NUTRIENTS, SUSPENDED SEDIMENT, AND PESTICIDES IN WATERS OF THE RED RIVER OF THE NORTH BASIN, MINNESOTA, NORTH DAKOTA, AND SOUTH DAKOTA, 1970-90

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Conversion Factors

Multiply	By	To obtain
inch (in.)	25.4	millimeter
foot (ft)	.3048	meter
square mile (mi^2)	2.590	square kilometer
cubic foot per second (ft^3/s)	.02832	cubic meter per second
quart (qt)	.9464	liter
ounce, fluid (fl. oz)	.2957	liter
pound, avoirdupois (lb)	4.536	kilogram

Temperatures given in this report in degrees Fahrenheit (°F). Celsius (°C) can be converted to degrees Fahrenheit as follows:

$$°C = (°F - 32)/1.8$$

Abstract

Available data on nutrients (phosphorus and nitrogen), suspended sediment, and pesticides in the Red River of the North Basin, a study unit under the U.S. Geological Survey National Water-Quality Assessment (NAWQA) Program, are reviewed. These data were collected by several agencies during 1970-90. Nutrient concentrations in surface water are higher downgradient from agricultural and urban areas than in other areas, but generally do not exceed U.S. Environmental Protection Agency (USEPA) Maximum Contaminant Levels (MCLs). The 10 milligram per liter (mg/L) drinking water MCL for nitrate (as nitrogen) was rarely exceeded. Some of the largest nutrient inputs to the surface-water system appear to come from the Fargo-Moorhead area. The highest nitrogen concentrations usually were found in the Red River of the North. Nitrogen composition was mostly organic nitrogen with some nitrate. Ammonia nitrogen was negligible except during mid-winter, when concentrations could exceed 1.0 mg/L. Streams draining the corn-dominated cropland in the southern part of the basin had relatively high nitrogen concentrations compared to parts of the basin where small-grain crops, forests, and wetlands predominate. The Pembina River in the northern part of the basin had a large range in nitrogen concentrations that often exceeded those in the Red River of the North. The highest phosphorus concentrations generally were found in of the Red River of the North, although tributary streams occasionally had peak concentrations that exceeded those in the Red River of the North. Median nitrate concentrations in ground water were less than 1.0 mg/L as nitrogen in all counties in the basin except in Otter Tail and Becker Counties in Minnesota. Half of the wells in Otter Tail County had nitrate-nitrogen concentrations exceeding 2.8 mg/L. Shallow, surficial aquifers tended to have the highest nitrate concentrations.

Median suspended-sediment concentrations were less than 100 mg/L except in the Red River of the North near the Canadian border at Emerson, Manitoba and the Pembina River. The Pembina River occasionally had high suspended sediment concentrations; about 10 percent of the samples exceeded 2,000 mg/L.

For both surface and ground water, available pesticide data were limited in spatial and temporal coverage. The majority of pesticide analyses for the Red River of the North Basin show no concentrations above laboratory reporting limits. Reported concentrations usually were below USEPA MCLs. Only a few analyses of pesticides in ground water had concentrations above laboratory reporting limits. Wells that had reportable levels are mainly in the southern and southeastern part of the basin, where atrazine was the most commonly detected pesticide.

A relatively large fraction of stream samples had detectable quantities of 2,4-D, α- and γ-HCH, and atrazine. These samples covered time spans of as much as 15 years and were from sites downstream from large drainage basins; however, concentrations were well below USEPA MCLs. One county-level study showed higher 2,4-D concentrations at upstream sites than at the outlet from a small basin. This indicates that downstream sites may fail to show impaired water-quality and the fate of pesticides used in the basin. Following the 1972 ban on DDT, concentrations of DDT in fish samples from the Red River of the North quickly decreased. Fish concentrations of DDE and DDD decreased more slowly. Low levels of DDE and DDD were detected in fish 14 years after the DDT ban.

Introduction

The Red River of the North (referred to herein as the Red River) drainage basin (fig. 1) encompasses areas of rich agricultural lands, forests, wetlands, prairie, and large numbers of lakes, and prairie potholes. The Red River Basin was selected as a study unit under the U.S. Geological Survey's National Water-Quality Assessment (NAWQA) Program because (1) the basin 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 basin 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.

This report is a review of selected data collected by several agencies during 1970-90 in the Red River Basin. Stoner and others (1993) provide a general description of the environmental setting of the basin as it relates to water quality, including major land-use and cropping patterns. A synopsis of that report follows.

Environmental Setting

The general physical, hydrological, and ecological setting of the Red River Basin is diverse in ways that could significantly control the areal distribution and flow of water and, therefore, the distribution and concentration of constituents that affect water quality. Continental glaciers generally deposited 150 to 300 feet of unconsolidated material over the basin and shaped a landscape of very flat

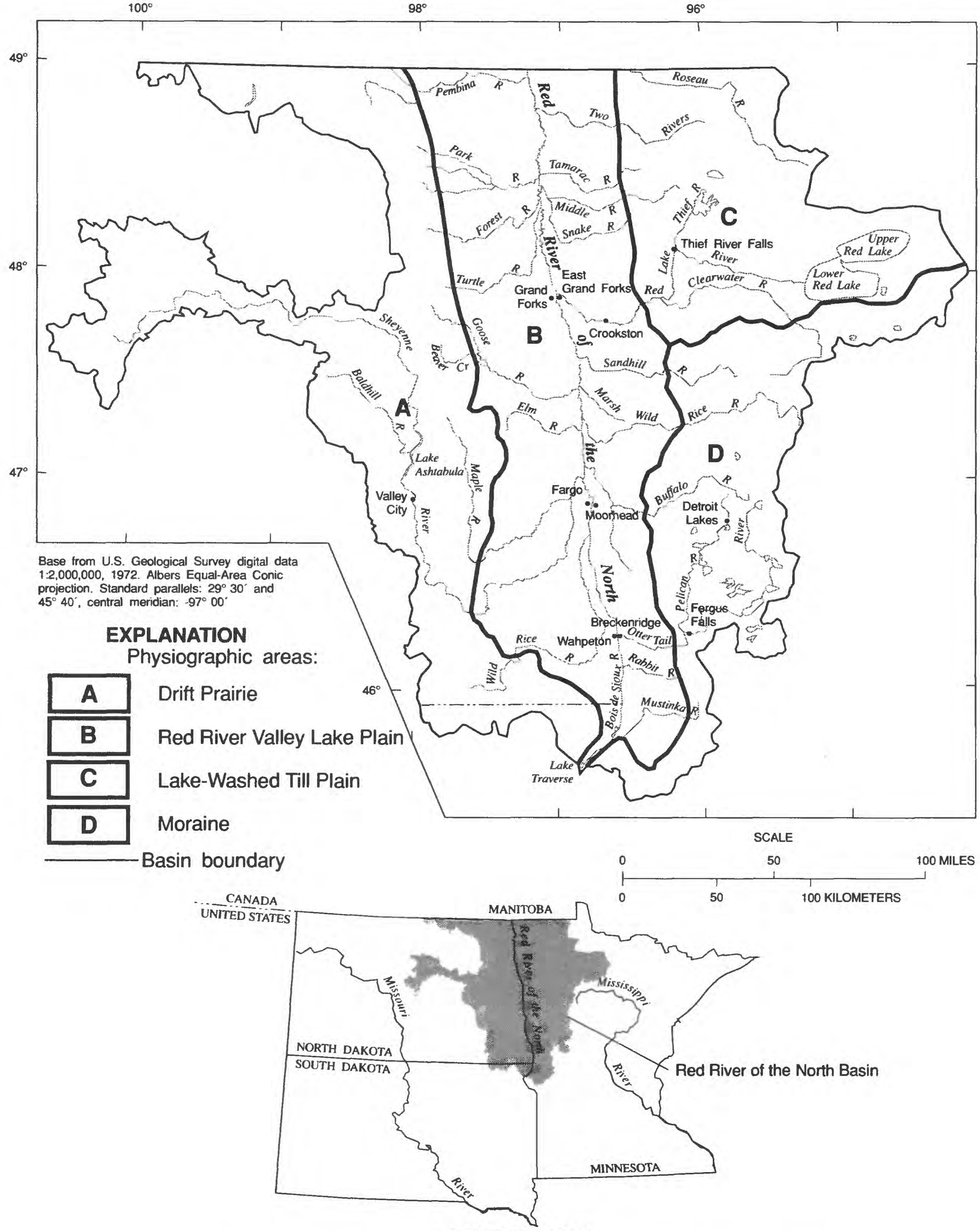


Figure 1.--Red River of the North Basin and physiographic areas. [Modified from Maclay and others, 1972 and Winter and others, 1984]

lake plains near the center of the basin, and gently rolling uplands, lakes, and wetlands along the basin margins. The fertile black, fine-grained soils and landscape are conducive to agriculture; productive cropland covers 66 percent of the land area. Pasture, forests, open water, and wetlands comprise most of the remaining land area. The 1990 population of 511,000 represents an 8 percent increase since 1980. Almost one-third of the population lives in the cities of Fargo and Grand Forks, North Dakota and Moorhead, Minnesota. The climate of the Red River Basin is continental and ranges from dry subhumid in the North Dakota part of the basin to subhumid in the Minnesota part. The mean monthly temperature ranges from -1 degrees Fahrenheit (°F) in January near the United States-Canadian border to 73°F in July in the southern part of the Red River Basin.

From its origin, the Red River meanders northward for 394 miles (mi) to the United States-Canadian border, a path that is nearly double the straight-line distance. The Red River receives over 75 percent of its annual flow from its eastern tributaries as a result of regional patterns in precipitation, evapotranspiration, soils, and topography. Annual runoff is greatly variable. Most runoff 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. Lakes, prairie potholes, and wetlands are abundant in most physiographic areas outside of the Red River Valley Lake Plain. An extensive drainage system of ditches has been constructed in the lake plain to promote spring runoff and rapid drainage of the clay-rich soils.

Ground water available to wells, streams, and springs primarily comes from sand and gravel aquifers near land surface or buried within the glacial drift that mantles the entire Red River Basin (fig. 2). Water moves through the system of bedrock and glacial-drift aquifers in a regional system generally toward the Red River and in complex local flow systems controlled by local topography. Many of the bedrock and glacial-drift aquifers are hydraulically connected to streams in the region. These connections can affect the hydrologic-flow regime, water quality, and water development of the basin.

The total water use in 1990, about 196 million gallons, was mostly for public supply and irrigation. About 52 percent of the water used in 1990 came from ground-water instead of surface-water sources. Most municipalities obtain their water from ground-water sources. However, the largest cities (Fargo, Grand Forks, and Moorhead) have surface-water sources and most of this water is derived from the Red River.

Concentrations of dissolved chemical constituents in surface waters generally are low during spring runoff and after thunderstorms. At times of low flow, when water in streams is largely from ground-water seepage, the water quality closely reflects the chemistry of the glacial-drift aquifer system. Water in the Red River generally has dissolved-solids concentrations less than 600 milligrams per liter (mg/L) with mean values ranging from 347 mg/L near the headwaters to 406 mg/L at the Canadian border near Emerson, Manitoba. Calcium and magnesium are the principal cations and bicarbonate is the principal anion along most of the reach of the Red River. Dissolved-solids concentrations generally are lower in the eastern tributaries than in the tributaries draining the western part of the basin. However, the annual loading of chemical constituents from each side of the basin is fairly-well balanced as a result of the larger contribution of runoff from the Minnesota side.

The quality of water in glacial drift is variable and depends on the position of the sampling point within the ground-water flow system. Ground water in the surficial aquifers commonly is a calcium bicarbonate type with dissolved-solids concentrations generally between 300 and 700 mg/L. However, water from deeper in the glacial drift tends to become more mineralized. As the ground water moves downgradient along flow paths, dissolved-solids concentrations increase, and the water becomes a dominately magnesium and sulfate type. Water in sedimentary bedrock aquifers is a predominantly sodium and chloride type and is characterized by dissolved-solids concentrations in excess of 1,000 mg/L.

Small grains including wheat, oats, rye, and barley are grown throughout most of the Red River Basin. These often are rotated with other crops in regional patterns based on differences in soils, topography, and climate. Corn and soybeans are grown primarily in the southern part of the basin. Occasionally, small patches of soybeans are planted in other parts of the basin. Sunflowers, hay, and small grains are grown on the drift prairie in the western part of the basin. Sugar beets, small grains, and soybeans are grown in the Red River Valley Lake Plain very near the Red River. These areas, especially in the northern half of the basin, 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.

Erosion of soil by wind and water can be increased by cultivation practices and by streambank trampling by livestock. Nitrate-nitrogen concentrations also can increase locally in surficial aquifers beneath cropland that is fertilized, and especially where it is irrigated. Nitrogen and phosphorus in surface runoff from cropland

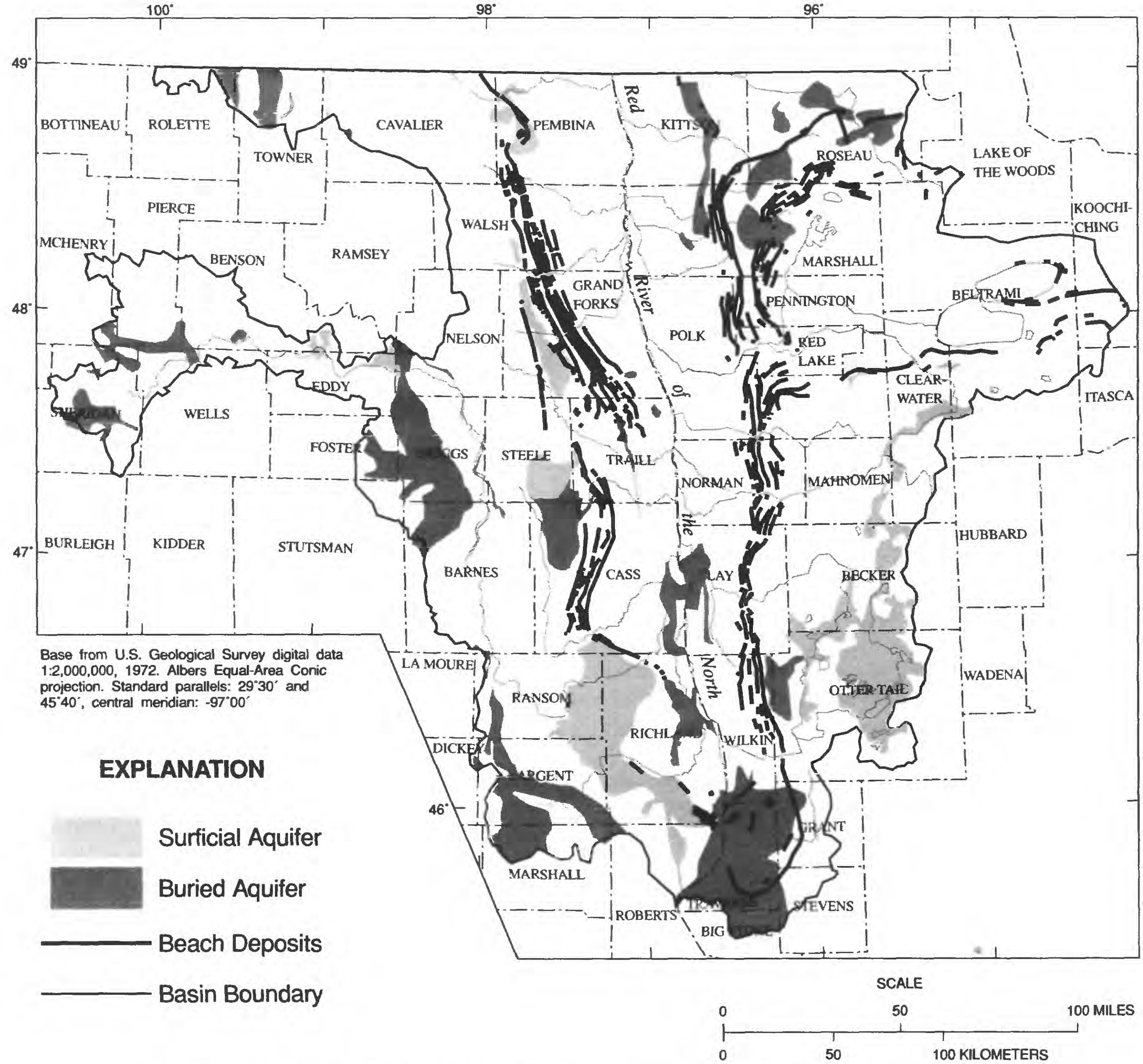


Figure 2.--Major surficial and buried sand and gravel aquifers in glacial drift in the Red River of the North Basin. [Modified from Stoner and others, 1993]

fertilizers and nitrogen from manure have the potential to contribute nutrients to lakes, reservoirs, and streams. However, nitrate and other nitrogen species have not been identified as a regionally widespread problem in the basin. Some of the more persistent pesticides applied to crops, such as atrazine, have been detected in the Red River.

Urban runoff and treated effluent from municipalities are discharged into streams. These point discharges contain some quantity of organic compounds from storm runoff, turf-applied pesticides, and trace metals. The largest releases of treated-municipal wastes are from the population centers along the Red River and its larger tributaries. Sugar-beet refining, potato processing, poultry and meat packing, and milk, cheese, and cream processing are among the principal food processing operations from which treated wastes are released to streams, mostly in or near the Red River.

Dams, drainage ditches, dikes, natural flood-plain obstructions, and wetlands can alter the residence time of water, thereby affecting the amount of sediment, biota, and dissolved constituents carried by the water. These features can also affect habitat for aquatic biota by altering populations and community structure.

Use and Sources of Nutrients, Sediment, and Pesticides

Agricultural practices can affect nutrient, suspended-sediment, and pesticide concentrations in natural waters. Application of fertilizers can result in increased nutrient concentrations in surface water and ground water. Tillage practices can affect erosion of soil and transport of sediment to surface water. Pesticides, which include herbicides, insecticides, and fungicides, routinely are applied to control various pests. In recent years, about 2×10^8 kilogram (kg) of herbicides were used annually in the United States (Gianessi and Puffer, 1990).

Alexander and Smith (1990) summarized estimates of fertilizer usage by county for the entire United States. The county-level data in this report were determined from statewide reporting of chemical fertilizer use, and partitioned to each of the counties on the basis of percent of agricultural land within each county. Although estimates made by this method could be imprecise for certain areas, it provides useful, relative application rates of chemical nitrogen and phosphorus fertilizers. The resultant numbers were provided as total nitrogen and phosphorus usage for the entire county. The most recent data (1985) from Alexander and Smith (1990) for counties in, or partially within, the Red River Basin are shown in table 1. These data have been normalized using county area and reported as kilograms per square mile (kg/mi^2).

In a related effort, R.B. Alexander (USGS, written commun., 1993) is compiling a list of nitrogen and phosphorus production from manure for counties throughout the United States. For this effort, county-level livestock population census data from 1987 was combined with nitrogen and phosphorus content of animal wastes and the rates at which those livestock produce waste. Assuming that all the livestock wastes produced within a county are applied as fertilizer within that county, the data should be a reasonably reliable indication of nitrogen and phosphorus from animal wastes. The data shown for manure in table 1 also have been normalized by county area to provide estimated application in kg/mi^2.

Adding nutrient input from chemical sources to nutrient input from manure provides the total input from these two sources. Table 1 shows the total nitrogen and phosphorus application and is ordered by decreasing calculated application rates. Although the table indicates that chemical inputs of nitrogen and phosphorus are largest in Norman County, the manure that may be applied in Stevens County would cause nitrogen and phosphorus application rates to exceed those of Norman County.

Figures 3 and 4 show the relative ranking of the counties in or near the Red River Basin based on quartiles of the data shown in table 1 for nitrogen and phosphorus, respectively. The highest use areas are near the center of the basin and primarily in the Red River Valley Lake Plain. The counties directly adjacent to the Red River tend to have the highest application rates.

It is uncertain why the top 12 counties based on nitrogen and phosphorus application are all on the Minnesota side of the basin. This could reflect different agricultural policies and practices, including how the data are reported, compensation for increased plant growth and nutrient uptake, or compensation for increased rainfall with resulting wash-off or leaching of applied nutrients that need to be replaced.

Fertilizers (including manure from different livestock) can contain varying ratios of nitrogen to phosphorus. Table 1 and figures 3 and 4, however, show that generally these differences would not change the relative ranking of most of the counties. The counties would rank about the same whether they were ordered by nitrogen application or phosphorus application.

Statistics on pesticide use periodically are compiled by the Minnesota Department of Agriculture, the North Dakota State University Extension Service, and the South Dakota Department of Agriculture. Different methods for collecting and reporting usage statistics are used by these agencies and, therefore, these data cannot be readily combined and compared. These statistics, however, can be used to estimate relative usage rates for pesticides. The most commonly used pesticides in the Red River Basin are summarized in tables 2 and 3. More complete descriptions of pesticide usage in the Red River Basin are given by McMullen and others (1990), and by the South Dakota Department of Agriculture (1988).

Pesticide usage changes through time. New pesticides are developed, some pesticides are banned because of health concerns, and some are replaced with more effective alternatives. Such shifts may have beneficial implications for water quality and ecosystem integrity; many earlier pesticides (especially organochlorines) degrade slowly in the environment and bioaccumulate. Some of these chemicals have been replaced with more toxic compounds applied at lower rates. These compounds may be less persistent in the environment, but have unknown ecological effects. Various pests can become tolerant to certain pesticides over many generations, thus requiring different pesticides for effective control. Major insect infestations can result in high insecticide usage. Data for the state of North Dakota indicate that the total agricultural

Table 1.--Estimates of nitrogen and phosphorus application for counties in the Red River of the North Basin (Modified from Alexander and Smith, 1990)

[units in kilograms per square mile]

County	Nitrogen				Phosphorus			
	From chemicals	From manure	Total	Per area of agriculture	From chemicals	From manure	Total	Per area of agriculture
Stevens, Minn.	16,700	4,100	20,800	24,500	3,300	1,700	5,000	5,800
Norman, Minn.	19,200	900	20,100	23,700	3,700	280	4,000	4,700
Traverse, Minn.	17,500	1,700	19,200	21,800	3,400	670	4,100	4,600
Wilkin, Minn.	18,400	550	19,000	21,300	3,600	220	3,800	4,300
Clay, Minn.	16,400	1,600	18,000	21,900	3,200	500	3,700	4,500
Polk, Minn.	16,000	820	16,800	22,500	3,100	230	3,300	4,500
Marshall, Minn.	12,900	4,000	16,800	25,500	2,500	1,200	3,800	5,700
Grant, Minn.	15,100	1,700	16,800	21,300	2,900	640	3,600	4,500
Big Stone, Minn.	13,500	2,300	15,800	21,600	2,600	930	3,600	4,900
Red Lake, Minn.	13,600	1,800	15,400	21,400	2,700	480	3,100	4,400
Pennington, Minn.	14,200	1,100	15,400	20,500	2,800	310	3,100	4,100
Kittson, Minn.	12,900	590	13,500	20,800	2,500	180	2,700	4,100
Cass, N.Dak.	9,900	900	10,800	12,400	2,000	300	2,300	2,700
Traill, N.Dak.	10,100	240	10,400	11,500	2,100	94	2,200	2,400
Steele, N.Dak.	9,800	300	10,100	11,600	2,000	88	2,100	2,400
Richland, N.Dak.	8,500	1,300	9,800	12,100	1,700	440	2,200	2,700
Pembina, N.Dak.	8,600	480	9,100	10,700	1,800	190	1,900	2,300
Walsh, N.Dak.	8,500	570	9,100	10,400	1,700	180	1,900	2,200
Grand Forks, N.Dak.	8,500	570	9,000	11,300	1,700	180	1,900	2,400
Otter Tail, Minn.	5,400	3,400	8,800	20,500	1,100	790	1,800	4,300
Roseau, Minn.	7,900	890	8,800	17,600	1,500	240	1,800	3,500
Mahnomen, Minn.	6,700	1,200	7,900	18,700	1,300	350	1,600	3,900
Barnes, N.Dak.	6,900	950	7,800	9,700	1,400	290	1,700	2,100
Sargent, N.Dak.	5,900	1,600	7,600	11,200	1,200	560	1,800	2,600
Cavalier, N.Dak.	7,000	230	7,200	8,500	1,400	71	1,500	1,800
Ransom, N.Dak.	5,200	1,800	7,100	9,000	1,100	600	1,700	2,100
Griggs, N.Dak.	5,800	1,200	7,000	9,200	1,200	360	1,500	2,000
Roberts, S.Dak.	3,800	3,000	6,700	11,400	760	980	1,700	3,000
Foster, N.Dak.	5,000	1,400	6,300	8,200	1,000	400	1,400	1,800
Becker, Minn.	4,500	1,800	6,300	19,100	870	460	1,300	4,000
Nelson, N.Dak.	5,300	600	5,900	7,800	1,100	170	1,300	1,700
Wells, N.Dak.	4,800	1,000	5,900	7,400	980	290	1,300	1,600
Towner, N.Dak.	5,400	300	5,700	6,600	1,100	92	1,200	1,400
Ramsey, N.Dak.	5,400	280	5,700	7,400	1,100	83	1,200	1,500
Stutsman, N.Dak.	4,200	1,400	5,700	8,500	860	400	1,300	1,900
Eddy, N.Dak.	3,000	1,400	4,500	6,300	620	420	1,000	1,500
Benson, N.Dak.	3,300	1,100	4,400	6,000	680	300	970	1,300
Marshall, S.Dak.	3,400	470	3,900	7,700	700	130	830	1,600
McHenry, N.Dak.	2,300	1,500	3,800	7,200	470	430	900	1,700
Rolette, N.Dak.	2,600	1,100	3,800	6,500	540	330	860	1,500
Pierce, N.Dak.	2,300	1,000	3,300	4,800	460	280	740	1,100
Clearwater, Minn.	1,600	1,200	2,800	19,700	300	320	620	4,400
Sheridan, N.Dak.	1,400	1,100	2,500	4,700	290	300	590	1,100
Beltrami, Minn.	620	410	1,000	12,900	120	100	220	2,800
Itasca, Minn.	680	220	900	17,900	130	68	200	4,000
Lake of the Woods, Minn.	720	130	840	9,400	140	37	180	2,000
Koochiching, Minn.	440	99	540	13,600	87	28	110	2,900

