	25th percentile	Median	50th percentile	Maximum	Number of samples
9. Wild Rice River at Twin Valley, Minnesota:						
Ammonia, dissolved	<0.015	0.0200	0.0350	0.0900	0.38	38
Nitrite, dissolved	<.010	<.0100	<.0100	.0100	.13	38
Ammonia plus organic nitrogen, dissolved	.600	.7000	.8000	.9000	1.50	38
Ammonia plus organic nitrogen, total	.600	.8000	.9000	1.1000	2.00	38
Nitrite plus nitrate nitrogen, dissolved	<.050	<.0500	.0830	.2300	4.80	38
Phosphorus, total	<.010	.0300	.0650	.1200	.31	38
Phosphorus, dissolved	<.010	.0100	.0300	.0600	.15	38
Orthophosphate, as phosphorus	<.010	.0100	.0250	.0500	.11	38
10. Snake River above Alvarado, Minnesota:						
Ammonia, dissolved	20	.0400	.0800	.1550	1.40	32
Nitrite, dissolved	<.010	.0000	.0200	.0550	.21	32
Ammonia plus organic nitrogen, dissolved	.900	1.0000	1.2000	1.3000	2.70	32
Ammonia plus organic nitrogen, total	.800	1.1500	1.4000	1.6000	2.60	36
Nitrite plus nitrate nitrogen, dissolved	<.050	.0040	.1750	.9600	3.10	32
Phosphorus, total	.040	.1200	.1850	.2700	.57	36
Phosphorus, dissolved	<.010	.0600	.1150	.1900	.42	32
Orthophosphate, as phosphorus	<.010	.0650	.1000	.1750	.38	32
11. Bois-De Sioux River near Doran, Minnesota:						
Ammonia, dissolved	<.010	.0300	.0800	.2500	1.60	26
Nitrite, dissolved	<.010	<.0100	.0200	.0500	.31	26
Ammonia plus organic nitrogen, dissolved	.600	1.0000	1.2000	1.4000	3.10	26
Ammonia plus organic nitrogen, total	.900	1.2000	1.4000	1.9000	3.30	26
Nitrite plus nitrate nitrogen, dissolved	<.050	<.0500	.0980	.8600	5.20	26
Phosphorus, total	.070	.1700	.2950	.4900	1.30	26
Phosphorus, dissolved	.030	.0700	.2000	.4500	.81	26
Orthophosphate, as phosphorus	.010	.0700	.1750	.4300	.74	26
12. Red River of the North above Fargo, North Dakota:						
Ammonia, dissolved	<.015	.0400	.0500	.1000	.36	17
Nitrite, dissolved	<.010	<.0100	.0200	.0400	.19	17
Ammonia plus organic nitrogen, dissolved	.500	.6000	.9000	.9000	1.20	17
Ammonia plus organic nitrogen, total	.700	.9000	1.1000	1.2000	1.80	17
Nitrite plus nitrate nitrogen, dissolved	<.050	.1500	.3100	.7500	3.80	17
Phosphorus, total	.020	.1500	.1700	.3200	.51	17
Phosphorus, dissolved	.030	.0500	.0600	.1800	.28	17
Orthophosphate, as phosphorus	.010	.0500	.0700	.1900	.26	17

Table 17. Summary of nutrient concentration at stream sites in the Red River of the North Basin study unit, by site

[Note: concentrations given in milligrams per liter; site number referenced on figure 2]

Constituent	Concentrations					Number of samples
	Minimum	25th percentile	Median	50th percentile	Maximum	
13. Red River of the North at Halsted, Minnesota:						
Ammonia, dissolved	0.010	0.0500	0.0800	0.2400	1.20	23
Nitrite, dissolved	<.010	.0100	.0200	.0500	.27	23
Ammonia plus organic nitrogen, dissolved	.500	.7000	.8000	.9000	1.60	18
Ammonia plus organic nitrogen, total	.800	.9000	1.1000	1.4000	2.50	24
Nitrite plus nitrate nitrogen, dissolved	.098	.3000	.5600	.9800	4.90	23
Phosphorus, total	.070	.2100	.2750	.3600	.84	24
Phosphorus, dissolved	.050	.1100	.1300	.2400	.37	23
Orthophosphate, as phosphorus	.060	.1000	.1200	.2200	.36	23
14. Red River of the North at Grand Forks, North Dakota:						
Ammonia, dissolved	.020	.0400	.0600	.1300	.38	25
Nitrite, dissolved	<.010	<.0100	.0100	.0200	.27	25
Ammonia plus organic nitrogen, dissolved	.600	.8000	.8000	.9000	1.50	25
Ammonia plus organic nitrogen, total	.700	.9000	1.0000	1.2000	1.70	25
Nitrite plus nitrate nitrogen, dissolved	.130	.2300	.3500	.5000	4.60	25
Phosphorus, total	.030	.1200	.1800	.2600	.49	25
Phosphorus, dissolved	.030	.0700	.1100	.2000	.37	25
Orthophosphate, as phosphorus	.030	.0600	.0900	.1700	.33	25
15. Red River of the North at Emerson, Manitoba:						
Ammonia, dissolved	<.015	.0300	.0400	.1250	.37	44
Nitrite, dissolved	<.010	<.0100	.0100	.0300	.24	44
Ammonia plus organic nitrogen, dissolved	.600	.7000	.8000	1.0000	1.50	39
Ammonia plus organic nitrogen, total	.700	.9000	1.1000	1.2000	1.90	45
Nitrite plus nitrate nitrogen, dissolved	<.050	.2700	.3950	.8350	5.80	44
Phosphorus, total	.060	.1600	.2100	.3300	.55	45
Phosphorus, dissolved	.040	.0900	.1400	.1950	.36	44
Orthophosphate, as phosphorus	.030	.0700	.1300	.1750	.35	44

[1] Censoring level chosen to account for differences in method detection limits and analytical recovery differences among the pesticides.

☆ U.S. GOVERNMENT PRINTING OFFICE: 1997 - 673-268 / 26501 REGION NO. 8