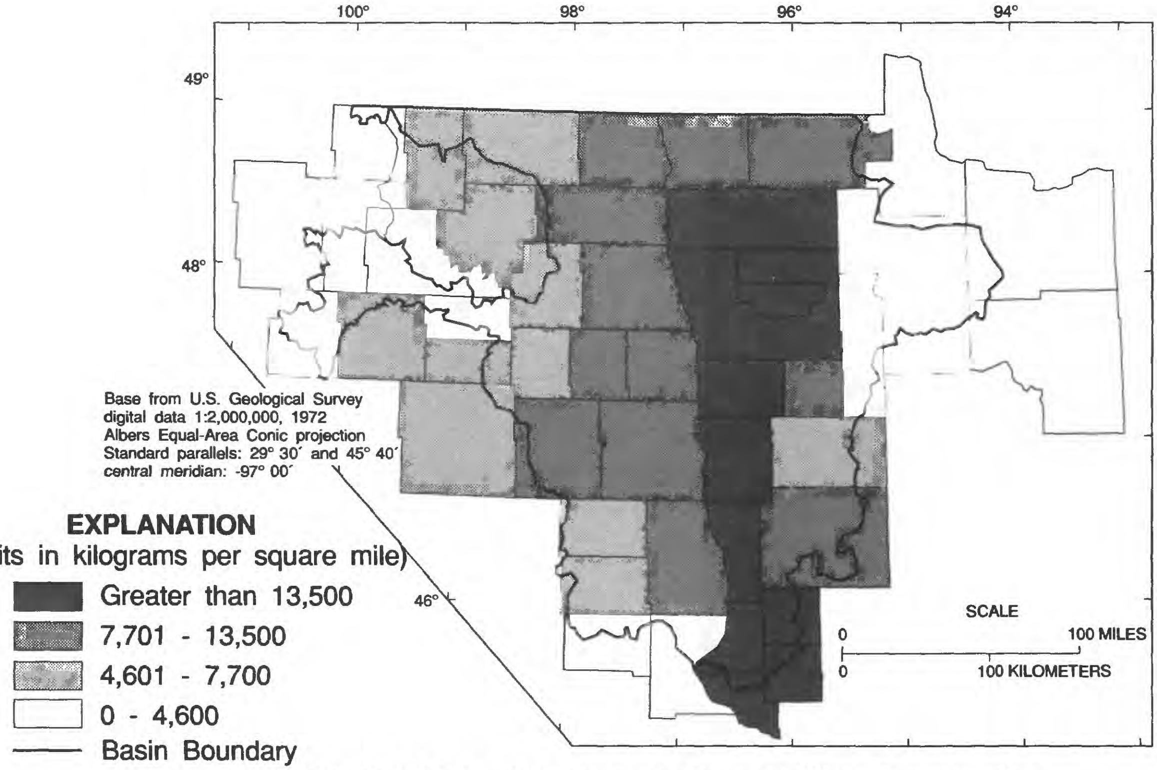


Figure 3.--Estimated total nitrogen applied as fertilizer for counties in and near the Red River of the North Basin. [Modified from Alexander and Smith, 1990]

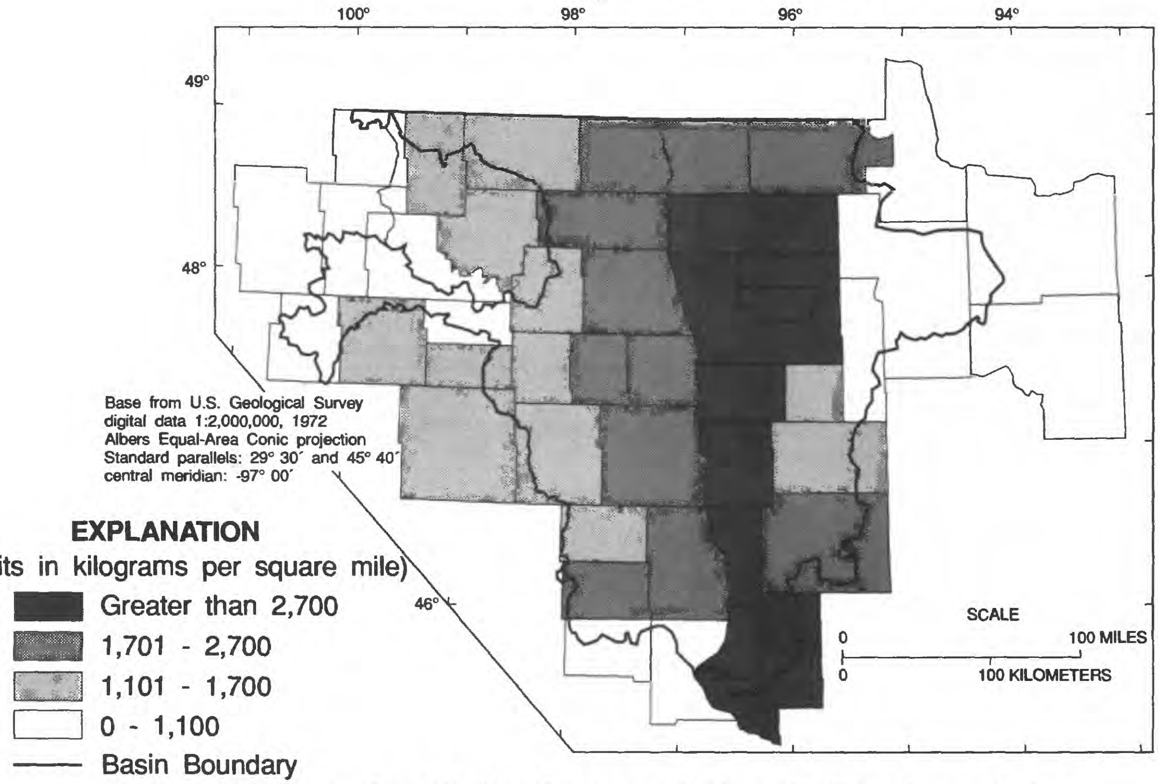


Figure 4.--Estimated total phosphorus applied as fertilizer for counties in and near the Red River of the North Basin. [Modified from Alexander and Smith, 1990]

Table 2.--Pesticide applications in North Dakota for 1989 (from McMullen and others, 1990).

[All values in thousands of acres applied]

Fungicides			
Triphenyltin hydroxide	173	Sulfur	6.7
Mancozeb	165	Benomyl	4.1
Propiconazole	163	Thiabendazole	3.4
Maneb	67		
Metiram	24		
Herbicides			
2,4-D, 2,4-D amine, and 2,4-D ester	8107	Imazamethabenz	91
MCPA, MCPA amine, and MCPA ester	4384	Pendimethalin	79
Trifluralin	4077	Barban	60
Dicamba	3085	Metolachlor	55
Metsulfuron	1190	Metribuzin	33
Triallate	1021	Cycloate	32
Diclofop	1833	Chloramben	30
Ethalfluralin	725	Propanil	23
Bromoxynil	646	Diethatyl	23
Chlorsulfuron	427	Endothall	19
Bentazon	411	Paraquat	10
Glyphosate	406	Butylate	9.8
EPTC	350	Diallate	9.0
Desmedipham	296	Tridiphane	8.3
Cyanazine	204	Fluazifop-P	6.0
Phenmedipham	200	Amitrol	5.8
Sethoxydim	190	Quizalofop	3.7
Picloram	180	Ethofumesate	3.3
Fenoxaprop-ethyl	149	Benefin	3.2
Clopyralid	128	Propachlor	3.1
Acifluorfen	111	Diquat	2.2
Atrazine	110	Lactofen	1.3
Difenzoquat	103	Imazethapyr	.2
Alachlor	97		
Insecticides			
Carbofuran	530	Dimethoate	14
Ethyl parathion	348	Aldicarb	12
Fenvalerate	280	Trichlorfon	4.4
Esfenvalerate	261	Pyrethroid	4.4
Methyl Parathion	210	Disulfoton	4.1
Terbufos	132	Oxamyl	2.5
Malathion	101	Fonofos	1.9
Carbaryl	80	Methidathion	1.6
Chlorpyrifos	72	Azinphos-methyl	.6
Phorate	69	Acephate	.1
Phosphamidon	68	Chlordane (technical)	.1
Endosulfan	34		

Table 3.--Relative area of herbicide and insecticide applications for Minnesota counties in the Red River of the North Basin, 1989. (Note: the data are tabulations of survey statistics, and are not extrapolated to estimate the total chemical usage in the region. These data are presented only to show relative usage rates. (From J.W. Hines, written commun., 1992))

[All values in thousands of acres applied]

Herbicides			
MCPA, MCPA amine, and MCPA ester	84	Imazethapyr	10
Bromoxynil	68	Acifluorfen	10
Trifluralin	48	Atrazine	8.9
2,4-D, 2,4-D amine, and 2,4-D ester	43	Chlorsulfuron	7.1
Diclofop-methyl	32	Difenzoquat	6.7
Trifensulfuran (thiameturon-methyl)	32	Fenoxaprop	5.9
Bentazon	29	Clopyralid	5.2
Dicamba	27	Fluazifop-P-butyl	4.4
Desmedipham	25	Metribuzin	3.5
Phenmedipham	22	Metolachlor	2.6
Triallate	21	Pendimethalin	2.4
Sethoxydim	18	Cycloate	2.4
Imazamethabenz	18	Glyphosate	2.1
Ethafluralin	14	Propanil	1.4
EPTC	13	Lactofen	1.4
Cyanazine	13	Barban	.4
Alachlor	12		
Insecticides			
Terbufos	81		
Chlorpyrifos	36		
Phorate	23		
Parathion	18		
Fonofos	14		
Carbofuran	8.1		
Esfenvalerate	7.3		
Carbaryl	7.3		
Malathion	5.9		
Tefluthrin	4.2		
Permethrin	3.3		
Dimethoate	.7		
Acephate	.7		
Diazinon	.4		

lands on which herbicides, insecticides, and fungicides are used have increased substantially from 1978 to 1989 (McMullen and others, 1990).

Agricultural practices affect soil erosion and sediment transport. Erosion can be influenced by many factors, including frequency and timing of tillage, tillage of steep lands and gullies, the direction of plowing with respect to the land slope, and over grazing, which can damage plant cover. Many practices have been developed to minimize soil erosion. These include reduced-tillage farming, contour farming, maintaining untilled buffer strips on steep lands and near streams, and planting cover crops.

Agricultural effects on water quality are often interdependent. Reduced-tillage farming methods, for example, may result in greater competition for water and nutrients by weeds. This could result in greater use of herbicides to control weeds.

Other influences also can affect nutrient, suspended-sediment, and pesticide concentrations in natural waters. Sewage effluent can substantially increase nutrient concentrations. Runoff and natural erosion mobilize nutrients and sediment, and land disturbance, such as construction, exacerbates these processes. Fertilizers and herbicides applied to golf courses and lawns also can affect nutrient and pesticide concentrations in nearby waters.

Purpose and Scope

This report summarizes selected data on nutrients, suspended sediment, and pesticides in the Red River Basin; identifies sources of these constituents; and identifies areas where data currently are not sufficient to characterize water quality. The constituents described in this report are nitrogen and phosphorus nutrient species, suspended sediment in streams, and synthetic organic pesticides that were sampled during 1970-90. Supplementary pesticide data collected during the 1960s and 1991-92 are included in this report.

This basin-wide analysis of water-quality data will provide a basis for future water-quality studies in the basin, such as those by the NAWQA program and by water-resource managers and investigators from the Red River Basin. Information from this report will be synthesized with data from similar NAWQA studies across the country to assess water quality at a national scale.

The data evaluated here are generally from within the Red River Basin although ground-water data collected near (but outside) the basin boundary are included. Even though quality-assurance methods for earlier data may not meet current standards, or may not be adequately documented, the earlier data were included for comparative purposes.

Method of Data Review

Inclusion of data for this report generally depended on several factors. Accessibility of data in a computerized data base was an important consideration. Because pesticide data for the Red River Basin were sparse, additional effort was made to review data from selected written reports. Data collected to characterize chemical spills or point sources are not included in this report. Data from different sources generally are treated separately in this report. Some nutrient data from the USEPA's STORET (STOrage and RETrieval) data base were not separated according to sampling program or differences in methods, because this information was not readily available.

Reported concentrations of chemicals in natural waters are dependent on sampling methods and vary among agencies and over time. For example, stream hydraulics affect the distribution of chemicals and suspended sediment at a stream cross-section. Water samples collected near the surface at the stream center may not contain the same chemical concentrations as water samples collected using depth- and width-integrated sampling methods (Martin and others, 1992).

Differences in analytical methods also confound direct comparison of water-quality data among and within agencies as methods change over time. Because of the many factors that affect analytical results, there has been an increasing awareness of the importance of using quality-assurance methods to substantiate environmental analytical data (Keith and others, 1983). Data that are not quality assured are of limited value because they have not been demonstrated to fall within a defined margin of error of true analyte concentrations. The environmental chemistry literature contains much data that were later shown to be biased, sometimes by several orders of magnitude (Patterson and Settle, 1976). Such bias might have been detected if rigorous quality-assurance methods had been in place.

Another consideration is the method used for determining the reporting limit for each analyte; different methods may be used by different agencies or by the same agency over time. In the 1960s and 1970s, laboratories commonly reported the concentration of an analyte as zero if the analyte was not detected. As detection limits were rigorously defined and brought into common use (American Chemical Society Committee on Environmental Improvement, 1980; Long and Winefordner, 1983), the concentration of an analyte was reported as less than a specified detection limit (for example, <0.1 mg/L) if the analyte was not detected. Because analytical data that are equal to or slightly higher than detection limits are imprecise, many laboratories use a limit of quantitation, which is a concentration that is several times higher than the detection limit (American Chemical Society Committee on Environmental Improvement, 1980). Thus, when an analyte is either not detected, or is detected at or above the detection limit (but below the limit of quantitation), its concentration is reported as less than a specified limit of quantitation. In some data bases it is common to see reporting limits for analytical methods increase over time due to the introduction of these procedures.

Improvements in sampling and analytical methods can result in lower detection limits, and therefore lower reporting limits. Improved methods can yield data that, when combined with earlier data, show spurious downward temporal trends in chemical concentrations (Flegal and Coale, 1989).

Because of temporal changes in reporting limits, pesticide data used in this report were examined and screened before use. When data for a given chemical show increases in reporting limits over time, all data are censored at the highest reporting limit. This was done not only because the earlier reporting limit may not have been rigorously defined, but also to allow for the application of more valid statistical tests (Helsel and Hirsch, 1992, p. 369). When reporting limits decrease over time, and the decreases can be ascribed to improved sampling methods such as elimination of sample contamination, pesticide data are not censored at the highest reporting limit.

Reporting limits also complicate the interpretation of nutrient concentrations. Because of the difficulty in determining the appropriate reporting limit for each nutrient analyzed for each laboratory that may have analyzed a sample and which method they might have used, nutrient data used in this report were not censored. Data shown in illustrations and in tables are presented as they are stored in the source data base. As a guide to the readers of this report, the reporting limit for the most common nutrient analyses performed by the USGS National Water-

Quality Laboratory in Arvada, Colorado are provided with the data where appropriate. The reader needs to be aware that this reporting limit may not be applicable to all the data shown, and that any data less than the displayed reporting limit could be, but are not necessarily, inaccurate.

Most of the data in this report were analyzed using the Statistical Analysis System (SAS; Release 6.07) on a Data General Unix workstation[1]. SAS was used to store and manipulate data, produce statistical summaries, and produce preliminary copies of most of the data plots shown in this report.

Much of the data in this report are summarized graphically as truncated box plots (Helsel and Hirsch, 1992). Box plots concisely show skewness, central tendency, and range. Where more than 15 data values are available, the box plots are truncated at the 10th and 90th percentiles so that extreme values are not displayed. Where 10 to 15 data values were available, box plots are generally truncated at the 25th and 75th percentiles. Where fewer than 10 data values were available individual data points are displayed. Sample sizes (number of values) are shown with each box plot.

Data Sources

Several State and local agencies monitor water quality of streams and lakes for regulatory purposes and ambient monitoring. Federal agencies, including the USGS, commonly collect water-quality data for monitoring or for addressing specific water-quality issues. The USEPA often collects water-quality samples through contracts with State or local agencies. Table 4 shows the sources of water-quality data known to be available for the Red River Basin. Data from all these sources were not included in this report, but will be evaluated more completely as study continues in the Red River Basin.

Several data sources were used for this report. Most data were obtained from computerized data bases. These include the USEPA STORET system, which is used as a repository for water-quality data by the Minnesota Pollution Control Agency (MPCA), the North Dakota Health Department, and other agencies; and the USGS National Water Information System (NWIS). Additional data were acquired from Environment Canada and the North Dakota State Water Commission (NDSWC) data bases, and, for selected pesticide data, from written reports and journal articles.

The STORET and NWIS data bases were searched for about 350 different constituents that encompass most organic pesticides used presently and historically in the Red River Basin. Because of the various media (water, bottom sediment, and biological tissue) sampled and the various degradation products and isomers that are measured, more than one value may exist for a given pesticide.

Acknowledgments

Several individuals and state agencies contributed data or technical advice to this work. John Hines and Bruce Montgomery of the Minnesota Department of Agriculture, and Gregory Dahl and Bruce Seelig of the North Dakota Extension Service provided information on pesticide usage. Stanley Smith of the U.S. Fish and Wildlife Service provided information on the National Contaminant Biomonitoring Program work that has been conducted at a site on the Red River. Tom Klaseus provided several reports of the Minnesota Department of Health efforts on monitoring of pesticides. Val Chacko of Environment Canada provided reports and data from their monitoring efforts. David Ripley assisted in providing data collected by the North Dakota State Water Commission. Dave Wall of the Minnesota Pollution Control Agency provided useful background information about nitrogen in ground water. Members of the Red River Basin NAWQA liaison committee also provided information included in this report.

Nutrients

Nutrients in ground and surface waters, although present from natural sources including phosphatic minerals and nitrogen fixed from the atmosphere, can increase because of human activities. Agricultural practices including livestock production and application of fertilizers can cause increased nutrient concentrations in natural waters when they leach into the ground water or run off into nearby streams or lakes. Urban areas are also sources of nutrients including sewage effluent, lawn fertilization, and storm runoff. Nitrate nitrogen can be a substantial part of the acid precipitation that results from the burning of fossil fuels. Ammonia nitrogen also can be transported through the atmosphere.

When nutrients are enriched in natural waters, the density of plants often will increase because plant growth is enhanced. This can lead to eutrophication of lakes and streams and cause high variability in dissolved-oxygen concentrations and pH as the plants alternately photosynthesize and respire. Increased plant density can decrease light penetration, reduce stream velocities, and ultimately alter the stream ecosystem.

[1] The use of brand or trade names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

Table 4.--Sources of water-quality data for the Red River of the North Basin

Agency	General purpose and availability of data for water-quality assessment
	Federal agencies
U.S. Army Corps of Engineers	Samples are collected for comprehensive studies to evaluate impacts of water-regulations projects. The data, which may be accessible from computer files, include field measurements of reservoir profiles and at stream sites downstream from reservoirs. Some data are available through the Reservoir Operating Plan Evaluation (ROPE) program.
U.S. Bureau of Indian Affairs	Samples have been collected in cooperation with individual Indian tribes and reservations to describe the quality of water resources. Data may be available for the Reservations of Fort Totten, Red Lake, Lake Traverse, Turtle Mountain, and White Earth.
U.S. Bureau of Reclamation	Data are collected to assess impacts of irrigation and water delivery systems on water quality. Most data collected after the 1980's are available on computer files.
U.S. Department of Energy - National Uranium Resource Evaluation Program	Water samples from wells and bottom material samples from streams were collected to assess national uranium resources. Data are computerized and accessible, but include only concentrations of inorganic constituents.
U.S. Environmental Protection Agency (USEPA) STOrage and RETrieval system (STORET)	Data are collected by the Minnesota Pollution Control Agency, North Dakota Department of Health, and South Dakota Department of Water and Natural Resources for general water research and for regulatory programs. The data are computerized and accessible. Information is available about the quality of surface water, ground water, sediment, fish tissue, and some effluents. Other water-quality data are available from BIOS (biological data system), PCS (permit compliance system), and Reach (hydrographic mapping and graphing program); some bioassessment data also may be available from paper files.
U.S. Fish and Wildlife Service	Samples are collected for special projects and to measure trends. Data include contaminant residues (metals, pesticides, and polynuclear aromatic hydrocarbons) in tissues of fish, migratory birds, and aquatic organisms. Some pesticide data from wetlands outside of the Red River Basin to evaluate toxicity effects are available in paper files for some sites in North Dakota. Specific data for Kelly's Slough and Tewaukon Wildlife Refuges are available.
U.S. Geological Survey (USGS) National Water Information System (NWIS)	Data are collected for water-quality studies, networks, and general research and are readily accessible from computerized data bases. Information about stream, aquifer, and well conditions commonly are available. Much of these data were collected in cooperation with other Federal, State and local agencies.
Canadian Agencies	Data are collected to monitor and help regulate the health of natural resources. Data on hydrology, land use and land cover, water use, and water quality collected by federal and provincial governments and private contractors are available. Many years of data, some resulting from intense sample collection, are available for the Red River at Emerson, Manitoba. Data also are available for the Pembina and Roseau River subbasins. Agencies include the Water Survey of Canada, Environment Canada, and several agencies from Manitoba. Much of the Environment Canada data is available in computerized data bases.
	State and local agencies - Minnesota
Department of Agriculture	Concentrations of pesticides and nutrients are measured statewide to monitor trends and to determine the effects of agricultural practices on water quality. Data include samples from wells, surface water, and precipitation; and six years of quarterly samples for 20 wells outside the Red River Basin. Data are available and computerized in several formats.
Department of Health	Pathogens, nitrate, and some toxic compounds are measured to define the health of public and some private drinking-water supplies. Most data are for concentrations of common ions, especially before 1974. Data for special studies include volatile organic compounds for all community and some nontransient noncommunity wells; heavy metals and radiochemicals for many ground-water systems; and pesticides (Safe Drinking Water Act parameters at all community systems using surface water, plus pesticides and selected breakdown products for many wells and some aquifers). Data from special studies and samples from new wells are accessible from computer files, other data are in paper files.

Table 4.--Sources of water-quality data for the Red River of the North Basin (Continued)

Agency	General purpose and availability of data for water-quality assessment
Department of Natural Resources, Fish and Wildlife Division	Data are collected to aid in the management of State game and wildlife, including data on physical and chemical parameters to assess fisheries in lakes and streams. Data are available in STORET and D-base IV computer files.
Pollution Control Agency	Data are collected for regulatory programs, to describe ambient water-quality conditions, and for general water research. This agency cooperates with USEPA in populating the STORET and PCS data bases and administers the Clean Water Partnership programs that produce water-quality data for watersheds in the state, such as the Clearwater River study of agricultural-chemical runoff.
Municipalities	Data are collected for regulatory and water-treatment process control functions. Includes the cities of Moorhead, Fergus Falls, Thief River Falls, and Crookston.
Red Lake Indian Reservation	Data have been collected to monitor the status and trends of water quality in lakes. Ground-water quality near selected landfills has been monitored in cooperation with USEPA. Data is available from STORET, although some data are in Lotus files.
Universities and Colleges	The data collected have been for specific water research. Most of this data is available only from paper files. Likely sources of data include the Crookston and Morris campuses and the Water Resources Research Institute of the University of Minnesota, as well as Bemidji State University, Concordia College, and Moorhead State University.
White Earth Indian Reservation	Pathogens, inorganic constituents, and nitrates have been sampled to determine the quality of drinking water supplies. Much of these data was collected in cooperation with the Indian Public Health Service and the U.S. Bureau of Indian Affairs. Some aquatic biological data has been collected for 31 lakes, and includes fish tissue analyses. Water quality measurements have been made on most streams, and some chemistry data is available for ground water near landfills. Most data are available from STORET.
	State and local agencies - North Dakota
Department of Health	Data are collected to support regulatory and monitoring functions. Measurements of pathogens and general water chemistry are available from paper files. Ambient stream quality data are stored in STORET. Ground-water data have been collected since the 1940's.
Game and Fish Department	This agency collects data necessary to manage State game and fish resources. Water chemistry, measurements of fish populations, and tissue analyses are available. The data are kept in paper files.
Fort Totten Indian Reservation	Data that have been collected to describe water resources are available from USGS computer files.
Municipalities	Data are collected for regulatory and water treatment and for process control functions. The cities of Fargo, Grand Forks (which has its own laboratory), Wahpeton, and Valley City are involved in this monitoring.
State Water Commission	This agency has an extensive monitoring network operated to determine status and trends in the State's ambient water quality. Data also are collected to support research and special projects. Measurements mostly include common ions for surface and ground waters. Their data are available in a computerized form.
Universities	Data are collected for specific water research and generally is disseminated in theses and through dissertations. Probable sources include North Dakota State University and the University of North Dakota and the Water Resources Research Institute of the University of North Dakota.
	State and local agencies - South Dakota
Department of Water and Natural Resources	Data are collected to describe and regulate water resources; some of these data are available from STORET.
Lake Traverse Indian Reservation	Data have been collected to characterize Reservation water resources; these data are available from USGS computer files.
Universities	Data are collected for specific water research and generally is disseminated in theses and through dissertations. Probable sources include the Water Resources Research Institute of the University of South Dakota.

Nitrite and nitrate nitrogen have been shown to cause health problems and even death to human infants and livestock when concentrations are excessive (Wall and Montgomery, 1991). Wall and Montgomery (1991) also describe in more detail some of the health effects and the implications of elevated nitrogen concentrations.

Surface Water

Although numerous stream sites throughout the Red River Basin have been sampled, the number of samples collected and analyzed often are inadequate to fully characterize stream quality at a particular site. Full characterization of constituent concentrations is difficult because concentrations of a stream can change substantially over time. Samples collected during base streamflow conditions usually indicate much different stream quality than samples collected during a flood. Because the streamflow regimes that were sampled generally are unknown, much of the data provided here should be considered as only a general characterization of the quality of the streams.

Another consideration in reviewing the data provided in this report is that streams throughout the Red River Basin have not been sampled during concurrent time periods. Changes in land use, climate, and hydrologic variability within stream basins could confound comparisons of stream-water quality across the basin.

Several criteria were used to optimize the comparability between streams and along streams. These criteria are that (1) the site has at least two years of data, (2) at least eight samples were analyzed for the constituent evaluated, (3) the samples were collected quarterly or more frequently, (4) the sampling was done during 1970-90, and (5) the site was not sampled to monitor a point-source input. Figure 5 shows the location of stream-sampling sites included in this report. The stream sites included in this report are listed in table 5.

Comparison of the physiographic areas shown in figure 1 with the distribution of sampling sites shown in figure 5 shows that the majority of sampling sites are primarily along the Red River and in the Red River Valley Lake Plain. Very few sampling sites were situated in or near the other physiographic areas. Sampling sites that were in other areas usually were only on one stream, and that stream may not represent the water quality of the entire area. This limited distribution of sampling sites prevents making generalizations about the water quality within and comparisons of the water quality among the various physiographic areas in the Red River Basin.

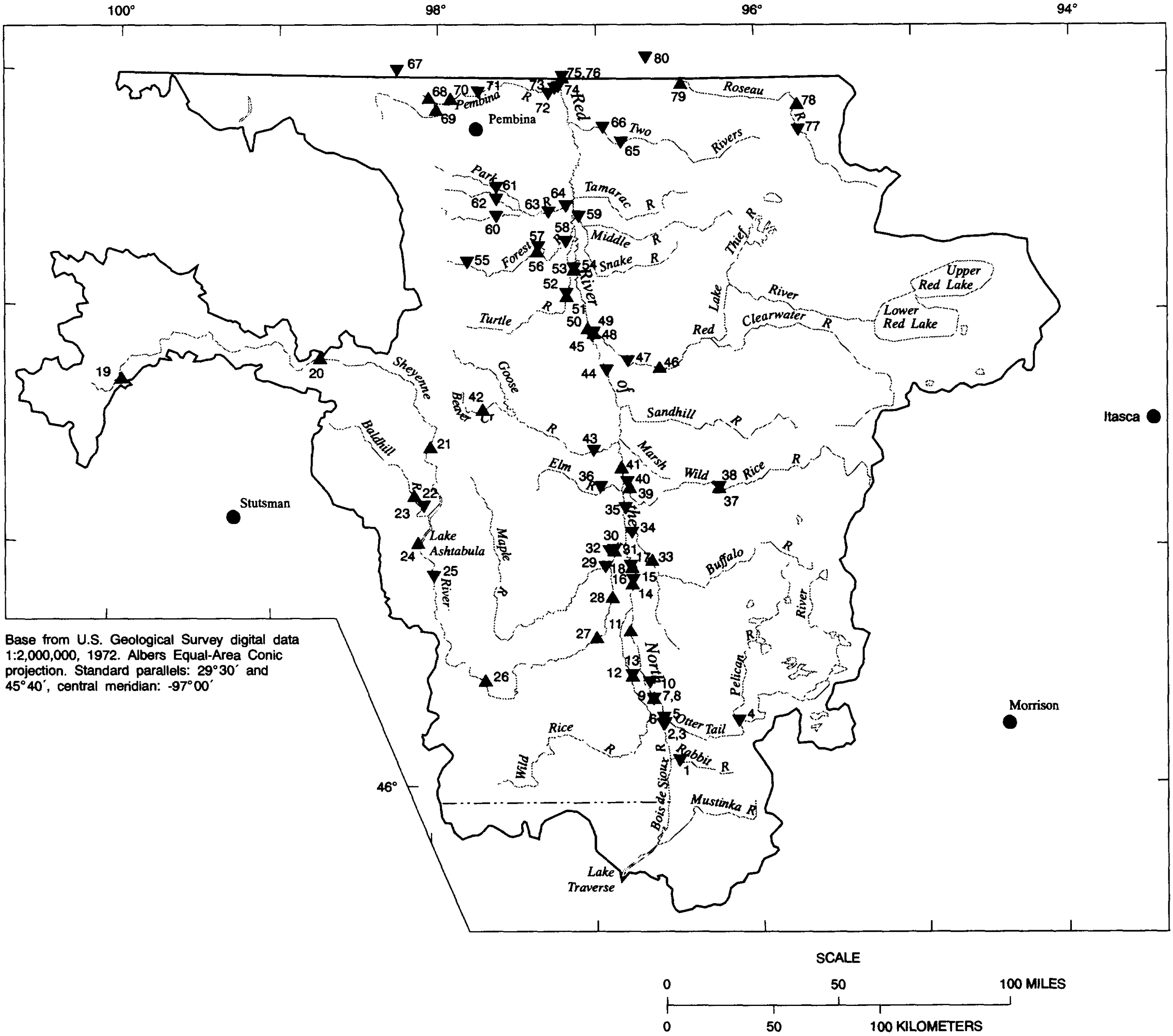
Figure 6 shows the distribution of sample dates for USGS stream water-quality monitoring sites summarized in this report. Data collected from several sites sampled for long time periods (decades) and with sufficient frequency can be used to identify water-quality trends and long-term averages. Sites 9 (on the Red River) and 30 (on the Sheyenne River) have been sampled for relatively short, but concurrent time periods, and could be used to compare the quality between the two basins. It could be misleading, however, to compare the water quality between these two sites with the water quality of the Sheyenne River at site 27 which was sampled many years later. Although it is most prudent not to compare data from different time periods, few sample sites would remain if strict selection criteria were applied. It would be difficult to describe the water quality of an area the size of the Red River Basin with data from only a few sites.

Nitrogen

Total nitrogen concentrations in streams ranged from below detection (0.1 mg/L) to more than 20 mg/L measured at the Red River at Halstad, Minn. Dissolved nitrogen concentrations ranged from below detection to 3.4 mg/L and averaged about 78 percent of the total nitrogen. Fewer data were available to compute dissolved nitrogen concentrations, but those that were computed had a distribution similar to but slightly less than that for total nitrogen. Only ten sites had sufficient data for inclusion in figure 7, which shows the distribution of nitrogen concentrations for USGS stream sampling sites in the basin. Median nitrogen concentrations were high at two sites on the Red River; Halstad, Minn. and Emerson, Manitoba. Sites on the Sheyenne River also tended to have higher median nitrogen concentrations than other tributary streams. The largest range in nitrogen concentrations was found on the Pembina River.

Considerably more data were available to describe nitrate concentrations than for total nitrogen concentrations throughout the basin, partly because of its health-related effects and because some assumptions were made to maximize the amount of data available. Nitrite-nitrogen concentrations were almost always negligible (often below detection) and comprised a minor portion of the nitrite plus nitrate frequently determined in analyses. Because of its high solubility, total nitrate was about the same as dissolved nitrate. Also, for USGS data, it has been determined that there essentially is no difference between paired analyses for total versus dissolved analyses of nitrite plus nitrate (David Rickert, USGS, written commun., 1992).

Figure 8A shows the distribution of nitrate concentrations in streams in the Red River Basin. The highest median concentrations of nitrate were found in the Sheyenne River, especially near the mouth, and the



EXPLANATION

Surface-water monitoring site, number is indentification for this report

▲9 Monitored by USGS

▼1 Monitored by other agencies

● Atmospheric deposition Monitoring site

Figure 5.--Stream sampling sites and atmospheric deposition monitoring sites in the Red River of the North Basin.

Table 5.-- Stream sites sampled for analysis of nutrients, suspended sediment, and pesticides (listed in downstream order)

[DD, degrees; MM, Minutes; SS, seconds]

Map site identifier (figure 5)	USGS site identifier	Site name	Latitude DD MM SS			Longitude DD MM SS		
1		Rabbit River at US-75 near Campbell, Minn.	46	06	43	096	30	00
2		Bois de Sioux River at Wahpeton, N. Dak.	46	15	50	096	35	55
3		Bois de Sioux River at Breckenridge, Minn.	46	15	50	096	35	56
4		Otter Tail River near Fergus Falls, Minn.	46	16	32	096	08	21
5		Otter Tail River at Breckenridge, Minn.	46	16	02	096	35	23
6		Red River of the North at Wahpeton, N. Dak.	46	17	23	096	35	44
7		Red River of the North at Brushvale, Minn.	46	22	06	096	39	21
8		Red River of the North 6 mi N of Wahpeton, Minn.	46	22	11	096	39	23
9	05051510	Red River of the North below Wahpeton, N. Dak.	46	22	30	096	39	25
10		Whiskey Creek at US-75 at Kent, Minn.	46	26	22	096	40	46
11	05051522	Red River of the North at Hickson, N. Dak.	46	39	35	096	47	44
12	05053000	Wild Rice River near Abercrombie, N. Dak.	46	28	05	096	47	00
13		Wild Rice River, near Abercrombie, N. Dak.	46	28	05	096	47	00
14	05054000	Red River of the North at Fargo, N. Dak.	46	51	40	096	47	00
15		Red River of the North at Moorhead, Minn.	46	52	26	096	46	35
16	05054020	Red River of the North below Fargo, N. Dak.	46	55	50	096	47	05
17		Red River of the North at Fargo, N. Dak.	46	56	02	096	47	28
18		Red River of the North near Fargo, N. Dak.	46	56	02	096	47	28
19	05054500	Sheyenne River above Harvey, N. Dak.	47	42	10	099	56	55
20	05056000	Sheyenne River near Warwick, N. Dak.	47	48	20	098	42	57
21	05057000	Sheyenne River near Cooperstown, N. Dak.	47	25	58	098	01	38
22	05057200	Baldhill Creek near Dazey, N. Dak.	47	13	45	098	07	28
23		Bald Hill Creek near Dazey, N. Dak.	47	10	56	098	03	52
24	05058000	Sheyenne River below Baldhill Dam, N. Dak.	47	01	50	098	05	50
25		Sheyenne River at Valley City, N. Dak.	46	53	02	097	59	48
26	05058700	Sheyenne River at Lisbon, N. Dak.	46	26	49	097	40	44
27	05059000	Sheyenne River near Kindred, N. Dak.	46	37	54	097	00	01
28	05059400	Sheyenne River near Horace, N. Dak.	46	48	13	096	54	13
29		Maple River near Fargo, N. Dak.	46	55	44	096	56	44
30	05060600	Sheyenne River near Harwood, N. Dak.	47	00	05	096	53	40
31		Sheyenne River at Harwood, N. Dak.	47	00	05	096	53	40
32		Rush River near Harwood, N. Dak.	46	59	50	096	55	18
33	05062000	Buffalo River near Dilworth, Minn.	46	57	40	096	39	40
34		Buffalo River at Georgetown, Minn.	47	04	32	096	47	03
35		Red River of the North near Perley, Minn.	47	10	47	096	49	27
36		Elm River near Grandin, N. Dak.	47	16	01	096	58	33
37	05062500	Wild Rice River at Twin Valley, Minn.	47	16	00	096	14	40
38		Wild Rice River at Twin Valley, Minn.	47	15	56	096	14	51
39	05064000	Wild Rice River at Hendrum, Minn.	47	16	05	096	47	50
40		Wild Rice River near Hendrum, Minn.	47	17	21	096	48	42

Table 5.-- Stream sites sampled for analysis of nutrients, suspended sediment, and pesticides (listed in downstream order)--Continued

Map site identifier (figure 5)	USGS site identifier	Site name	Latitude DD MM SS			Longitude DD MM SS		
41	05064500	Red River of the North at Halstad, Minn.	47	21	10	096	50	50
42	05064900	Beaver Creek near Finley, N. Dak.	47	35	40	097	42	18
43		Goose River near Hillsboro, N. Dak.	47	25	12	097	01	02
44		Red River of the North south of Grand Forks, N. Dak.	47	45	37	096	56	15
45		Red River of the North at Grand Forks, N. Dak.	47	54	28	097	01	32
46	05079000	Red Lake River at Crookston, Minn.	47	46	32	096	36	33
47		Red Lake River at Fisher, Minn.	47	48	04	096	48	13
48	05082200	Red Lake River at East Grand Forks, Minn.	47	55	24	097	00	59
49		Red Lake River at East Grand Forks, Minn.	47	55	24	097	01	00
50	05082500	Red River of the North at Grand Forks, N. Dak.	47	56	34	097	03	10
51	05083000	Turtle River at Manvel, N. Dak.	48	04	43	097	11	03
52		Turtle River near Manvel, N. Dak.	48	05	13	097	11	02
53	05083500	Red River of the North at Oslo, Minn.	48	11	35	097	08	25
54		Red River of the North at Oslo, Minn.	48	11	39	097	08	26
55		Forest River near Fordville, N. Dak.	48	13	00	097	48	23
56	05085000	Forest River at Minto, N. Dak.	48	16	10	097	22	10
57		Forest River near Minto N. Dak.	48	17	09	097	21	47
58		Forest River E of Minto, N. Dak.	48	18	26	097	11	23
59		Snake River N of Big Woods, Minn.	48	24	50	097	06	26
60		South Br. Park River E of Park River, N. Dak.	48	24	51	097	37	23
61		North Br. Park River E. of Hoople, N. Dak.	48	32	07	097	37	25
62		Middle Br. Park River S of Hoople, N. Dak.	48	29	06	097	37	33
63		Park River N of Oakwood, N. Dak.	48	25	58	097	17	54
64		Park River at U.S. I-29 near Oakwood, N. Dak.	48	27	30	097	11	24
65		So. Branch Two Rivers 6.5mi SE of Hallock, Minn.	48	43	41	096	50	33
66		Middle Br. Two Rivers 1 mi N of Hallock, Minn.	48	47	24	096	57	24
67		Pembina River near Windygates, Manitoba	49	01	53	098	16	40
68	05099380	Pembina River near Vang, N. Dak.	48	55	00	098	03	23
69	05099400	Little South Pembina River near Walhalla, N. Dak.	48	51	55	098	00	20
70	05099600	Pembina River at Walhalla, N. Dak.	48	54	50	097	55	00
71		Pembina River near Leroy, N. Dak.	48	56	25	097	44	30
72		Tongue River SW of Pembina, N. Dak.	48	56	06	097	18	08
73		Pembina River near Pembina, N. Dak.	48	57	30	097	15	33
74		Red River of the North at Pembina, N. Dak.	48	57	54	097	14	13
75		Red River of the North at Emerson, Manitoba	49	00	30	097	12	40
76	05102500	Red River of the North at Emerson, Manitoba	49	00	30	097	12	40
77		Roseau River at Malung, Minn.	48	46	34	095	43	29
78	05105300	Roseau River below Roseau, Minn.	48	53	28	095	43	50
79	05112000	Roseau River below S.D. 51 near Caribou, Minn.	48	58	54	096	27	46
80		Roseau River at Gardenton, Manitoba	49	05	20	096	41	00

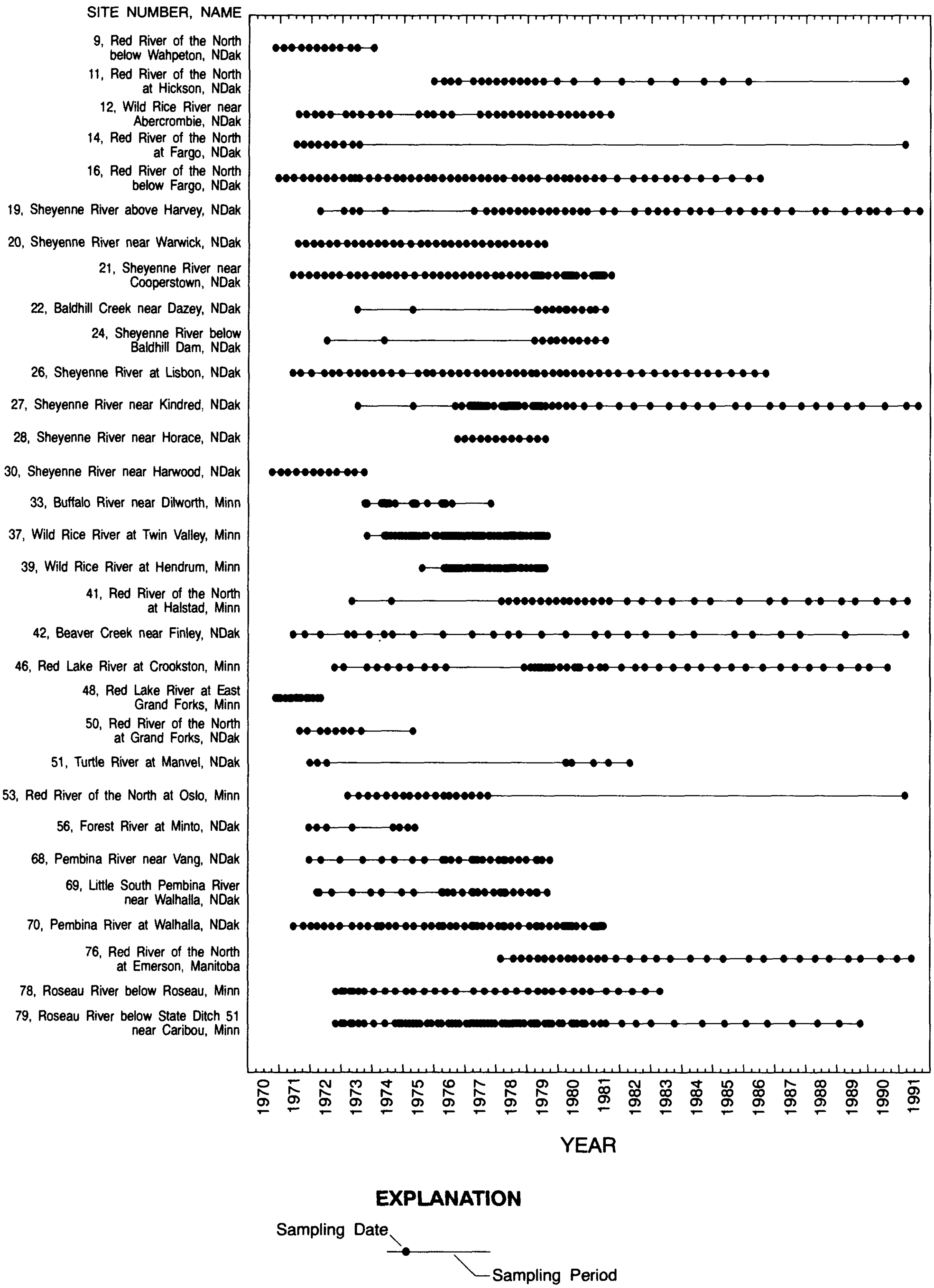
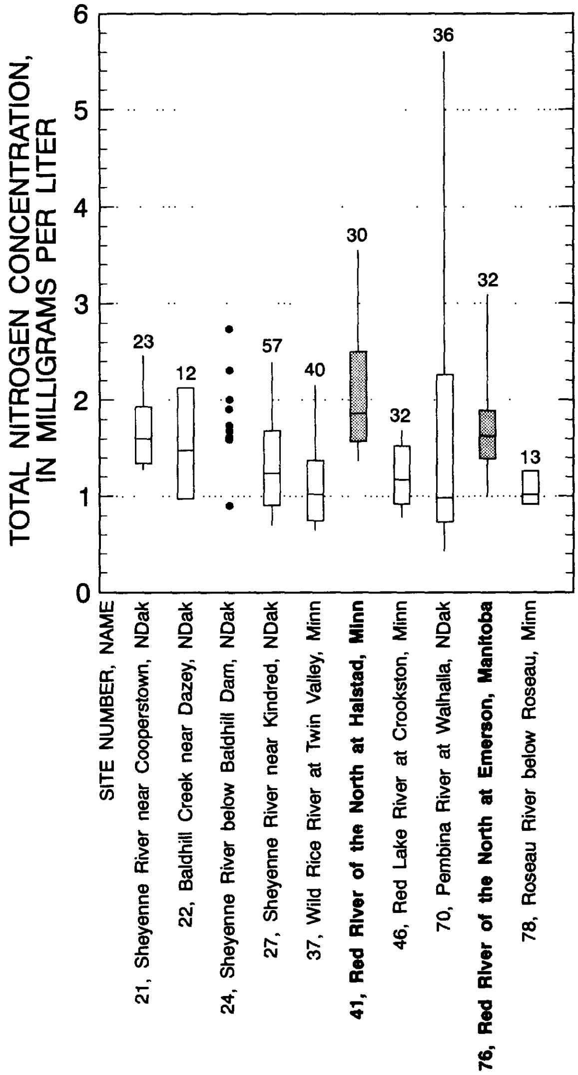


Figure 6.--Distribution of sample-collection dates for selected U.S. Geological Survey stream sites in the Red River of the North Basin.



EXPLANATION

Sites with more than 15 data values:

23 Number of observations

90th Percentile

75th Percentile

50th Percentile (Median)

25th Percentile

10th Percentile

Sites with 10-15 data values have no whiskers shown.

Sites with less than 10 data values have individual data values shown.

Shaded boxes indicate a site on the Red River of the North.

Figure 7.--Distribution of total nitrogen concentrations for selected U.S. Geological Survey stream sites in the Red River of the North Basin.

Pembina River (as high as 0.81 mg/L). Nitrate concentrations also were high in the Red River at Halstad, Minn. and Emerson, Manitoba.

The largest ranges in nitrate concentration were found at the three Pembina River sites (fig. 8A). This river drains some of the steepest agricultural land in the basin. This probably contributes to more rapid runoff of nutrients. This would cause frequent, high, and short-term runoff that results in a large range in nitrate concentrations.

Median ammonia concentrations shown on the box plots in figure 8B were above 0.2 mg/L at two sites on the Sheyenne River and two sites on the Red River. The Red River below Fargo, N. Dak. had the highest median ammonia concentration of more than 0.4 mg/L, and also had the largest range in values. This could be attributed to wastewater discharges from the Moorhead sewage treatment plant and other discharges from the Fargo-Moorhead area. The Fargo sewage treatment plant on the Sheyenne River probably contributed to the relatively high concentrations of ammonia detected downstream at the Harwood, N. Dak. site.

The high ammonia concentrations at the Red River at Halstad, Minn. and the Sheyenne River below Baldhill Dam are more difficult to interpret. At Halstad, it is possible that increased ammonia from the Fargo-Moorhead area is still present in the Red River, particularly during the winter months when re-aeration would be minimal. Also during the winter, elevated ammonia below Baldhill Dam on the Sheyenne River probably is caused by anoxic conditions in Lake Ashtabula. High ammonia concentrations near lake sediments may be present throughout the year, but the entire lake may build up high ammonia concentrations under ice cover (Wetzel, 1975). To verify this seasonality, ammonia concentrations from sites having high median concentrations (site 24 on the Sheyenne River and sites 16 and 41 on the Red River) were compared by month. Median ammonia concentrations during November through March were about or well above 0.5 mg/L, but during April through October ammonia concentrations were about 0.2 mg/L or less.

Analyses were available for ammonia plus organic nitrogen as total (TKN), dissolved (DKN), or both (TKN and DKN). More data were available for total ammonia plus organic nitrogen than for dissolved. Because the distribution of TKN and DKN concentrations are about the same, only TKN will be discussed in this report. Likewise, the organic nitrogen component of TKN can be determined only when ammonia concentrations are available. Because both values often are not available, TKN will be discussed.

About two thirds of the nitrogen in the rivers of the Red River Basin is TKN. Figure 8C shows that the distribution of TKN at each site and between sites is similar to the

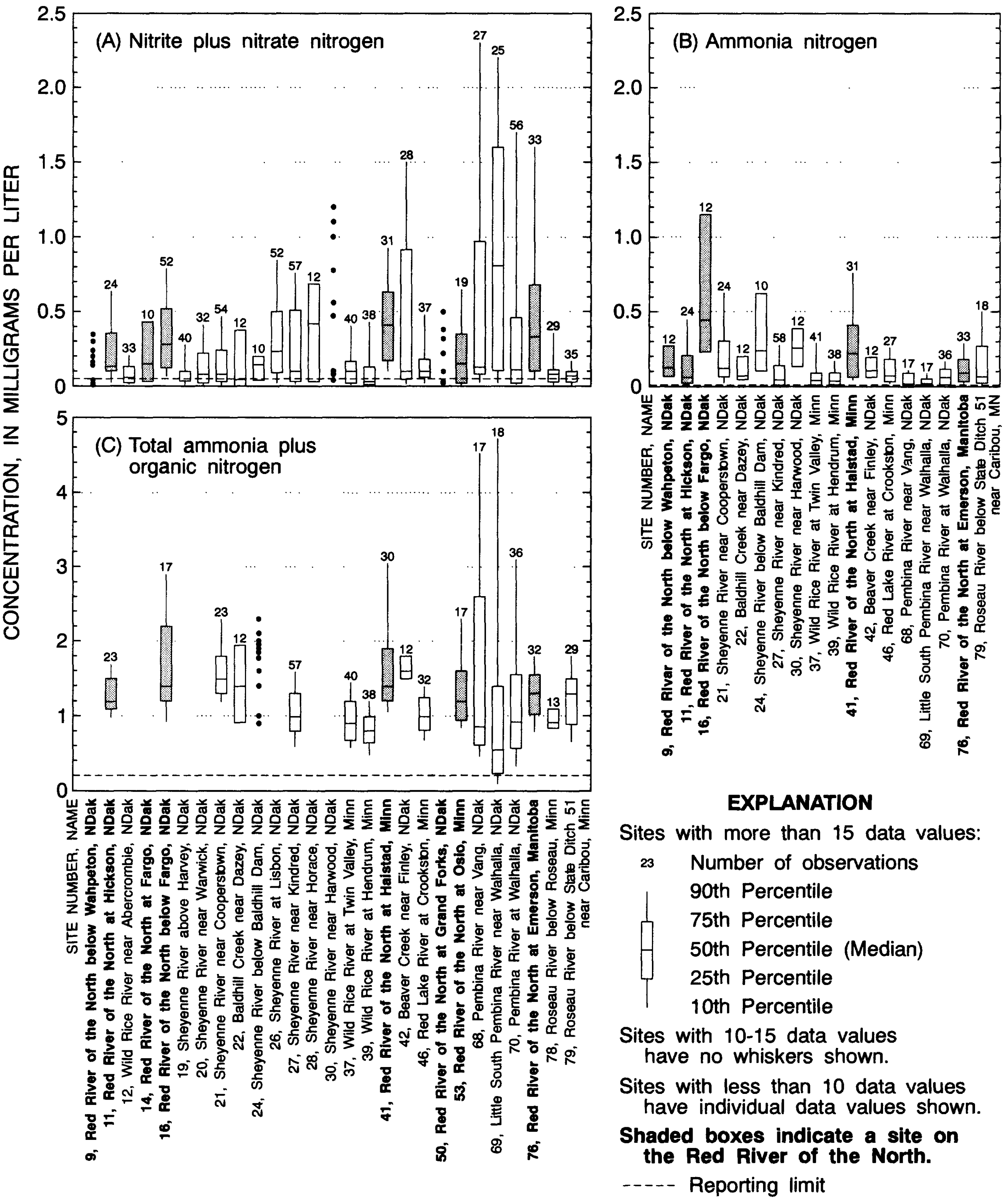


Figure 8.--Distributions of (A) nitrite plus nitrate nitrogen, (B) ammonia nitrogen, and (C) total ammonia plus organic nitrogen concentrations for selected U.S.Geological Survey stream sites in the Red River of the North Basin.

distribution of total nitrogen in figure 7. This is because most of the total nitrogen is TKN. About 90 percent of the TKN in the Red River Basin is organic nitrogen. Data were available at many more sites for TKN concentrations than were available to compute total nitrogen.

TKN concentrations tend to be highest in the Red River, Beaver Creek, and the Sheyenne River. A notable decrease in TKN concentration is evident at the Sheyenne River at Kindred, N. Dak. This can be attributed to dilution by ground water discharging into the Sheyenne River from the Sheyenne Delta aquifer upstream of Kindred. Downey and Paulson (1974) showed that discharge to the Sheyenne River from this aquifer can be as high as 29 cubic feet per second (ft^3/s), which can be a large percentage of the streamflow measured at Kindred. Data were insufficient to determine the effect of the Sheyenne Delta aquifer on other forms of nitrogen.

The large range in concentrations evident for nitrate in the Pembina River also is evident for TKN concentrations. This probably results also from runoff of nitrogen from agricultural areas.

The criteria used to increase comparability between sample sites for the USGS data also were applied to the data retrieved from the STORET data base. USGS samples often were collected from the same rivers, but at different sites. Substantial amounts of STORET data, however, are for smaller streams. This probably reflects an interest in more focused sampling to study problem areas. Therefore, the STORET data might show more of the high and low concentrations that are present in the Red River Basin.

Enough data to compute and discuss total nitrogen concentrations were available only at 16 sampling sites in the basin. The box plots in figure 9A show that median total nitrogen concentrations were below 2 mg/L at most sites and were lowest in the Wild Rice River in Minnesota. The highest median concentrations were found on the Rabbit River, the Red River downstream of the Fargo-Moorhead area, and the Snake River in northwestern Minnesota. The much higher concentrations and range in values on the Rabbit River suggest that this stream is substantially affected by agricultural runoff. Corn and soybeans are the predominant crops in this area. Corn requires substantial nitrogen fertilizer and soybeans produce excess nitrogen; some of this nitrogen probably is getting into the Rabbit River.

Sufficient data to discuss nitrate (nitrite plus nitrate) concentrations were available for 27 sites in the Red River Basin (fig. 9B). It is apparent that the highest median nitrate concentrations typically are found on the Red River and average about 0.4 mg/L. The largest ranges in concentration were found at sites on the Red River, and on some tributary streams. Nitrate concentrations in the Rabbit River, Whiskey Creek, Snake River, and Two Rivers (all in Minnesota, fig. 5) exceeded 1.2 mg/L in more than ten percent of the samples analyzed. Insufficient data were available from the STORET or North Dakota State Water Commission (NDSWC) data bases to supplement the USGS data showing the high nitrate concentrations for the Pembina River.

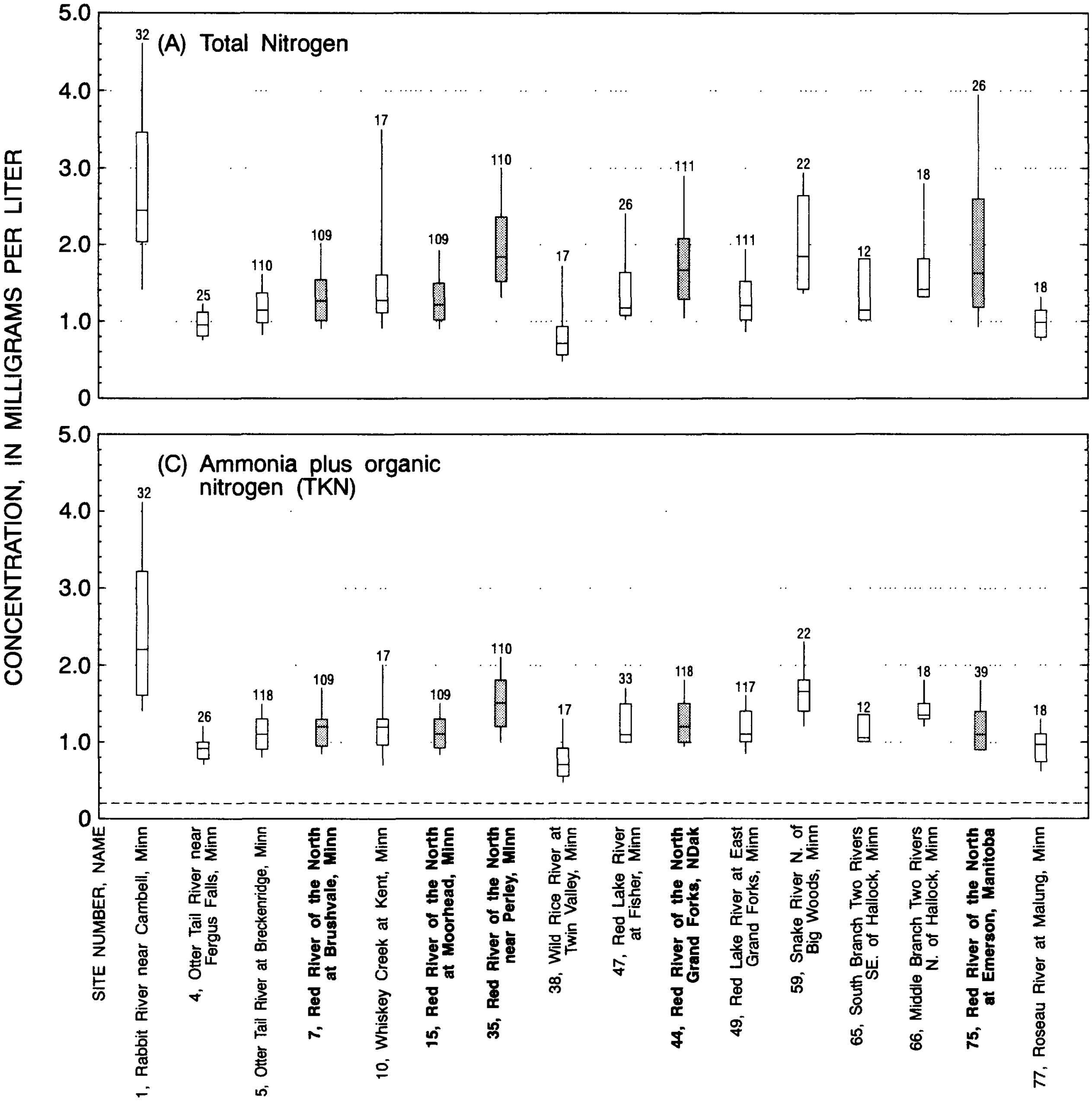
Sixteen sites from the STORET data base had sufficient TKN concentration data to consider in this report (fig. 9C). Most of the sites had median concentrations of about 1 mg/L or slightly higher. The Wild Rice River in Minnesota had the lowest median TKN concentration with only 0.7 mg/L. Notably high median TKN concentrations were found on the Red River downstream of the Fargo-Moorhead area and on the Snake River near the mouth, having 1.5 and 1.6 mg/L respectively. The highest median, 2.2 mg/L, and largest range, 3.7 mg/L, of TKN concentrations were measured in the Rabbit River, and probably are caused by intense agriculture in that area.

Median ammonia nitrogen concentrations were below 0.2 mg/L at most sites in the basin, and 90 percent of the values measured at most of these sites were below about 0.5 mg/L (fig. 9D). Larger ammonia concentrations were found at sites on the Red, Snake, and the Middle Branch Two Rivers. At the Red River below the Fargo-Moorhead area, the Middle Branch Two Rivers, and on the Park River, more than ten percent of the ammonia concentrations were greater than 1.0 mg/L and at some sites were greater than 1.5 mg/L. Urban effects may have contributed to the high concentrations at the Fargo-Moorhead area on the Red River and below Grafton on the Park River; however, at sites less affected by urban areas it is suspected that livestock operations may have affected water quality.

Another potential source of nitrogen to the watershed is from atmospheric sources. Although the atmosphere is 78 percent nitrogen, it is in a free gaseous form and not readily available for biological reactions until it has been converted to some other form of nitrogen by nitrogen-fixing bacteria. Other forms of nitrogen such as ammonia and nitrate, however, are available for biological reactions and are found in the atmosphere.

Atmospheric loading of two forms of nitrogen (ammonia and nitrate) to the Red River Basin were determined from measurements of wet deposition taken at National Atmospheric Deposition Program (NADP) sites operated in or near the basin. The location of these sites is shown in figure 5. All these sites have been operated at least since 1984, but only data collected during 1984-90 were used.

Because of the varying distances of each of these sites from the study unit basin, the nitrogen deposition measured at these sites was weighted based on the distance from the



EXPLANATION

Sites with more than 15 data values:

32 Number of observations
90th Percentile
75th Percentile
50th Percentile (Median)
25th Percentile
10th Percentile

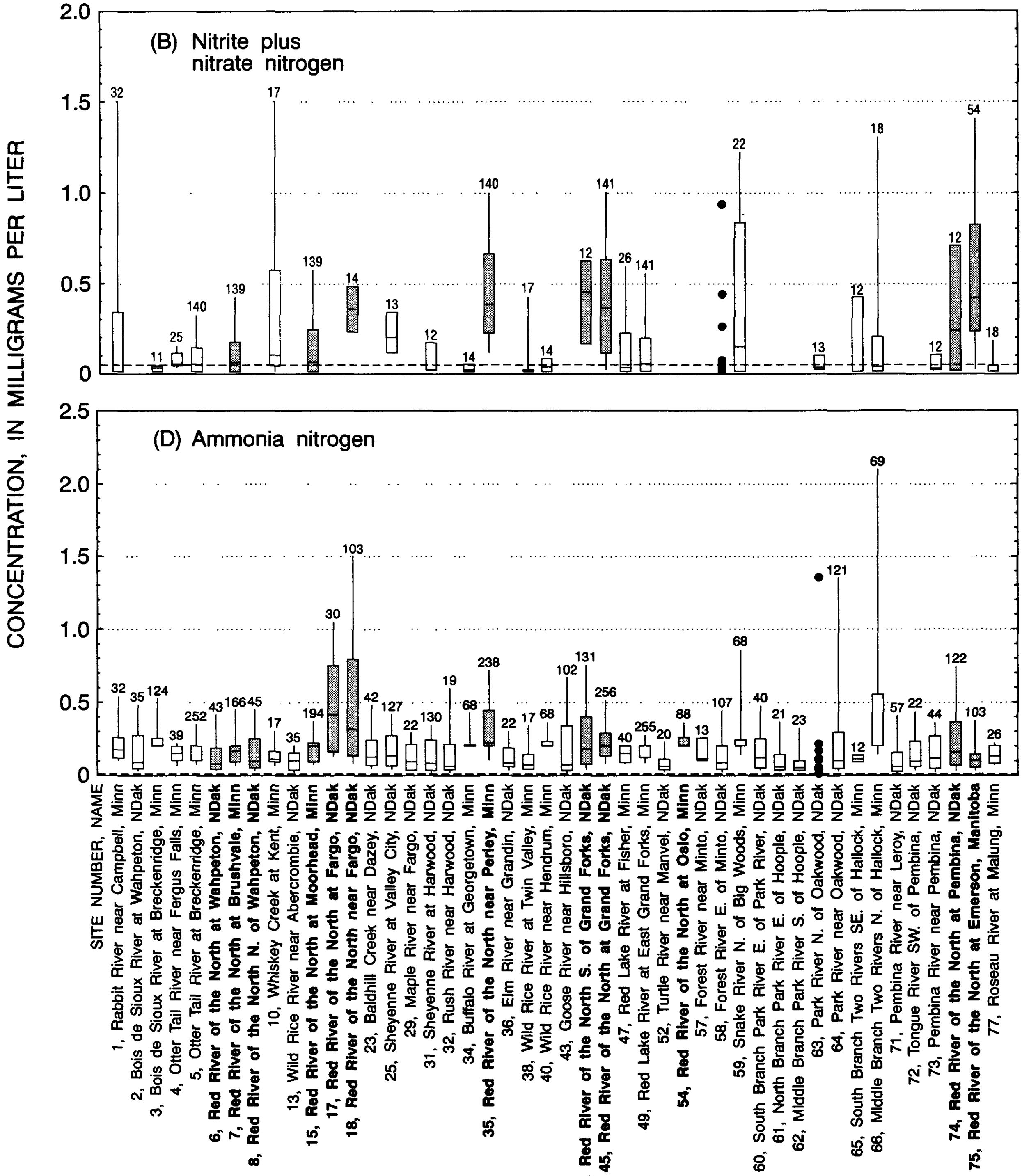
Sites with 10-15 data values have no whiskers shown.

Sites with less than 10 data values have individual data values shown.

Shaded boxes indicate a site on the Red River of the North.

----- Reporting limit

Figure 9.--Distributions of (A) total nitrogen, (B) nitrite plus and (D) ammonia nitrogen concentrations for selected RETrieval stream sites in the



nitrate nitrogen, (C) ammonia plus organic nitrogen (TKN), U.S. Environmental Protection Agency STOrage and Red River of the North Basin.

geographic center of the study unit. This was determined to be a point about 22 miles south of Grand Forks, N. Dak.

The relation between wet and dry deposition reported by D.L. Sisterson (1990) was applied to the wet deposition values to determine the amount of dry atmospheric deposition occurring in the basin. The different regional ratios of wet to dry deposition for each state were applied to data based on the state the site was located in. Urban differences, however, were not applied because only 3 percent of the basin is urban and Sisterson's (1990) data indicate no urban effect for atmospheric deposition in North Dakota.

Table 6 shows the average annual atmospheric deposition of ammonia nitrogen and nitrate nitrogen to the Red River Basin. Data were not available to compute the loads of other forms of nitrogen or loads of phosphorus. It is apparent that of the nitrogen shown in table 6, most arrives with the rainfall and most of that is ammonia nitrogen. An average of about 1.4×10^7 kilograms of ammonia and nitrate nitrogen are deposited annually over the entire 36,400 square mile catchment of the study unit basin.

Table 6.-- Average annual distance-weighted load of ammonia and nitrate nitrogen to the geographic center of the Red River of the North Basin study unit, 1984-90

[units in kilograms per square mile]

	Deposition		
	Wet	Dry	Total
Ammonia nitrogen	137	78	215
Nitrate nitrogen	112	67	179
Total	249	145	394

Phosphorus

Total phosphorus concentrations at USGS sampling sites are shown in figure 10A. The lowest median concentrations, less than 0.1 mg/L, were measured in the Wild Rice, the Red Lake, and the Roseau Rivers in Minnesota, with high variability in the Roseau River. Median concentrations of 0.3 mg/L or higher were found below Fargo, N. Dak. and at Halstad, Minn. on the Red River and the most downstream site on the Sheyenne River. The Red River sites are downstream from treated-sewage effluent of the cities of Fargo, N. Dak. and Moorhead, Minn. The Sheyenne River site is downstream from treated-sewage effluent of Fargo, N. Dak. only (fig. 5).

Data were available at more sites and streams for dissolved phosphorus concentrations. The plots in figure 10B show that the highest median concentrations of dissolved phosphorus and the widest range in values were measured in the Wild Rice River in North Dakota. Because no large communities are located above this site near Abercrombie, N. Dak., it is suspected that agricultural practices, including livestock operations or runoff from some other agricultural areas, are affecting the water quality in the Wild Rice River. Livestock operations also could explain the high concentrations on the Sheyenne River near Harvey, N. Dak. The lowest median concentrations were found in Baldhill Creek, N. Dak. and in the Wild Rice, Red Lake, and Roseau Rivers in Minnesota.

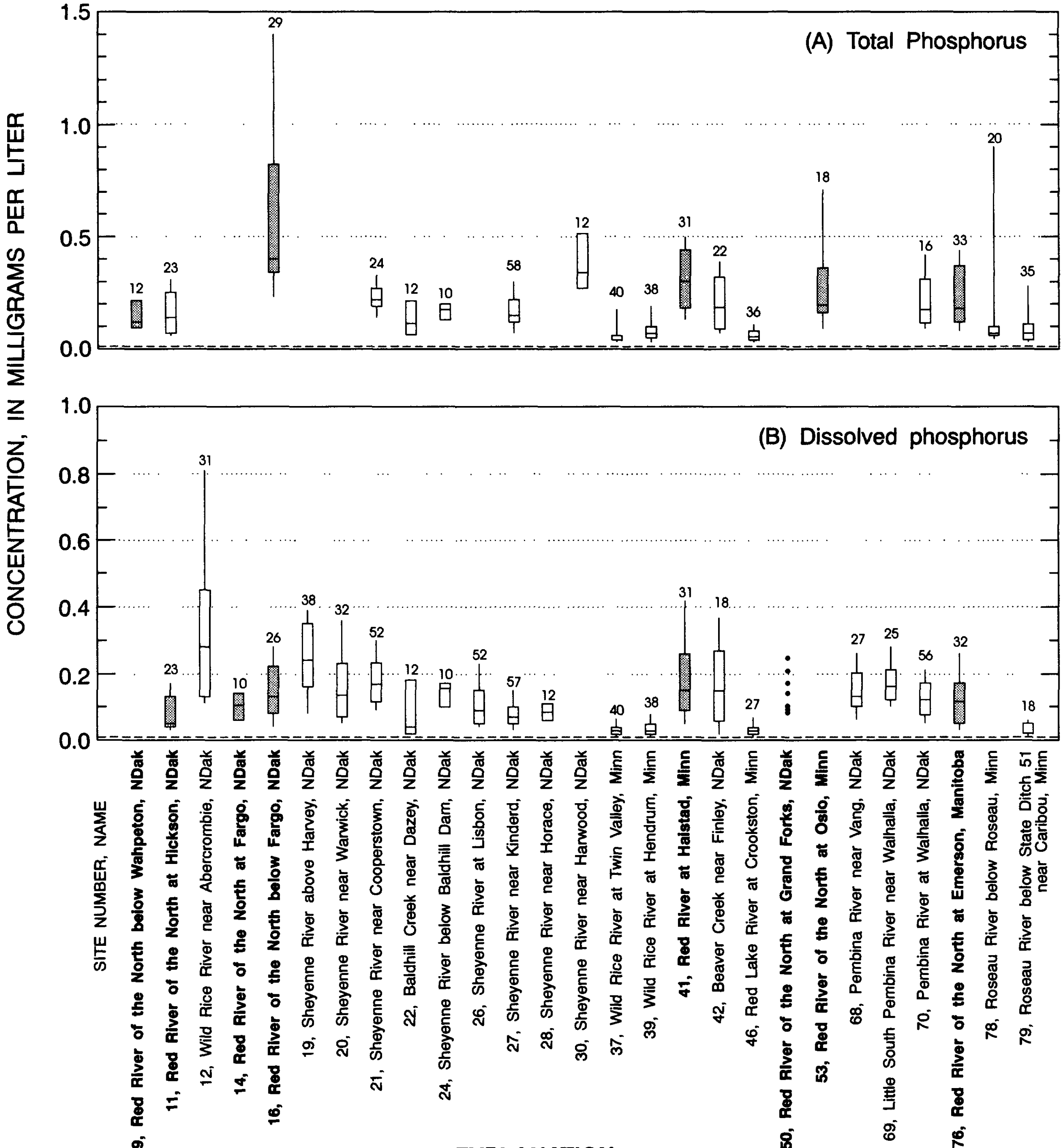
The streams that carried the highest concentrations of total phosphorus did not have notably high concentrations of dissolved phosphorus. Most of the phosphorus at those sites probably was particulate, being attached to suspended particles or within algal cells.

Data from the STORET data base are available for more sites, and generally show the same distribution of phosphorus concentrations as the USGS data. Total phosphorus concentrations were determined more often than dissolved. The distributions of total phosphorus concentrations for this data set are shown in figure 11.

The highest median total phosphorus concentration, 0.5 mg/L, was found in the Rabbit River where more than ten percent of the concentrations were higher than 1.0 mg/L. Apparently some characteristic of the soils or agricultural practices in the watershed of this stream are causing much more phosphorus to enter this stream than in other watersheds in the basin.

The Red River near Perley, Minn. also had phosphorus concentrations that were high and variable. This site is several miles downstream from the Fargo-Moorhead area and probably shows the effect of effluent from these communities.

The lowest phosphorus concentrations and the lowest ranges were found in the Wild Rice River, the South Branch Two Rivers, and the Roseau River in Minnesota. On the Middle Branch Two Rivers, below the confluence with the South Branch Two Rivers, phosphorus concentrations are much higher than on the South Branch and the range in values (10th to 90th percentiles) is the highest for any of the sampling sites shown. Although both these sites, above and below the confluence, were sampled during non-overlapping time periods, this difference is probably real. It is possible that livestock operations on the Middle Branch are affecting the quality of the stream at this site. Also, Hallock is only about one mile upstream from the site on the Two Rivers having the increased phosphorus and these data possibly show the effects of sewage effluent, fertilizer storage, or some other source in the town.



EXPLANATION

Sites with more than 15 data values:

23 Number of observations

90th Percentile

75th Percentile

50th Percentile (Median)

25th Percentile

10th Percentile

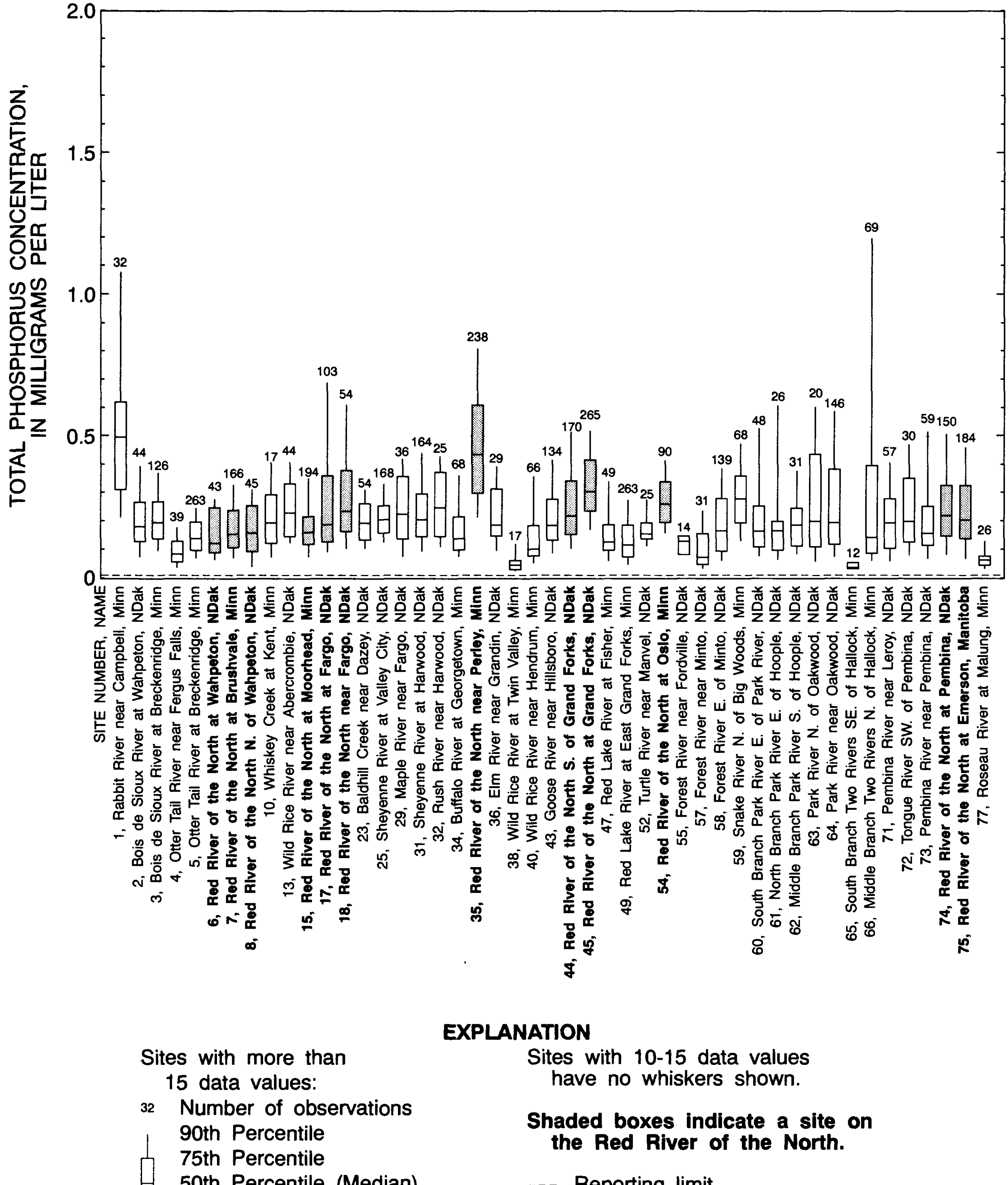
Sites with 10-15 data values have no whiskers shown.

Sites with less than 10 data values have individual data values shown.

Shaded boxes indicate a site on the Red River of the North.

--- Reporting limit

Figure 10.--Distributions of (A) total phosphorus and (B) dissolved phosphorus concentrations for selected U.S. Geological Survey stream sites in the Red River of the North Basin.



EXPLANATION

Sites with more than 15 data values:

32 Number of observations
90th Percentile
75th Percentile
50th Percentile (Median)
25th Percentile
10th Percentile

Sites with 10-15 data values have no whiskers shown.

Shaded boxes indicate a site on the Red River of the North.

--- Reporting limit

Figure 11.--Distribution of total phosphorus concentrations for selected U.S. Environmental Protection Agency STOrage and RETrival stream sites in the Red River of the North Basin.

Seasonality of nutrient concentrations

With seasonality of fertilizer application, some degree of seasonality might be expected for nutrients measured in streams draining farmed croplands. Data at most sites are not sufficient to analyze the monthly variability. However, Environment Canada has collected data from some sites near the U.S. border with Canada at a relatively high frequency.

Monthly concentrations of total nitrogen for the Red River at Emerson, Manitoba are summarized in figure 12A. The most noticeable seasonality occurs during April and June through July. The high peak in April probably corresponds to snowmelt runoff; whereas the rise during summer probably is caused by runoff of cropland fertilizers. Figure 12B shows that nearly all the April increase is caused by a large increase in the concentration of nitrate (nitrite plus nitrate) nitrogen. The source of this nitrate is uncertain, but could result in part from oxidation of ammonia nitrogen. Figure 12C shows that ammonia concentrations tend to be very high in January. This probably results from microbial degradation of nitrogen-containing organic matter, and is enhanced by low oxygen concentrations as oxygen lost to biochemical oxygen demand is not adequately replaced during periods of ice cover. As sunlight penetrates the ice during February and March, more oxygen may be produced by phytoplankton, and the ammonia could become oxidized to nitrate. Bacterial processes mediate oxidation and reduction reactions of nitrogen species, and the population dynamics of various microbial species may play an important role in the detected peaks in ammonia and nitrate concentrations.

The buildup of ammonia in streams during winter under ice appears to be a fairly common occurrence and has interesting implications for sampling design. The Roseau River is sampled quarterly by the USGS near the Canadian border at Caribou, Minn. as part of the National Stream Quality Accounting Network (NASQAN) program. During part of this time, Environment Canada collected samples monthly from the same river about 22 miles downstream at Gardenton, Manitoba. Ammonia nitrogen concentrations resulting from these concurrent samplings are shown in figure 13. Based on USGS quarterly data, the Roseau River had negligible ammonia concentrations except during one apparently anomalous year when the ammonia concentration reached 1.3 mg/L. The more frequent data collected by Environment Canada, however, show that increased ammonia in the winter is an annual occurrence that is apparent when the sampling frequency is sufficient.

Figure 14A shows monthly concentrations of total phosphorus at the Red River at Emerson, Manitoba, measured by Environment Canada. This site is also sampled by the USGS, but Environment Canada has sampled it more frequently, so these data allow for more complete analysis. Phosphorus concentrations are high and variable during December and January, showing the effect of sewage effluent because of low streamflow or releases from sediments that may have become anoxic under ice. Concentration decreases during February and March may result from reduced waste-water inputs or dilution from snowmelt. The high concentrations in April probably occurred as the last of the snowmelt and spring rains mobilized phosphorus from bare soils and likely coincides with high concentrations of suspended sediment and spring flooding, or releases from sewage treatment plants. Sewage treatment plants often are permitted to store much of their effluent during winter and release it during spring snowmelt runoff when streams have a greater capacity to dilute the effluent. High phosphorus concentrations during the early summer probably are caused by storm runoff of fertilizers applied to cropland.

Total phosphorus concentrations (fig. 14B) were lowest during October through December and increased during January through April. The increase in phosphorus concentrations could result from releases from anoxic sediments or transport during snowmelt runoff in the spring. Snowmelt runoff typically occurs during March through April. The increased phosphorus concentrations during June, July, and August probably are caused by runoff from fertilized cropland.

Data for other sites in the Red River Basin both from the USGS and STORET data bases also were analyzed, but are not shown. Similar seasonal patterns were apparent, but were inconclusive because the monthly distribution of data was inadequate.

Nutrient loading

The load of material carried by a stream provides critical information for characterizing stream quality. Loads provide an indication of the total amount of material carried out of a watershed. Streamflow is needed to determine the load of constituents past a stream site. One way to estimate the loading from water-quality samples collected without a streamflow measurement is to use streamflow data from a nearby USGS stream-gaging station. It often is difficult to find a stream gaging station near enough to the sampling site to adequately represent the streamflow at that site. Estimates of streamflow can be determined at sampling sites distant from gaging stations, but that is beyond the scope of this report.

Because loads are calculated as the product of concentration and streamflow, large rivers will carry a larger load while having the same concentration as a much

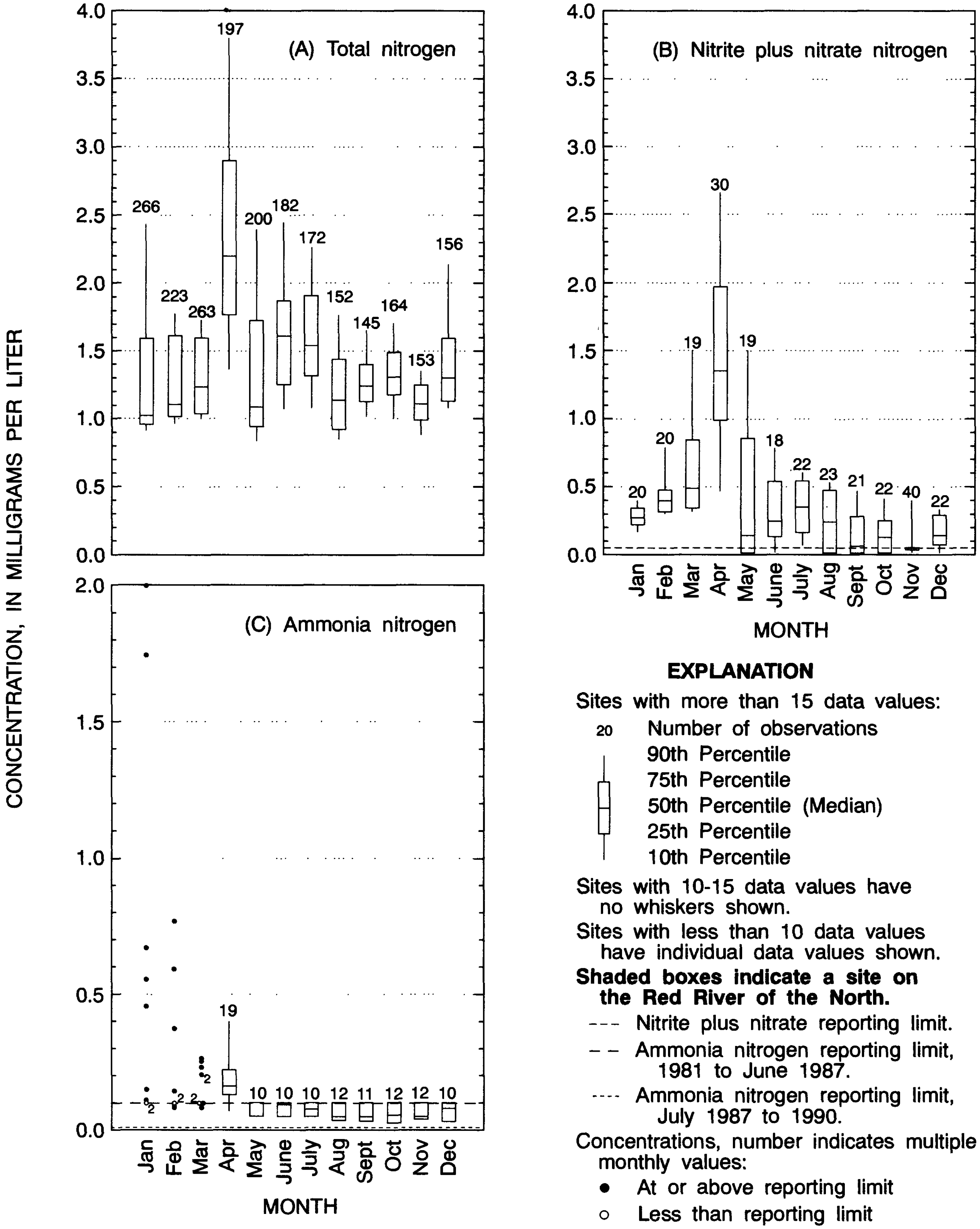
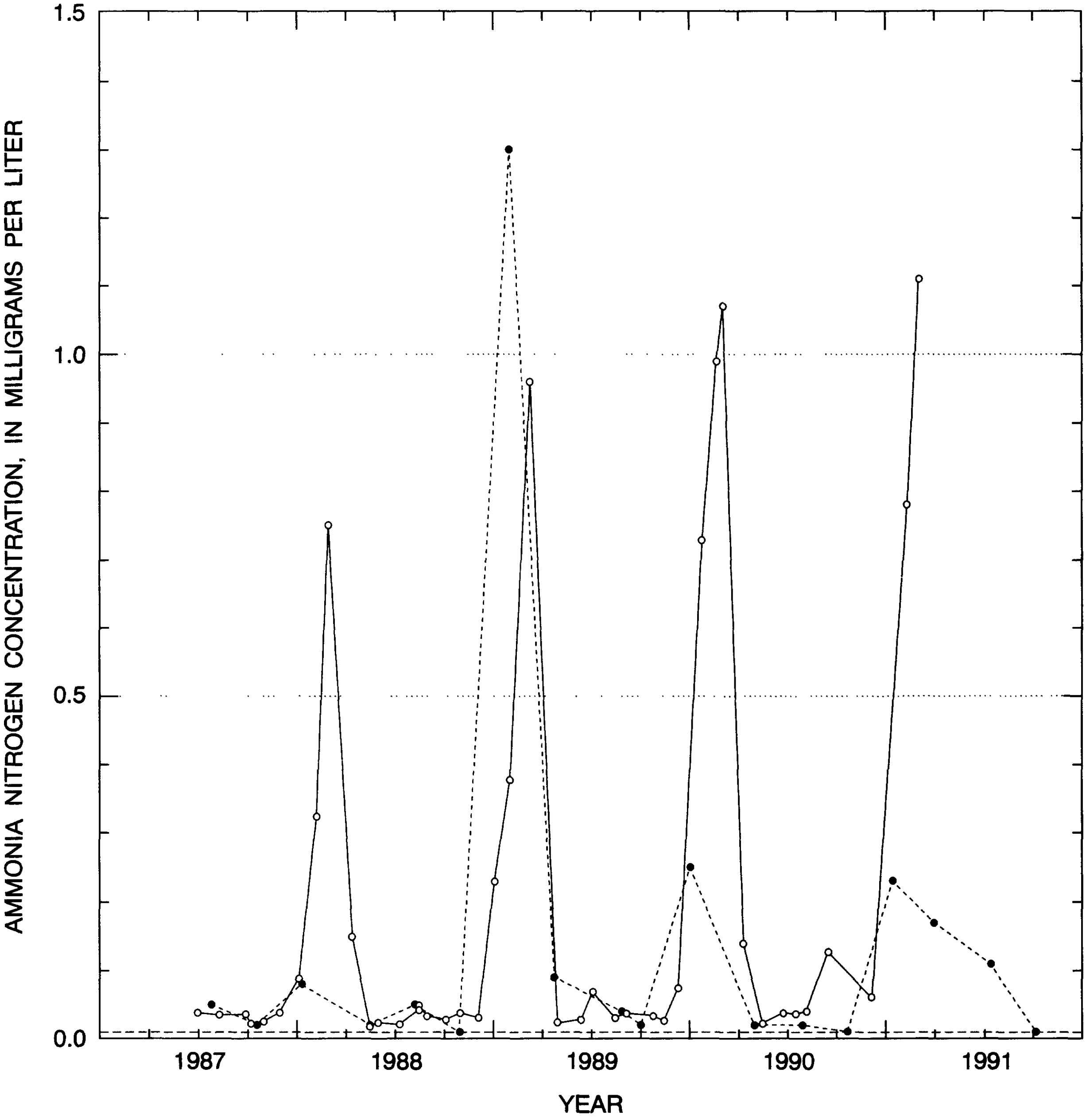


Figure 12.--Distributions of (A) total nitrogen, (B) nitrite plus nitrate nitrogen, and (C) total ammonia nitrogen concentrations for the Red River of the North at Emerson, Manitoba (Environment Canada data).



EXPLANATION

Caribou, Minnesota (USGS data)

Gardenton, Manitoba (Environment Canada data)

Reporting limit

Figure 13.--Ammonia nitrogen concentrations in the Roseau River at Caribou, Minnesota and Gardenton, Manitoba.

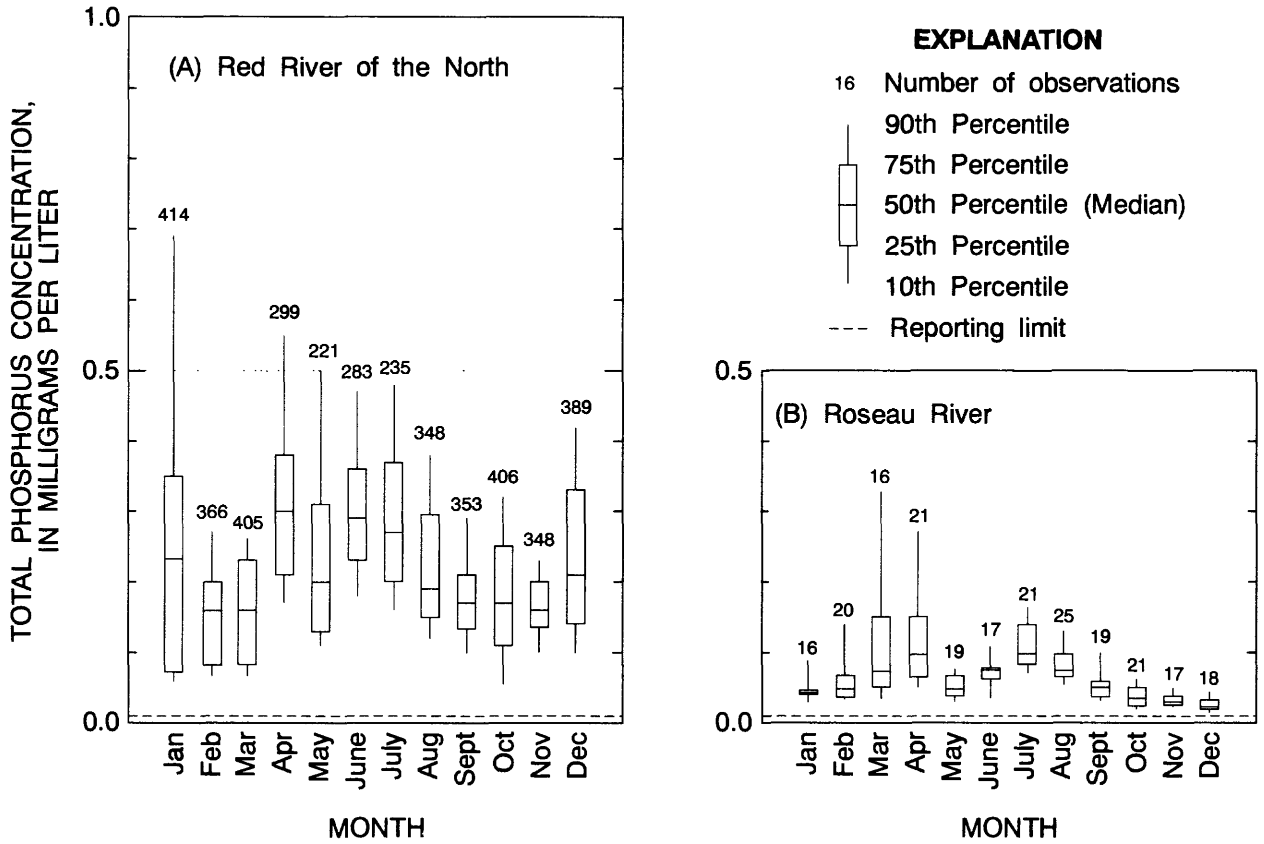


Figure 14.--Monthly distribution of total phosphorus concentrations for Environment Canada stream sites for (A) Red River of the North at Emerson and (B) Roseau River at Gardenton, Manitoba.

smaller stream. Conversely, small polluted streams can have a substantial effect on receiving waters. Another complication is that many streams, particularly on the western side of the basin, do not flow during part of the year. During periods of no streamflow, there is no record of zero load in the data base, which tends to skew high the load values for this type of stream. Analysis of loading data should take these factors into account.

Daily concentration data for constituents of interest generally are not available for most sites because collection of that data is prohibitively expensive. As an alternative, loads may be estimated based on the relation between constituent concentration (or load) and some other variable that may be measured daily, such as streamflow, water temperature, or specific conductance. Streamflow often relates closely to nutrient concentrations and can provide a reasonably accurate concentration or load estimate for many nutrients.

To develop estimates of nutrient concentrations from streamflow it is necessary to have nutrient concentration measurements from throughout the flow regimes of that stream. Unfortunately, samples from most stream gaging sites in the Red River Basin that were sampled for nutrient concentrations were collected only during low to moderate flows, and the higher flow regimes are inadequately represented. Estimation of loads during high flows where concentrations were not measured could be misleading because the largest load of many constituents is carried during high flows.

The only station in the Red River Basin that had adequate data to estimate nutrient loading was at the Red River at Emerson, Manitoba. Although sampled by several agencies, a large amount of dissolved nitrogen and total phosphorus concentration data has been collected from this site by Environment Canada. During limited time periods daily samples were collected.

Multiple linear regression models were developed for dissolved nitrogen and total phosphorus using the data from Emerson to relate concentration to streamflow. Trigonometric sine and cosine functions were used to compensate for seasonal cycles in concentration and constituent load. Regression models were chosen on the basis of residual plots and correlation coefficients, and were formulated using version 92.07 of a computer program called Estimator (Baier, Cohn, and Gilroy, U.S. Geological Survey, written commun., 1992). Estimator uses a minimum variance unbiased estimator (MVUE) to compensate for retransformation of logarithmic predicted values back to their original, untransformed units (Gilroy, Hirsch, and Cohn, 1990). The estimated loads shown in table 7 were calculated using a regression equation derived from the relation between constituent load and the streamflow. These regression equations are shown at the bottom of each part of the table. The equations were applied only to those years of streamflow data where concentration data for dissolved nitrogen and total phosphorus were available.

During 1980, 1981, and part of 1982 Environment Canada sampled dissolved nitrogen and total phosphorus daily, or almost daily. Results of this sampling, shown as measured load in table 7, indicate that load estimates are quite accurate, except during the lower flows of 1981 when load values appeared to be underestimated. Residual plots showed that the regression models were unable to account for occasional high nutrient concentrations during periods of low streamflow.

Table 7.-- Estimated total dissolved nitrogen and total phosphorus loads at Red River of the North at Emerson, Manitoba, (Environment Canada data).

[N, dissolved nitrogen load in kilograms per day; P, total phosphorus load; Q, stream flow in cubic feet per second; ln, natural logarithm; T, julian sampling date; π = 3.1416 (estimated values were multiplied by 365 to obtain load in kilograms per year)]

Year	Annual Streamflow, millions of acre-feet	Estimated value	95 percent prediction interval	Measured load	Number of days sampled	Nitrogen yield, in kilograms per square mile per year
Nitrogen load in millions of kilograms per year						
1979	6.22	24.7	20.8 -28.6			679
1980	1.32	2.02	1.64- 2.20	2.11	365	55.5
1981	1.11	1.18	1.14- 1.23	1.37	346	32.5
1982	3.37	6.10	5.57- 6.64	6.36	191	168
1983	3.10	4.69	4.39- 5.00			129
1984	3.10	5.74	5.23- 6.25			157
1985	3.83	5.33	5.05- 5.62			147
1986	5.13	10.9	10.4 -11.4			300
1987	3.00	6.16	5.85- 6.48			169
1988	.865	1.27	1.22- 1.32			34.8

Regression model:

$$\ln(N) = a + b*\ln(Q) + c*[\ln(Q)]^2 + d*\text{sine}(2*\pi*T) + e*\text{cosine}(2*\pi*T)$$

where: a = 8.41; b = 1.06; c = 0.110; d = 0.171; and e = 0.0940; coefficient of determination (r^2) = 0.93

Year	Annual Streamflow, millions of acre-feet	Estimated value	95 percent prediction interval	Measured load	Number of days sampled	Nitrogen yield, in kilograms per square mile per year
Phosphorus load in millions of kilograms per year						
1975	5.67	2.67	2.25 -3.10			73.4
1976	2.07	.851	.722 -.979			23.4
1977	.617	.174	.161-.186			4.77
1978	3.78	1.30	1.08 -1.53			35.8
1979	6.22	1.55	1.29 -1.82			42.7
1980	1.32	.489	.408-.570	.451	365	13.4
1981	1.11	.294	.270-.318	.390	347	8.08
1982	3.37	1.45	1.27 -1.63	1.65	191	39.9
1983	3.10	1.35	1.20 -1.50			37.1
1984	3.10	1.41	1.21 -1.61			38.6
1985	3.83	1.91	1.71 -2.10			52.3
1986	5.13	2.43	2.10 -2.75			66.6
1987	3.00	1.24	1.06 -1.41			34.0
1988	.865	.337	.285-.370			9.27

Regression model:

$$\ln(P) = a + b*\ln(Q) + c*[\ln(Q)]^2 + d*[\ln(Q)]^{0.5} + e*\text{sine}(2*\pi*T) + f*\text{cosine}(2*\pi*T)$$

where: a = 10.8; b = 3.42; c = 0.766; d = -0.0857; e = -0.0704; and f = -0.223; coefficient of determination (r^2) = 0.89

During the period shown in table 7 the estimated load of nitrogen and phosphorus varied considerably, more than two orders of magnitude for total phosphorus. The most nitrogen was carried out of the basin during 1979, almost 25 million kilograms. The most phosphorus was carried out of the basin during 1975, almost 2.7 million kilograms. The mean annual loading during these time periods was 6.81 million kilograms per year for dissolved nitrogen, and 1.25 million kilograms per year for total phosphorus.

The annual yields displayed in table 7 show that the potential loss of nutrients from the basin can be high. The yield of dissolved nitrogen from the Red River Basin during 1979 was nearly 680 kilograms per square mile. The yield of phosphorus from the basin during 1975 was more than 70 kilograms per square mile. The mean annual loads were 187 and 34 kilograms per square mile, respectively.

Ground Water

Samples for analysis of nutrients in ground water have been collected by several agencies throughout the Red River Basin. Most of the samples from North Dakota have been collected and analyzed by the NDSWC. Some samples were collected and analyzed by the USGS. Both agencies work cooperatively on ground-water data collection efforts and often share data. Although this resulted in duplicate analyses between the two data bases, duplicates were removed from the USGS data set before summarizing the data for this report. No ground-water quality data for North Dakota were found in the STORET data base, other than data collected by the USGS. Figure 15 shows the location of water wells having nutrient data included in this report.

The STORET data base had nutrient data for wells for most counties on the Minnesota side of the Red River Basin, but usually only one to two wells per county had data and no county had more than eight water wells with nutrient data. The NWIS data base, on the other hand, generally had nutrient data from several wells for most counties providing what should be a more diverse sampling distribution. Although nutrient data in the NWIS data base were available for many wells in several counties, some counties had no data. The heterogeneity of the spatial distribution of ground-water nutrient data (fig. 15) makes statistical analysis and summary difficult.

The only nutrient data for ground-water analyses reported by the NDSWC are values for phosphate and nitrate, but phosphate was analyzed in ground-water samples infrequently. Although the NDSWC analyzed for nitrite plus nitrate, they determined through occasional test samples that the nitrite concentrations were negligible. The NDSWC therefore reports nitrite plus nitrate concentrations as nitrate.

Reported nitrate concentrations (as nitrogen) in ground water on the North Dakota side of the Red River Basin ranged from zero (below detection) to more than 271 mg/L. Many samples in the NDSWC data base for wells scattered throughout the study area have high nitrate concentrations and probably represent samples of highly contaminated water (Dave Ripley, NDSWC, oral commun., 1992).

Figure 16 shows the statistical distribution of nitrate concentrations reported by the NDSWC summarized alphabetically by county. To produce this box plot, the mean nitrate concentration was determined for each well sampled before the statistical summaries were prepared. Summarizing the data in this way prevents skewing of the data by only a few wells that were sampled several times.

Median nitrate nitrogen concentrations in ground water for most counties in the North Dakota part of the Red River Basin were about 0.23 mg/L (NDSWC data). This corresponds to about 1 mg/L nitrate when reported as nitrate. One mg/L (as nitrate) was a common reporting value for many of the samples analyzed for nitrate because a quick, low cost analysis could be performed followed by a more precise analysis only when unusual concentrations were detected (Dave Ripley, NDSWC, oral commun., 1992). Many of the more precise results are reported below this limit of 1 mg/L (as nitrate) while many others are reported as zero; this explains much of the distribution of the data below the 0.23 mg/L (as nitrogen) median.

Median nitrate concentrations in ground water were greater than 0.23 mg/L in the North Dakota counties of Barnes, Cavalier, Eddy, Griggs, and Walsh. In most of these same counties, as well as Grand Forks, Pembina, and Steele Counties, more than ten percent of the wells sampled had average nitrate concentrations greater than 5 mg/L. Many of these counties have surficial aquifers, and some of these counties have small alluvial aquifers that could be susceptible to contamination. There appears to be no correlation between the nitrogen application rates shown in table 1 and figure 3 and nitrate concentrations found in ground water in North Dakota counties.

Nitrate concentrations in ground water also are available from the NWIS data base (North Dakota part of Red River Basin). The NDSWC analyzed many of the samples stored in the NWIS data base resulting in similar median values between the two data bases. The median nitrate concentrations in most of the counties were about 0.23 mg/L (using the 1 mg/L as nitrate reporting limit). Median concentrations above this 0.23 mg/L value occurred in Eddy, Foster, Grand Forks, Nelson, Richland, Rolette, Stutsman, and Traill Counties. Nitrate concentrations for Stutsman County were particularly high, but only a

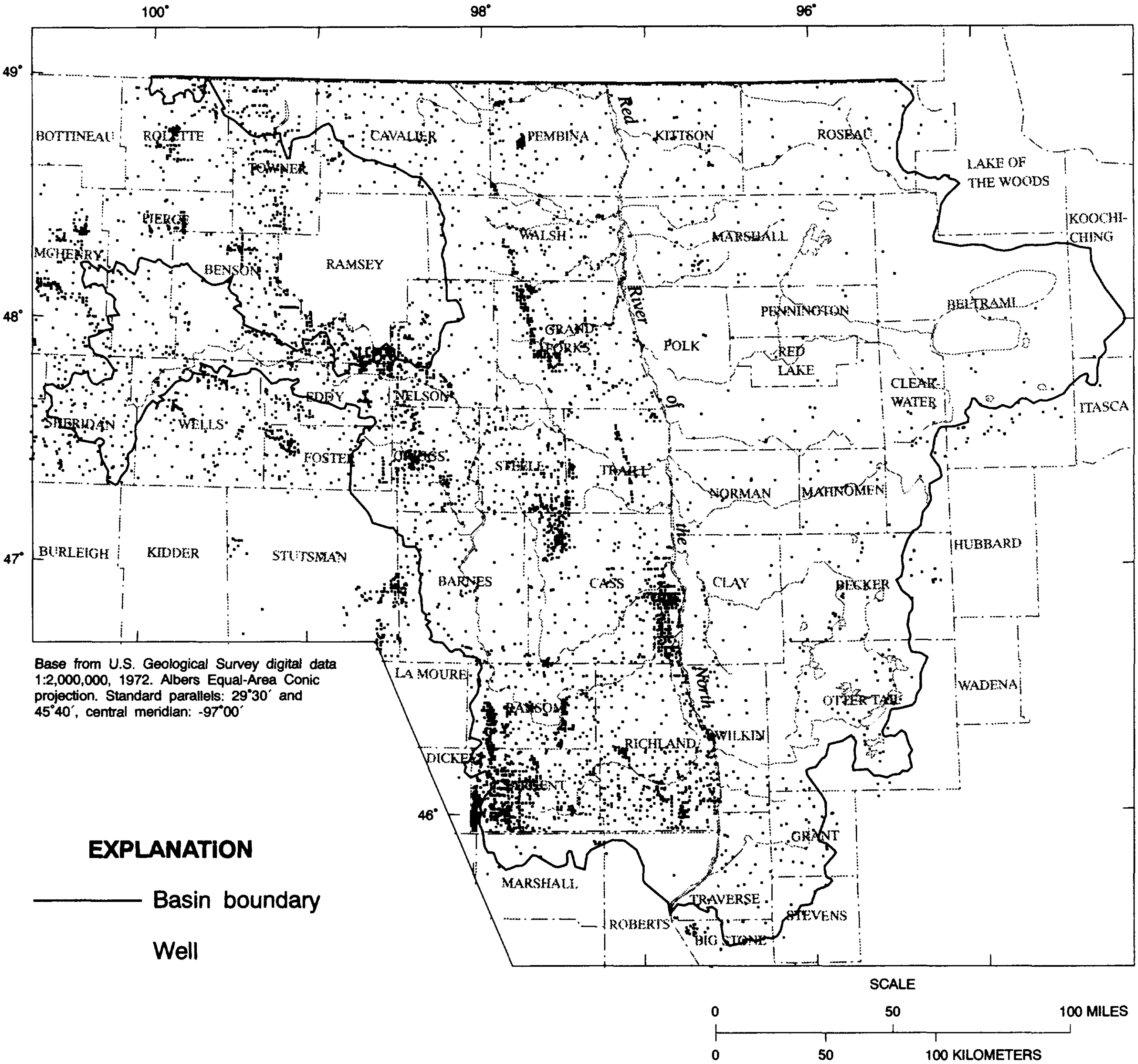


Figure 15.--Water wells sampled for nutrient concentrations in or near the Red River of the North Basin.

small part of this county is encompassed by the Red River Basin.

Examination of the data from the NWIS data base shows 8 counties in North Dakota where more than 25 percent of the sampled wells had average nitrate concentrations exceeding 1.0 mg/L. Nearly 25 percent of the sampled wells in Cass and Traill Counties also had more than 1.0 mg/L nitrate.

Data for phosphorus concentrations in ground water for North Dakota are limited. The only data related to phosphorus in ground water available from the NDSWC are phosphate concentrations. Phosphate is an important component of many minerals, but not necessarily indicative of total phosphorus concentration in ground water. In each county water from a few wells was analyzed for phosphate concentration, so any summary of that data would be skewed by the counties that have more data.Phosphate concentrations in ground water may be more a function of the mineral composition of the aquifers than of anthropogenic sources.

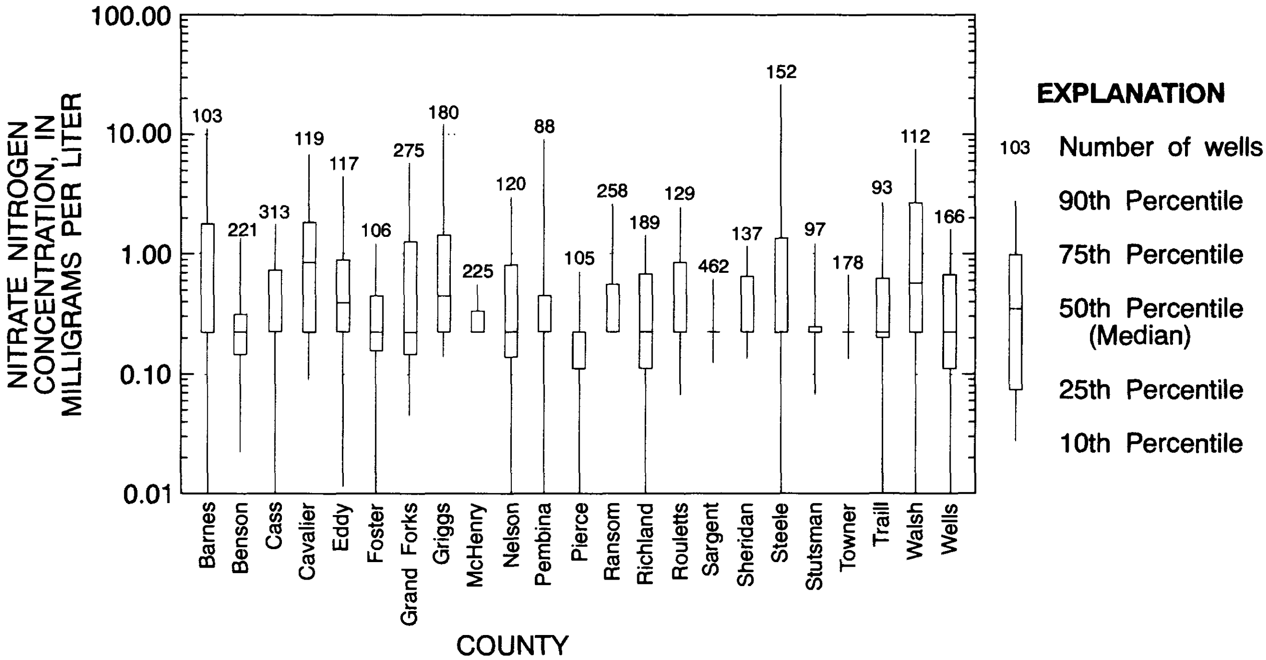


Figure 16.--Nitrate nitrogen concentrations in water wells in North Dakota counties in the Red River of the North Basin (North Dakota State Water Commission data).

Data for Minnesota ground water from STORET (fig. 17A) show that nitrate concentrations were higher in Otter Tail County than in ground water in other Minnesota counties. The median nitrate concentration for samples was 5 mg/L and two of these wells had nitrate concentrations higher than the 10 mg/L maximum contaminant level (MCL) for drinking water (U.S. Environmental Protection Agency, 1986).

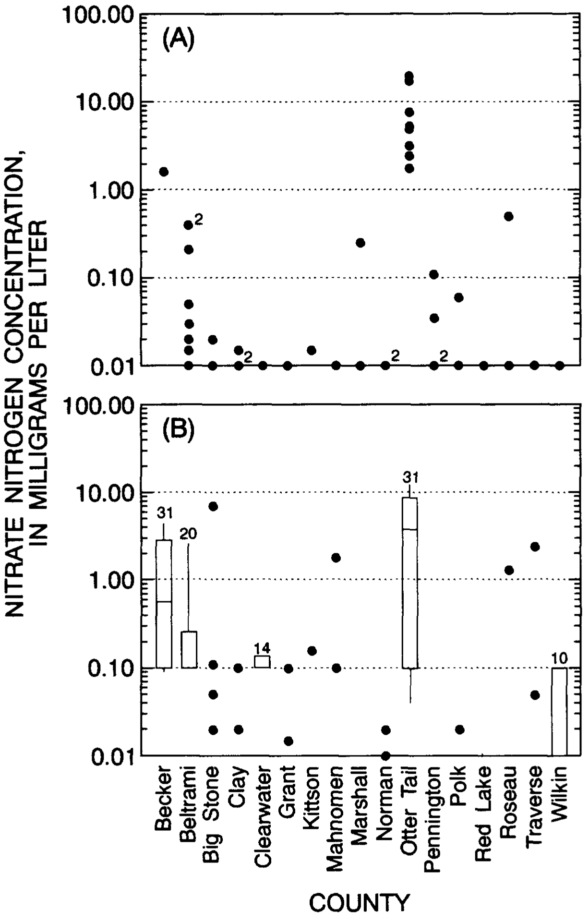
Ground water nitrate concentrations for Minnesota from the NWIS data base were highest in both Otter Tail and Becker Counties in Minnesota (fig. 17B). The highest median nitrate concentration (3.7 mg/L) occurred in Otter Tail County, and more than 3.0 mg/L nitrate was measured in almost 25 percent of the wells in Becker County. Table 1 shows that nitrogen application rates for these counties were relatively low compared to other counties, so application rates probably would not explain the high nitrate concentrations found in the ground water.

Otter Tail and Becker Counties have a relative abundance of ground water, much of it unconfined and shallow making it susceptible to contamination (fig. 2). Many of the crops in Otter Tail and Becker Counties are irrigated, suggesting that nitrogen-laden irrigation water is seeping into the ground water. The sampling program that provided the data summarized in figure 17, however, could have focused on contaminated aquifers resulting in average nitrate concentrations that are higher than if they were based on a random sampling.

Many of the northern counties on the Minnesota side of the basin have aquifers that are highly susceptible to contamination (MPCA, 1989). Data were inadequate during 1970-90 to determine whether ground-water quality has been affected. Near the southern part of the basin, counties that have high median nitrate concentrations in ground water also tend to have crops that require substantial nitrogen fertilization, such as corn, or crops that produce excess nitrogen, such as soybeans.

Based on data stored in the NWIS data base, relatively few ground water wells in the part of the Red River Basin in South Dakota were sampled for nutrients. Twelve wells were sampled for nitrate nitrogen and ten wells were sampled for dissolved phosphorus. Nitrate concentrations ranged from less than 0.01 to 2.0 mg/L with a median of 0.49 mg/L. Dissolved phosphorus concentrations ranged from less than 0.01 to 0.20 mg/L with a median of 0.04 mg/L. No nutrient data for ground water were found in the STORET data base for the South Dakota part of the Red River Basin.

Nitrate is the form of nitrogen most frequently analyzed from ground-water samples because the analysis is reasonably easy and a definite standard (the 10 mg/L MCL) exists against which to compare concentrations that are detected. Under anoxic conditions bacterially-mediated reactions can reduce nitrate to other forms that were not analyzed in samples. Nitrogen contamination of ground water may affect a much wider area than indicated, but it was not apparent because usually only nitrate (or nitrite plus nitrate) concentrations were determined



EXPLANATION

Sites with more than 15 data values:

31 Number of observations

90th Percentile

75th Percentile

50th Percentile (Median)

25th Percentile

10th Percentile

Sites with 10-15 data values have no whiskers shown.

Sites with less than 10 data values have individual data values shown. Number indicates multiple county values.

Figure 17.--Distribution of nitrate nitrogen concentrations in water wells in Minnesota counties in the Red River of the North Basin for (A) U.S. Environmental Protection Agency STOrage and RETrieval data and (B) U.S. Geological Survey data.

High nitrate concentrations in ground water may be related to susceptibility of the ground water to contamination (Wall and Montgomery, 1991). One way to determine whether this relation exists would be to compare nitrate concentrations in surficial aquifers with concentrations in deep or buried aquifers. Specific information about the aquifers sampled was not adequate to make comprehensive comparisons.

Another method to assess the effect of land-surface activities on shallow ground-water quality is to compare nitrate concentrations by well depth. Figure 18 shows the distribution of nitrate concentrations in shallow (less than or equal to 50 feet deep) water wells compared to the distribution of nitrate concentrations in deeper wells sampled in the Red River Basin by the USGS. The median nitrate concentration in the shallower wells was about 0.3 mg/L and nearly 10 percent had concentrations that exceeded the 10 mg/L MCL. The ground water in at least 75 percent of the deeper wells had nitrate concentrations that were at or below the commonly used 0.1 mg/L reporting limit. Only a low percentage of the deeper wells had detectable nitrate concentrations, and it is possible that some of the higher values indicated in figure 15 are anomalous or do not truly represent deep ground water.

Suspended Sediment

Sediment in surface waters may occur naturally from bank and upland soil erosion, particularly during major hydrologic events including floods. Soil disturbance, including construction and some agricultural practices, can cause increases in sediment transport from the land into nearby streams, lakes, and reservoirs. Stream-channel modifications also can increase the sediment-carrying capacity of a stream and lead to increased stream-bank erosion.

Increasing the amount of sediment in streams can have several adverse effects. Sediment accumulates in lakes and reservoirs, filling them over time. Sediment also can carry some nutrients and toxins sorbed to its surfaces, thereby creating a transport mechanism that might otherwise not exist.

Sediment transported by streams also can adversely affect aquatic ecosystems. Turbidity resulting from increased suspended-sediment concentrations can reduce light penetration, affecting the viability of aquatic plants. High concentrations of suspended sediment can clog fish gills, causing the fish to suffocate. Deposition of sediments can bury benthic organisms and fish eggs and change the benthic habitat. Nutrients, especially phosphorus, transported on sediment deposited in lakes and reservoirs can be released and augment plant growth.

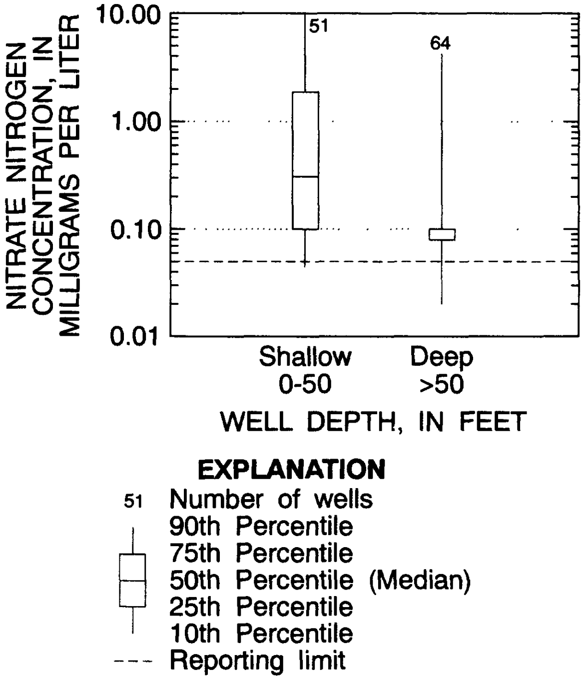


Figure 18.--Distribution of nitrate nitrogen concentrations for shallow and deep water wells (U.S. Geological Survey data).

Two common measurements of the suspended-material content in streams are suspended sediment (Guy, 1969) and suspended solids (Fishman and Friedman, 1989). Historically, the USGS has collected much more suspended-sediment data than suspended-solids data. Suspended sediment is collected as a depth-integrated sample from several verticals across the stream and the entire sample, often several liters, is analyzed without subsampling. Conversely, the suspended-solids method used by the U.S. Geological Survey subsamples from a composited depth- and width-integrated sample and the most dense particles (such as sand) may not be evenly dispersed in the composite sample, even with vigorous agitation. Laboratory analysts pipette a second subsample from the field sample, purposefully avoiding large particles that might clog the pipettes. Each subsampling may exclude the largest and most dense particles, biasing suspended-solids data relative to suspended-sediment data.

Figure 19 shows the relation between concentrations of suspended sediment and suspended solids in samples collected by the USGS in Minnesota and North Dakota. Suspended-solids data underestimates suspended-sediment content by more than a factor of two. There also is substantial scatter in the data. Because of the substantial difference between suspended-sediment and suspended-solids data and the difficulty trying to reliably relate the two values, this report focuses only on suspended-sediment data. The USGS and Environment Canada are the two agencies that have collected the suspended-sediment data included in this report.

Figure 20 shows the distribution of suspended-sediment concentrations for those sites in the basin where values meet the same criteria that were applied to nutrient data. Data were available for only a few sites, with limited spatial coverage of the basin. Median concentrations of suspended sediment in the Red River ranged from 46 mg/L below Fargo, N. Dak. to 108 mg/L at Emerson, Manitoba. Median sediment concentrations were lowest in Beaver Creek, N. Dak. and the Red Lake and Roseau Rivers, Minn. The highest suspended-sediment concentrations generally were found in the Pembina River, especially at Walhalla, N. Dak. Suspended-sediment concentrations in the Pembina River ranged from 3 mg/L to nearly 7,000 mg/L. The steep topography in the watershed of the Pembina River leaves the soils more susceptible to erosion. Also, the stream-bed gradient increases the sediment-carrying capacity of the stream. Other streams in the Red River Basin have the capacity to carry large quantities of suspended sediment, but data to quantify this were not available.

Data have been collected at only a few sampling sites to determine the amount of coarse material (sand and gravel) in proportion to the amount of finer material (clay and silt). The Red River at Emerson, Manitoba tended to carry the finest suspended sediment; in more than half the samples, 98 percent of the material was finer than sand. The site on the Red River at Halstad, Minn. also carried a high percentage of fine material. The Red River at sites below Fargo, N. Dak. and at Oslo, Minn. had median percentages finer than sand of 84 and 89, respectively, indicating that coarser material is transported at these sites. The Pembina River typically had about 85 percent of the suspended-sediment load as material finer than sand.

Additional data on suspended sediment, including daily sediment samples for several years, have been collected by the Water Survey of Canada for Environment Canada. Sites sampled on streams discussed in this report include the Pembina River at Windygates, the Red River at Emerson, and the Roseau River at Gardenton, all in Manitoba. Suspended-sediment data from these sites and from many other sites throughout Manitoba through 1985 are summarized in a report by Penner and others (1987). During the period of data analyzed by Penner and others (1987) the mean daily suspended-sediment concentration was 393 mg/L in the Pembina River, 223 mg/L in the Red River, and 35 mg/L in the Roseau River. The mean annual load in tons for each of these streams was 104,000 for the Pembina River, 952,000 for the Red River, and 10,700 for

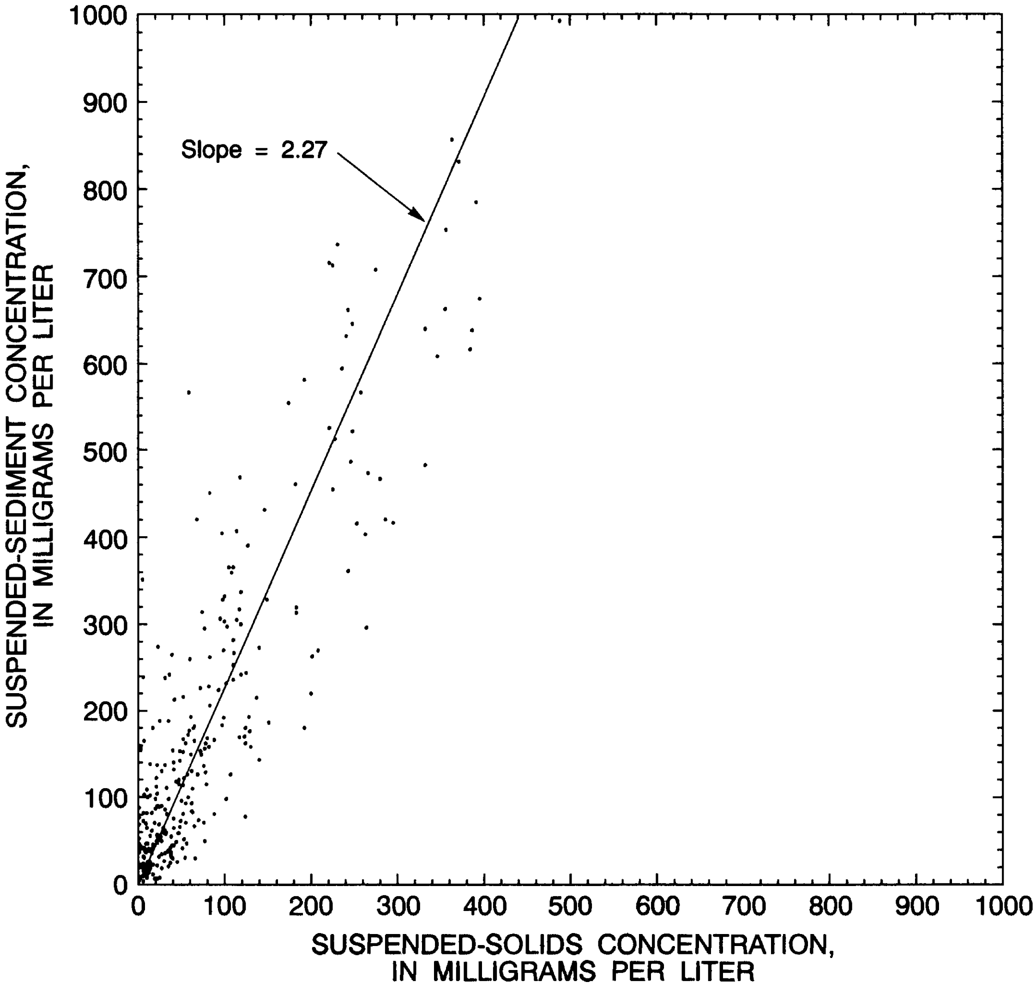


Figure 19.--Relation between suspended-sediment and suspended-solids concentrations (U.S. Geological Survey data).

the Roseau River. The mean annual yield in tons per square mile for each of these streams was 35.5 for the Pembina River, 23.5 for the Red River, and 6.12 for the Roseau River. A report by Hydrocon Engineering (Continental), Ltd. (1987) provides a detailed discussion of the sediment transport characteristics of the Pembina River at Windygates, Manitoba based on data collected by the Water Survey of Canada during 1962-84. A report by Glavic and others (1988) discusses sediment transport characteristics for the Red River at Emerson, Manitoba during 1978-86 and compares data collected by the USGS with data collected by the Water Survey of Canada.

Pesticides

This report is limited to a description of the presence of synthetic organic pesticides. Although inorganic compounds, such as copper sulfate (an algicide) and various arsenic compounds, have been used as pesticides, these chemicals will not be considered in this report. The term pesticides encompasses hundreds of commonly-used chemicals (herbicides, insecticides, fungicides, and other types) that have a large range in physical and chemical properties. Key factors that affect the movement and fate of pesticides in the environment are aqueous solubility, vapor pressure, lipophilicity (the tendency of a chemical to dissolve in lipids), and biological and chemical degradation processes. Extensive reviews of the properties and environmental behavior of pesticides have been published elsewhere (see, for example, Howard, 1991; Worthing and Hance, 1991).

Loading of pesticides to aquatic systems is related to usage or accidental release in contributing watersheds, and

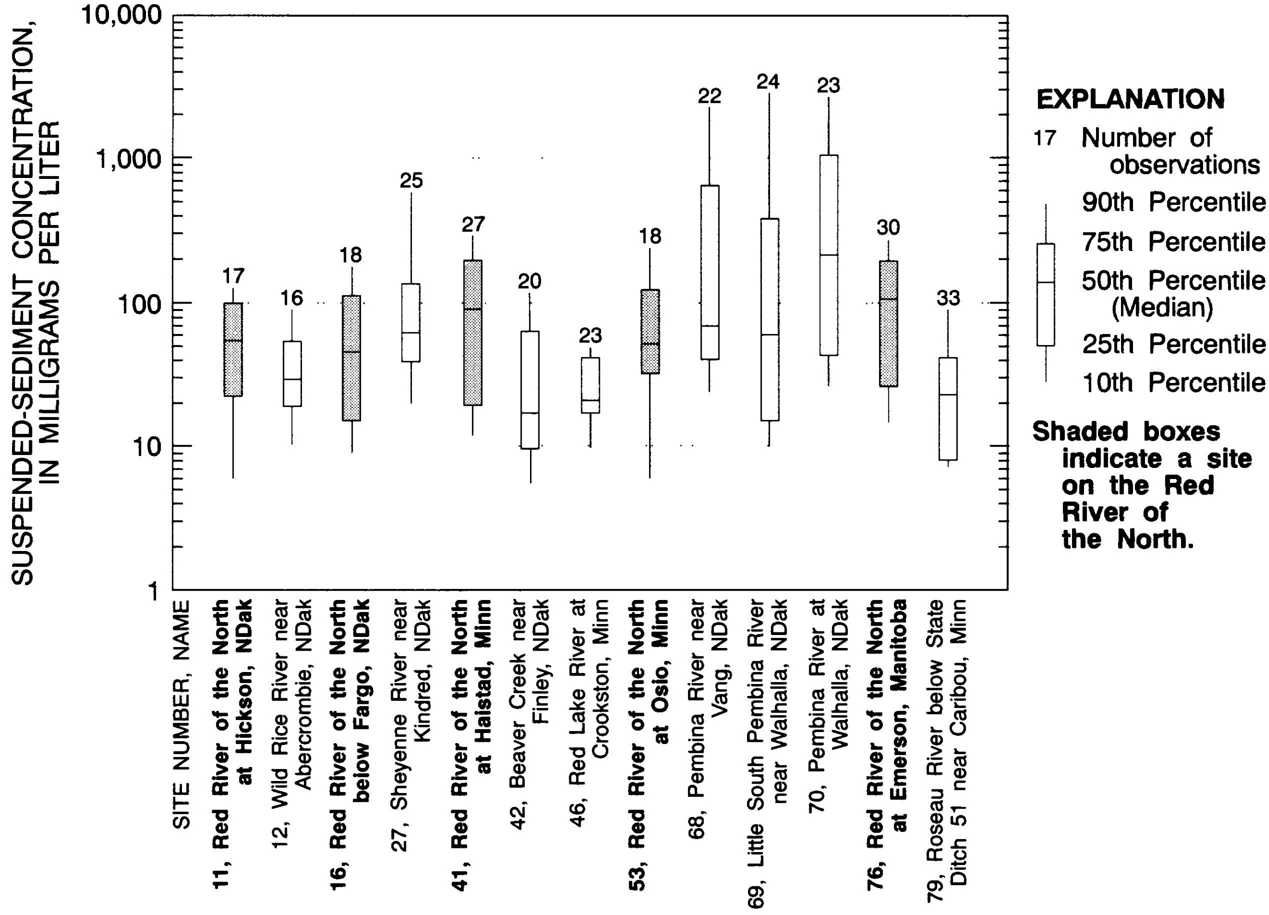


Figure 20.--Distribution of suspended-sediment concentrations for selected stream sites in the Red River of the North Basin (U.S. Geological Survey data).

other inputs such as atmospheric deposition. Loading also can be affected by aqueous solubility and adsorption to soils; loss mechanisms such as biological or chemical degradation and volatilization; and environmental factors such as runoff events and topography that affect transport of chemicals to aquatic systems. Occurrence of detectable levels of pesticides in water, aquatic sediments, or aquatic biological tissues thus depends on many factors, including loading rates, time since application, chemical half-life with respect to biological and chemical degradation, and physical and chemical properties of a chemical that influence its distribution among various media.

Because sampling programs vary greatly in analytes determined, time periods in which samples were collected, and sites or areas sampled, pesticide data are discussed separately for each sampling program (where sufficient data exist). Analytical capabilities can commonly allow chemicals to be measured at extremely low concentrations—levels that are well below established water-quality standards, guidelines, and criteria. The purpose of this report is to summarize available data whether or not criteria are exceeded. Measured concentrations are compared to established water-quality criteria, where appropriate. Analyses in which pesticides were not detected (below reporting limits) also are important in assessing contamination of water resources.

Relatively few sites in the Red River Basin have enough pesticide data to warrant statistical analyses and tests for trends in concentrations. Most of the data described in this section are from programs or surveys in which several sites over a large area are sampled infrequently, sometimes only once or several times over several decades. These data are insufficient to assess seasonal variations or long-term trends in pesticide concentrations, but are useful in providing an indication of which pesticides have been detected in surface and ground waters. However, seasonal and long-term patterns in concentrations are far more important in assessing potential contamination of water resources than a single measurement of a pesticide. Additionally, there are a number of commonly used pesticides, such as carbofuran and ethyl parathion (tables 2 and 3), which have been infrequently analyzed in water of the Red River Basin.

Where sufficient data exist, Wilkoxon rank-sum tests were performed to test for statistically significant differences between data sets. All differences herein described as "significant" are significant at the $\alpha = 0.01$ level (99 percent confidence level) using the rank-sum test.

Surface Water

The NWIS data base was searched for 350 constituents that include pesticides and pesticide-degradation products in water and bed sediments for surface-water sites sampled during 1960-91 in the Red River Basin. Pesticide data were found for 16 sites and 53 constituents (26 constituents in water samples and 27 in bottom-sediment samples) relating to 23 pesticides during 1968-82. DDE and DDD (metabolites of DDT) and heptachlor epoxide (a metabolite of heptachlor) were analyzed for some samples. These data are summarized in table 8. Many individual stations have data for only a few years and most data are from the early 1970s or late 1970s. Valid reporting limits were not used until later in the period of record; early data reported less-than-detectable concentrations as 0 micrograms per liter (µg/L). Data were censored at the higher reporting limit for the discussion in this report.

All samples for 13 pesticides had concentrations below their respective reporting limits. Nine of the remaining 10 pesticides had more than 90 percent of their data censored at the highest reporting limit. The herbicide 2,4-D in water was measured at concentrations at or above the reporting limit for 43 percent of 174 samples. These concentrations ranged from <0.01 (the highest reporting limit) to 0.40 µg/L. Figure 21A shows the distributions of 2,4-D concentration for each site.

The herbicide 2,4-D was detected over the entire period of record (1968-82); however, periods of record for individual stations are often less than 5 years. Two sites (Roseau River near Caribou, Minn. and Red River at Oslo, Minn.) had no samples that showed reportable levels of 2,4-D. Other sites on these rivers sampled by Environment Canada (discussed below), and the Red River at Hickson, sampled by the USGS, showed concentrations of 2,4-D greater than 0.01 µg/L during similar seasons and periods of record. Red River sites and Sheyenne River sites tended to have higher 2,4-D concentrations than the sites on other tributaries in the Red River Basin (fig. 21B).

Data from all sites were combined to yield a large enough statistical sample to examine seasonality in 2,4-D concentrations. March and June tended to have the highest concentrations; median concentrations exceeded the 0.01 µg/L reporting limit (fig. 21C):

The MPCA has pesticide data from 1967-79 (tab. 9) that are maintained in STORET. Most of the samples were analyzed for DDT only, or for DDT and its metabolites (DDD and DDE), and other chlorinated hydrocarbons. There are few analyses of other pesticides, with the exception of a survey that included malathion, a thiophosphate insecticide.

The MPCA has measured DDT (total, or individual isomers) and, less frequently, its degradation products DDD and DDE, in a total of 171 surface-water samples in the Red River Basin from April 1967 to September 1979. The analytical schedule was not consistent over this period. Several sites have had DDT, and sometimes its metabolites DDD and DDE, measured one or a few times during the period of record; some sites have DDT data for as many as thirteen dates. Thirteen Red River sites and twelve tributary sites are included in this data set. Of these samples, the *p,p'*-DDT isomer was detected at or above 0.10 µg/L (highest reporting limit) in 7 of 146 samples. Total DDT was detected at or above 0.05 µg/L (highest reporting limit) in only one of 43 samples. These data indicate that DDT contamination is not widespread in the region. In 1972, DDT was banned in the United States because it has deleterious effects on organisms. The highest concentrations of *p,p'*-DDT in this data base (>0.90 µg/L in three samples) were detected only before 1972.

The STORET data base also contains data from several MPCA surveys that focused on several more pesticides in stream bottom material and water samples. These surveys were conducted from 1977 to 1979, with most samples collected in October. A total of 12 stream-bottom material samples from 9 sites, and 26 water samples from 22 sites were collected from Red River Basin streams over this period (fig. 22). Samples from this survey were analyzed for DDT, DDD, DDE, chlordane, aldrin, HCH, lindane, dieldrin, endrin, methoxychlor, hexachlorobenzene, and malathion. Reporting limits for several of the analytes increased over this period. Some of these pesticides were in limited use at the time of the survey, and DDT had been banned in the United States. The October timing of this survey may not have detected the presence of pesticides that are applied earlier in the growing season. Malathion was detected in 21 of 26 surface-water samples at or above its lower reporting limit of 0.1 µg/L. For the 1979 samples, however, a reporting limit of 0.25 µg/L was established. Censoring all data at this higher limit, only 7 of 26 samples showed reportable concentrations of malathion, with a maximum concentration of 0.97 µg/L. These concentrations are well below the USEPA lifetime health

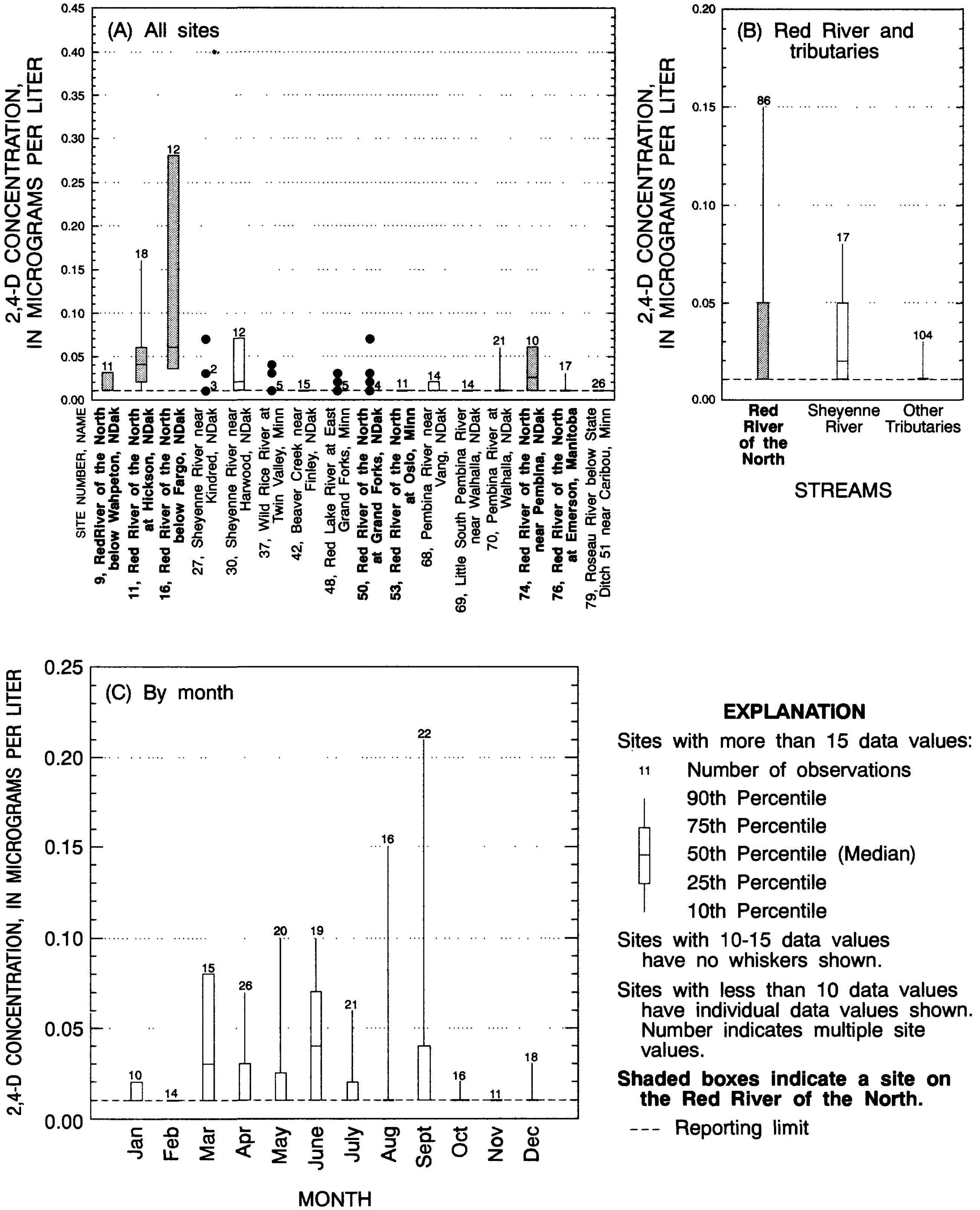


Figure 21.--Distribution of 2,4-D concentrations for selected U.S. Geological Survey stream sites in the Red River of the North basin (1968-82): (A) all sites, (B) Red River and tributaries, and (C) by month (all sites combined).

Table 8.--Summary of U.S. Geological Survey pesticide data from all surface-water sites in the Red River of the North Basin, 1968-82

[ND, not detected (reported concentration=0; detection limit not specified); µg/L, micrograms per liter; µg/kg, micrograms per kilogram dry solids; <, less than]

Chemical	Minimum reported concentration (µg/L)	Median reported concentration (µg/L)	Maximum reported concentration (µg/L)	Number of observations	Number of observations greater than reporting limit
		Water-column concentrations			
2,4,5-T, total	ND	ND	0.13	175	9
2,4-D, total	ND	ND	.40	174	75
Aldrin, total	ND	ND	<.01	196	0
Atrazine, total	ND	ND	ND	23	0
Chlordane, total	ND	ND	.10	174	4
DDD, total	ND	ND	.04	196	4
DDE, total	ND	ND	.02	195	4
DDT, total	ND	ND	.08	196	9
Diazinon, total	ND	ND	.26	149	6
Dieldrin, total	ND	ND	.03	196	8
Endosulfan, total	ND	ND	<.01	65	0
Endrin, total	ND	ND	<.01	196	0
Ethion, total	ND	ND	<.01	128	0
Heptachlor epoxide, total	ND	ND	.01	190	2
Heptachlor, total	ND	ND	.24	196	2
Lindane, total	ND	ND	.02	195	5
Malathion, total	ND	ND	<.01	145	0
Methoxychlor, total	ND	ND	.01	62	1
Methyl parathion, total	ND	ND	<.01	149	0
Methyl trithion, total	ND	ND	<.01	127	0
Mirex, total	ND	ND	<.01	40	0
Parathion, total	ND	ND	<.01	149	0
Silvex, total	ND	ND	.01	173	2
Simazine, total	ND	ND	ND	17	0
Toxaphene, total	ND	ND	<1.00	130	0
Trithion, total	ND	ND	<.01	127	0

Chemical	Minimum reported concentration (µg/kg)	Median reported concentration (µg/kg)	Maximum reported concentration (µg/kg)	Number of observations	Number of observations greater than reporting limit
		Bottom material concentrations			
2,4,5-T	ND	ND	ND	26	0
2,4-D	ND	ND	1.00	25	2
Aldrin	ND	ND	<.20	47	0
Atrazine	ND	ND	ND	6	0
Chlordane	ND	ND	1.00	47	1
DDD	ND	ND	.60	45	10
p,p'-DDD	.49	1.07	1.65	2	2
DDE	ND	ND	.57	47	9
DDT	ND	ND	2.15	46	4
Diazinon	ND	ND	ND	32	0
Dieldrin	ND	ND	.20	47	3
Endosulfan	ND	<.10	<.10	8	0
Endrin	ND	ND	<.20	47	0
Ethion	ND	ND	ND	30	0
Heptachlor	ND	ND	1.20	47	1
Heptachlor epoxide	ND	ND	<.20	47	0
Lindane	ND	ND	.20	47	2
Malathion	ND	ND	<.20	33	0
Methoxychlor	ND	ND	.20	28	2
Methyl parathion	ND	ND	<.20	33	0
Methyl trithion	ND	ND	ND	30	0
Mirex, total	ND	<.10	<.10	8	0
Parathion	ND	ND	<.20	34	0
Silvex	ND	ND	ND	27	0
Simazine	ND	ND	ND	6	0
Toxaphene	ND	ND	<10.00	42	0
Trithion	ND	ND	ND	30	0

Table 9.--Summary of Minnesota Pollution Control Agency pesticide data from all surface-water sites in the Red River of the North Basin (from STORET data base), 1967-79.

[ND, not detected (reported concentration=0; detection limit not specified); µg/L, micrograms per liter; µg/kg, micrograms per kilogram dry solids; NA, not applicable]

Chemical	Minimum reported concentration (µg/L)	Median reported concentration (µg/L)	Maximum reported concentration (µg/L)	Number of observations	Number of observations greater than reporting limit
		Water-column concentrations			
2,4-D, total	--	0.01	--	1	1
Aldrin, total	<0.01	<.01	0.2	33	3
α-HCH, total	<.02	<.02	<.02	26	0
Chlordane, total	<.1	<.1	<.1	26	0
cis-chlordane, total	<.02	<.02	<.02	26	0
trans-chlordane, total	<.03	<.03	<.03	26	0
Chlordane-nonachlor, *trans*, total	<.02	<.02	<.02	26	0
γ-chlordane, total	<.02	<.02	<.02	6	0
Chlorpyrifos, total	--	.21	--	1	1
DDE, total	<.01	<.01	.05	19	8
DDT, total	<.01	<.01	.1	44	1
o,p'-DDD, total	<.05	<.05	<.05	26	0
p,p'-DDD, total	<.05	<.05	<.05	26	0
o,p'-DDE, total	<.05	<.05	<.05	26	0
p,p'-DDE total	<.05	<.05	<.05	26	0
o,p'-DDT, total	<.1	<.10	<.1	30	0
p,p'- DDT, total	<.1	<.1	.9	146	7
Dieldrin, total	<.05	<.05	.19	35	5
Endrin, total	<.07	<.07	<.07	26	0
Heptachlor, total	.08	.09	.09	2	2
Heptachlor epoxide, total	--	.03	--	1	1
Hexachlorobenzene, total	<.05	<.05	<.05	30	0
Lindane, total[1]	<.01	<.01	<.01	20	0
Lindane, total[1]	<.05	<.05	<.05	4	0
Malathion, total	<.1	.19	.97	26	21
Methoxychlor, total	<.8	<.8	<.8	30	0
Mirex, total	--	<.5	--	1	0
Parathion, total	<50	<50	<50	12	0
Toxaphene, total	--	ND	--	1	1

Chemical	Minimum reported concentration (µg/kg)	Median reported concentration (µg/kg)	Maximum reported concentration (µg/kg)	Number of observations	Number of observations greater than reporting limit
		Bottom material concentrations			
Aldrin	<3	<3	<3	12	0
α-HCH	<3	<3	<3	9	0
Chlordane	<5	<5	<5	9	0
o,p' DDD	<30	<30	<30	9	0
p,p'-DDD	<30	<30	30	9	1
o,p'-DDE	<30	<30	30	9	1
p,p'-DDE	<30	<30	<30	9	0
o,p'-DDT	<60	<60	<60	12	0
p,p'-DDT	<20	<20	60	12	1
Dieldrin	<5	<5	<5	12	0
Endrin	<9	<9	<9	9	0
Hexachlorobenzene	<3	<3	<3	16	0
Lindane	<3	<3	<3	9	0
Methoxychlor	<50	<50	<50	12	0
Mirex, total	<1	<1	<1	7	0

[1] Data for total lindane in water were stored in the data base under two separate parameter codes, reflecting different methods of analysis.

advisory level of 200 µg/L (U.S. Environmental Protection Agency, 1993). However, the USEPA ambient stream-water criterion for the protection of aquatic organisms of 0.1 µg/L (chronic exposure level; U.S. Environmental Protection Agency, 1976) was exceeded frequently in samples from this study. North Dakota agricultural statistics show that reported malathion applications increased by over 15-fold from 1978 to 1984. Usage in 1989 was about the same as in 1984. Therefore, it may be of interest to assess malathion concentrations in the near future, to see if increases in usage result in high concentrations in streams of the Red River Basin. Bottom material samples from this survey showed that virtually none of the analytes were present. One sample (Red River at Moorhead) had DDT, DDD, and DDE concentrations that were lower than the highest reporting limit for the period, and thus may not be confirmed.

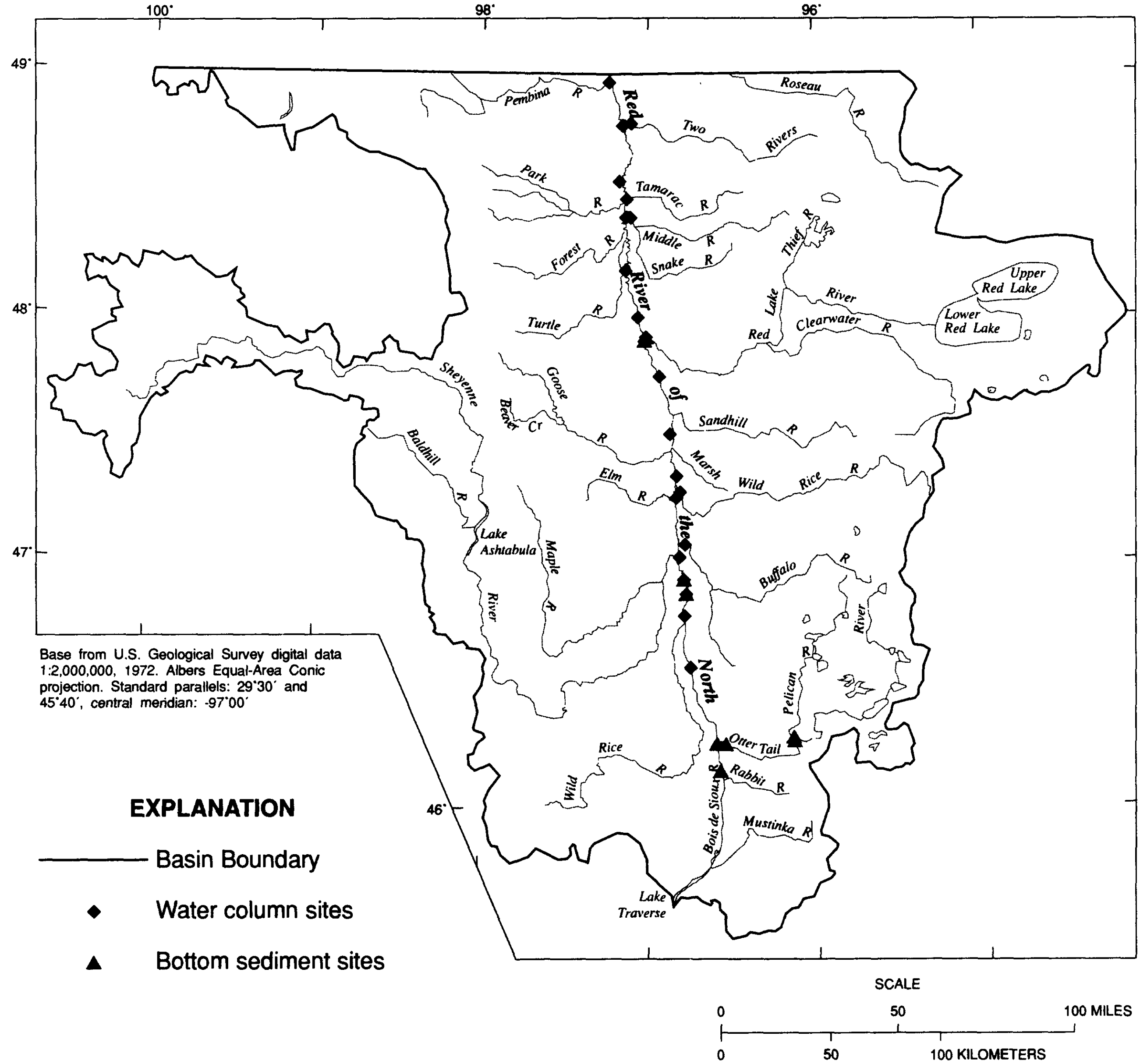


Figure 22.--Stream sampling sites for Minnesota Pollution Control Agency survey of pesticides in water and bottom sediments, 1977-1979.

Data from a drinking-water survey at four water treatment plants conducted in February 1975 are also in the STORET data base. Stream water was sampled before and after treatment at drinking-water treatment plants on the Otter Tail River, Red Lake River, and Red River. Analytes included several organochlorine insecticides, thiophosphates, and chlorophenoxy acids (tab. 10). The analytes included pesticides that are widely used in the region, and some that were no longer in use (such as DDT). Small amounts (0.01 µg/L) of the fungicide hexachlorobenzene were detected at two sites on the Red Lake River; otherwise all pesticide analytes were below reporting limits. This February sampling was at least one-half year after the peak period of pesticide application.

Data from the Red River at Emerson, Manitoba and the Roseau River at Gardenton, Manitoba were retrieved from Environment Canada's ENVIRODAT data base, which includes data from Environment Canada's NAQUADAT (National Water Quality Database). These are the most complete single-station records examined for pesticide data in this report. No significant tributaries contribute to either of these streams between the U.S.-Canada border and the sampling sites (fig. 5). For most of the time, monthly samples analyzed for pesticides have been collected from these sites since 1972 (Red River) and 1974 (Roseau

Table 10.--Summary of pesticide data for treated and untreated stream water from four drinking-water treatment plants in the Red River of the North Basin; data from U.S. Environmental Protection Agency Drinking Water Survey, February 1975

[µg/L, micrograms per liter; <, less than]

Chemical	Minimum reported concentration (µg/L)	Maximum reported concentration (µg/L)	Number of observations	Number of observations greater than reporting limit
Aldrin, total	<0.002	<0.002	8	0
Atrazine, total	<1	<1	8	0
Chlordane, total	<.002	<.002	8	0
Chlorobenzilate, total	<.01	<.01	8	0
Cyanazine, total	<1	<1	8	0
2,4-D, total	<.02	<.02	8	0
Dacthal (DCPA), total	<.003	<.003	8	0
o,p'-DDD, total	<.003	<.003	8	0
o,p'-DDE, total	<.003	<.003	8	0
o,p'-DDT, total	<.003	<.003	8	0
p,p'-DDD, total	<.003	<.003	8	0
p,p'-DDE, total	<.003	<.003	8	0
p,p'-DDT, total	<.003	<.003	8	0
Dieldrin, total	<.003	<.003	8	0
Dyfonate	<1	<1	8	0
α-endosulfan, total	<.005	<.005	8	0
β-endosulfan, total	<.005	<.005	8	0
Endrin, total	<.003	<.003	8	0
EPN, whole water, total	<1	<1	8	0
β-HCH, total	<.002	<.002	8	0
Heptachlor epoxide, total	<.002	<.002	8	0
Hexachlorobenzene, total	<.002	.006	8	3
Isodrin, total	<.003	<.003	8	0
Lindane, total	<.002	<.002	8	0
Methoxychlor, total	<.01	<.01	8	0
Methyl parathion, total	<1	<1	8	0
Mirex, total	<.005	<.005	8	0
2,4,5-T, total	<.01	<.01	8	0
Terbufos	<5	<5	8	0
Trifluralin, total recoverable	<.002	<.002	8	0
Trithion, total	<.02	<.02	8	0

River); this report reviews data collected through early 1990. Chacko and Ronmark (Environment Canada, written commun., 1990) have summarized the data from these sites in a draft report.

Several organochlorine insecticides and chlorophenoxy acid herbicides were analyzed in over 150 samples from the Red River at Emerson, Manitoba and over 120 samples from the Roseau River at Gardenton, Manitoba. Nitrogen-containing herbicides, including selected carbamates, thiocarbamates, triazines, and others, were analyzed in over 60 samples from the Red River at Emerson, Manitoba and in 18 samples from the Roseau River. Very few samples had concentrations above reporting limits for most of these pesticides. Twenty mono- and polychlorophenol compounds (several of which are used as fungicides, insecticides, and bactericides; pentachlorophenol is also a general herbicide and wood preservative) were analyzed in five monthly samples in 1990 at the Red River at Emerson, Manitoba; none were detected at concentrations at or above their reporting limits. The pesticide data are summarized in tables 11 and 12. Only four pesticide compounds were detected in a substantial fraction of samples. The herbicide 2,4-D was reported at concentrations at or greater than its higher reporting limit in 119 of 311 samples (38 percent). Alpha-hexachlorocyclohexane (α-HCH) was present in 241 of 298 samples (80 percent). Gamma-hexachlorocyclohexane (γ-HCH) was present in 121 of 309 samples (39 percent), (α-HCH and γ-HCH are components of technical lindane). Atrazine, an herbicide used for corn crops, was present above reporting limits in 35 of 83 samples (42 percent).

The analytical method for 2,4-D changed in 1985, with a concomitant increase in reporting limit from 0.004 to 0.03 µg/L. The fraction of samples with concentrations above reporting limits decreased substantially at each site after this change was implemented. For this report, all data were censored at the 0.03 µg/L reporting limit. Figures 23A and 23B show the presence of seasonal peaks in 2,4-D concentrations for the Red River at Emerson, Manitoba and the Roseau River at Gardenton, Manitoba. For the period of record, median 2,4-D concentration exceeded 0.03 µg/L only in the months of June-August for the Red River at Emerson, Manitoba, and in March and July for the Roseau River at Gardenton, Manitoba. Concentrations of 2,4-D were significantly higher at the Red River at Emerson, Manitoba than at the Roseau River at Gardenton, Manitoba (fig. 23C). Concentrations of 2,4-D at both sites were well below water-quality criteria.

Chacko and Gummer (1980) reported 2,4-D concentrations in the Red River at Emerson, Manitoba and downstream sites for 1972-77. Data from routine water-quality monitoring and from a special investigation of 2,4-D in water, suspended sediments, and bottom sediments showed that 2,4-D was frequently detected in water samples from the Red River. Occasionally, 2,4-D was detected in suspended sediments, but at low levels relative to water concentrations. None of the bottom sediment samples from this study had detectable levels of 2,4-D.

Two HCH isomers (α-HCH and γ-HCH) were analyzed in over 160 samples from the Red River at Emerson, Manitoba and over 130 samples from the Roseau River at Gardenton, Manitoba. γ-HCH was detected in nearly half the samples from the Red River at Emerson, Manitoba and in about 27 percent of the samples from the Roseau River at Gardenton, Manitoba. Concentrations of γ-HCH were significantly higher at the Red River at Emerson, Manitoba than at the Roseau River at Gardenton, Manitoba (fig. 24A). The alpha isomer was detected in many more samples from both sites: nearly 80 percent at the Red River at Emerson, Manitoba and 84 percent at the Roseau River at Gardenton, Manitoba. There was no significant difference in the concentrations of α-HCH between these two sites (fig. 24B). During the period of record, the monthly patterns of concentrations show an early-summer peak in γ-HCH concentration at the Red River at Emerson, Manitoba. During other seasons, nearly all concentrations were at or below the reporting limit. For the Roseau River at Gardenton, Manitoba median γ-HCH concentrations were below the reporting limit for all months. Conversely, median α-HCH concentrations were above the reporting limit for nearly all months for both sites (fig. 24C and 24D). HCH concentrations (α and γ isomers) have decreased since 1985 (fig. 25). The period from the mid-1970s to the mid-1980s has significantly higher concentrations than the mid-1980s to 1991. In the United States, nearly every lindane-containing agricultural product was either banned or subject to use restrictions in the mid-1980s. Therefore, decreased concentrations would be expected.

Several water-quality criteria and health guidelines exist for α-HCH and γ-HCH. An MCL has not been established for α-HCH. However, a quantitative carcinogenicity assessment has been made. The USEPA has classified α-HCH as a probable human carcinogen, and calculated a risk-specific dose (RSD) of 0.006 µg/L (10^{-6} risk level) for this compound (U.S. Environmental Protection Agency, 1993). This means that the excess cancer risk due to lifetime consumption of drinking water containing α-HCH at this concentration (0.006 µg/L) is estimated to be 1 in 10^6. Fifty-six of 298 samples (from both the Red River and Roseau River sites) had concentrations equal to or exceeding this value. An ambient stream water quality criterion for protection of human health (based on ingestion of water and aquatic organisms and a 10^{-6} risk level) was set at 0.0092 µg/L (U.S. Environmental Protection Agency, 1980). Fifteen of 298

Table 11.--Summary of Environment Canada pesticide data for the Red River of the North at Emerson, Manitoba

[μg/L, micrograms per liter; <, less than]

Chemical	Minimum reported concentration (μg/L)	Maximum reported concentration (μg/L)	Number of observations	Number of observations greater than reporting limit
Aldrin	<0.001	<0.001	159	0
Atrazine	<.05	.65	64	25
Barban	<.01	<.1	63	0
Benzoylprop-ethyl	<.025	<.025	63	0
α-chlordane	<.003	<.003	154	0
γ-chlordane	<.002	<.002	154	0
2,4-D	<.004	.82	179	87
2,4-DB	<.05	.2	178	1
p,p'-DDT	<.004	<.004	159	0
o,p'-DDT	<.001	<.004	152	0
p,p'-DDD	<.002	.002	159	1
p,p'-DDE	<.001	<.001	159	0
Diallate	<.01	.104	63	1
Dicamba	<.03	.04	75	1
Dichlorprop	<.03	.23	178	10
Dieldrin	<.002	<.002	159	0
α-endosulfan	<.001	<.001	159	0
β-endosulfan	<.003	<.003	159	0
Endrin	<.002	<.002	154	0
Fenoprop	<.03	<.03	154	0
γ-HCH	<.001	.02	171	83
α-HCH	<.001	.094	163	128
Heptachlor	<.001	<.002	159	0
Heptachlor epoxide	<.001	<.002	159	0
Hexachlorobenzene	<.001	<.001	151	0
Hoegrass	<.05	<.05	63	0
MCPA	<.2	.32	178	2
MCPB	<.05	<.05	75	0
Methoxychlor	<.01	<.012	159	0
Mirex	<.001	.001	152	1
Picloram	<.2	.20	158	4
2,4,5-T	<.05	.06	179	1
2,3,6-TBA	<.03	<.03	75	0
Triallate	<.01	.08	63	5
Trifluralin	<.005	.006	63	1

samples exceeded this criterion. A recalculated value for this criterion, based on more recent health data, was established at 0.0039 μg/L (U.S. Environmental Protection Agency, 1992c, 1993). This recalculated criterion was exceeded in 119 of 298 samples (40 percent). In the period from 1986-90, however, this criterion was exceeded in only 7 of 108 samples (6 percent). Ambient stream water quality criteria for protection of aquatic life are generally established for both acute toxicity and chronic toxicity. There are no aquatic life criteria for α-HCH specifically. For technical HCH (of which α-HCH is one component) the USEPA reported a lowest-observed-adverse-effect level (LOAEL) of 100 μg/L, in lieu of an aquatic-life criterion (data were not sufficient to establish an aquatic-life criterion) (U.S. Environmental Protection Agency, 1993). This LOAEL value is much higher than the measured concentrations in this data set. No chronic-toxicity criteria have been established for either α-HCH or technical HCH.

Because a larger number of samples had α-HCH concentrations above the RSD and the ambient water-quality criteria for protection of human health, a brief explanation of exposure assumptions used in calculating

Table 12.--Summary of Environment Canada pesticide data for the Roseau River at Gardenton, Manitoba

[μg/L, micrograms per liter; <, less than]

Chemical	Minimum reported concentration (μg/L)	Median reported concentration (μg/L)	Maximum reported concentration (μg/L)	Number of observations	Number of observations greater than reporting limit
2,4-D	<0.03	<0.03	0.4	132	32
2,4-DB	<.05	<.05	<.05	133	0
2,3,6-TBA	<0.03	<0.03	<0.03	40	0
2,4,5-T	<.05	<.05	.06	133	1
Aldrin	<.001	<.001	<.001	127	0
Atrazine	<.05	<.1	.13	19	10
Barban	<.1	<.1	<.1	18	0
α-HCH	<.001	.003	.06	135	113
γ-HCH	<.001	<.001	.004	138	38
Benzoylprop-ethyl	<.025	<.025	<.025	18	0
α-chlordane	<.003	<.003	<.003	127	0
γ-chlordane	<.002	<.002	<.002	127	0
o,p'-DDT	<.001	<.001	<.003	125	0
p,p'-DDT	<.004	<.004	<.004	127	0
p,p'-DDD	<.002	<.002	<.002	126	0
p,p'-DDE	<.001	<.001	<.001	127	0
Diallate	<.1	<.1	<.1	18	0
Dicamba	<.03	<.03	.27	41	3
Dichlorprop	<.03	<.03	.05	168	2
Dieldrin	<.002	<.002	<.002	127	0
α-endosulfan	<.001	<.001	<.001	127	0
β-endosulfan	<.005	<.005	<.005	127	0
Endrin	<.002	<.002	.006	127	1
Fenoprop	<.03	<.03	<.03	118	4
Heptachlor	<.001	<.001	<.001	127	0
Heptachlor epoxide	<.001	<.002	<.002	127	0
Hexachlorobenzene	<.001	<.001	<.001	125	0
Hoegrass	<.05	<.05	<.05	18	0
MCPA	<.2	<.2	<.2	133	0
MCPB	<.05	<.05	<.05	40	0
Methoxychlor	<.01	<.01	<.01	126	0
Mirex	<.001	<.001	<.001	125	0
Picloram	<.2	<.2	.2	99	2
Triallate	<.01	<.01	<.01	18	0
Trifluralin	<.005	<.005	<.005	18	0

these guidelines is warranted. In calculating the RSD for water, it is assumed that human exposure occurs by ingestion of water (2 L/day) by a 70 kg adult for 70 years. For calculation of the EPA water quality criterion for the protection of human health, it is assumed that human exposure occurs by both ingestion of water and ingestion of aquatic organisms (fish and (or) shellfish) that live in the water and bioconcentrate the contaminant. Thus, in addition to the exposure assumptions used for the RSD, it is also assumed that an average of 6.5 g of fish or shellfish that live in the contaminated water are consumed daily. In this report, the criteria are used for comparative purposes only. Both of these guidelines are based solely on carcinogenicity, and do not consider other health effects that may result from chronic, low-level exposure, other routes of exposure, and additive or synergistic adverse effects that may result from exposure to other contaminants. Also, contaminants may be removed from drinking water by various treatment processes. Thus, ambient stream-water concentrations may not necessarily reflect concentrations of the contaminant in drinking water.

The maximum observed γ-HCH concentration was 0.02 μg/L; this value is lower than most water quality standards and guidelines for protection of human health for this

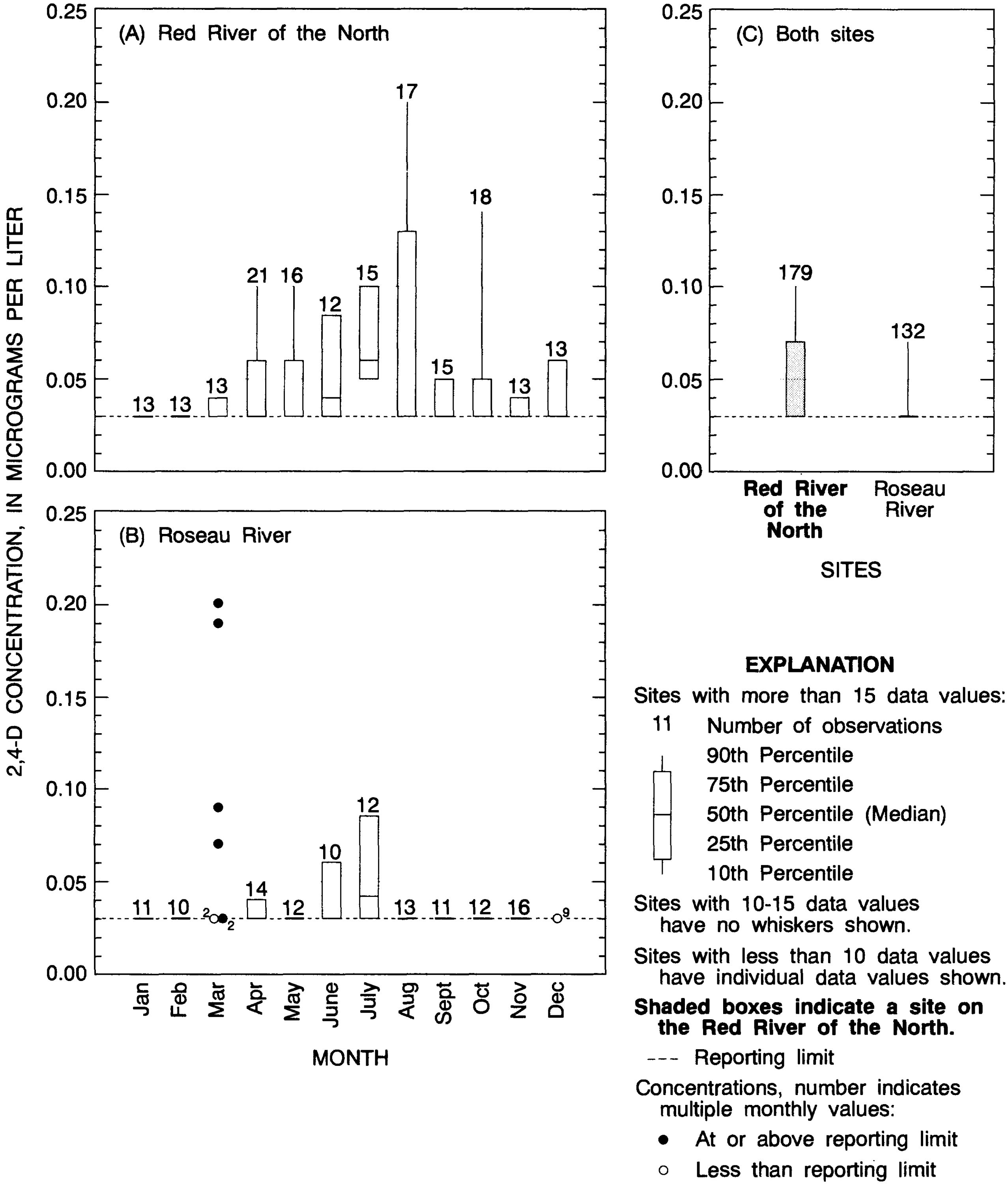


Figure 23.--Distribution of 2,4-D concentrations for Environment Canada stream sites (1975-90) (A) by month at the Red River of the North at Emerson, Manitoba, (B) by month at the Roseau River at Gardenton, Manitoba, and (C) both sites.

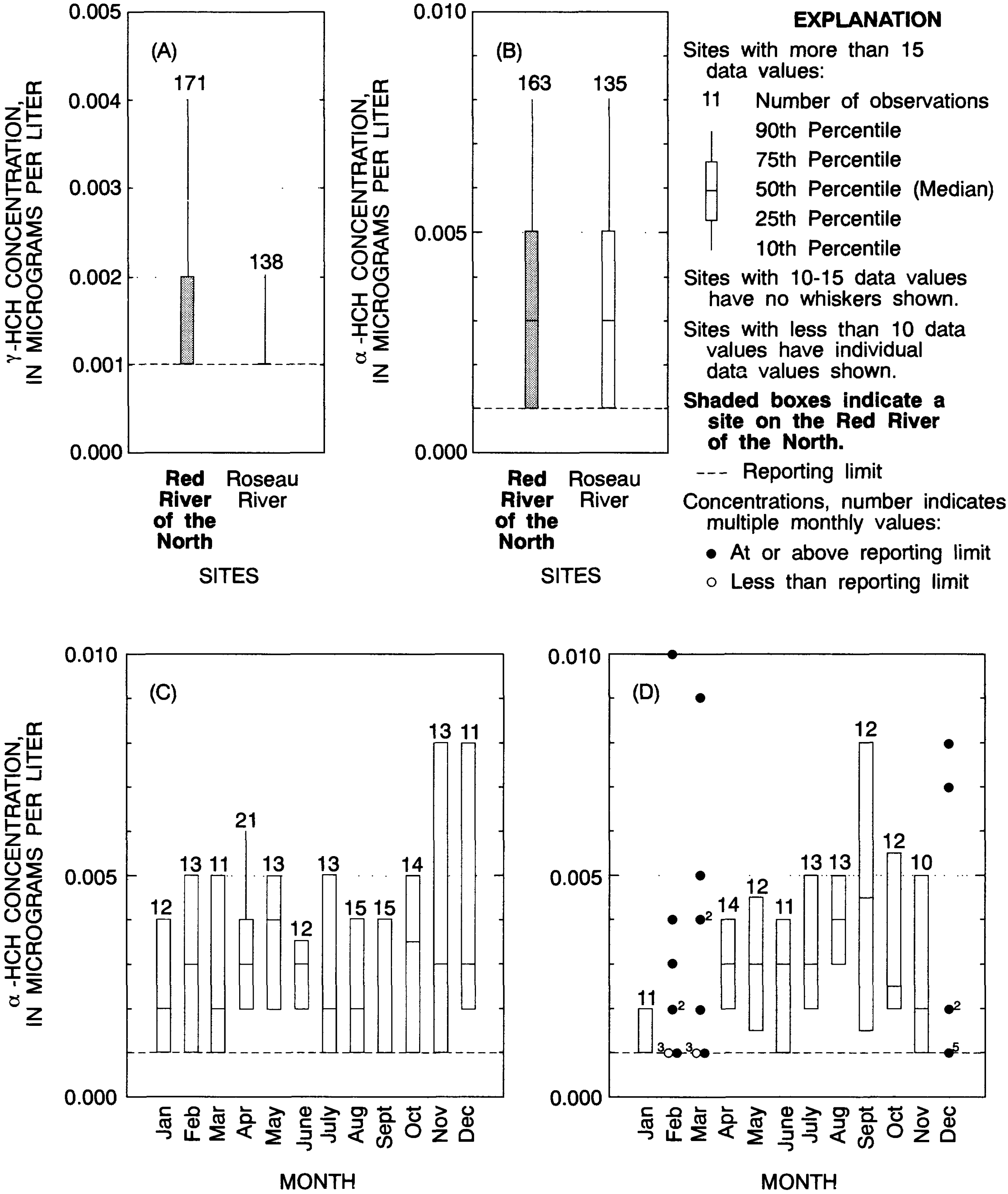


Figure 24.--Distributions of (A) gamma-hexachlorocyclohexane (γ-HCH) and (B) alpha-hexachlorocyclohexane (α-HCH) for Red River of the North at Emerson, Manitoba and Roseau River at Gardenton, Manitoba; monthly distribution of α-HCH concentrations for (C) Red River of the North at Emerson, Manitoba and (D) Roseau River at Gardenton, Manitoba, Environment Canada sites (1975-90).

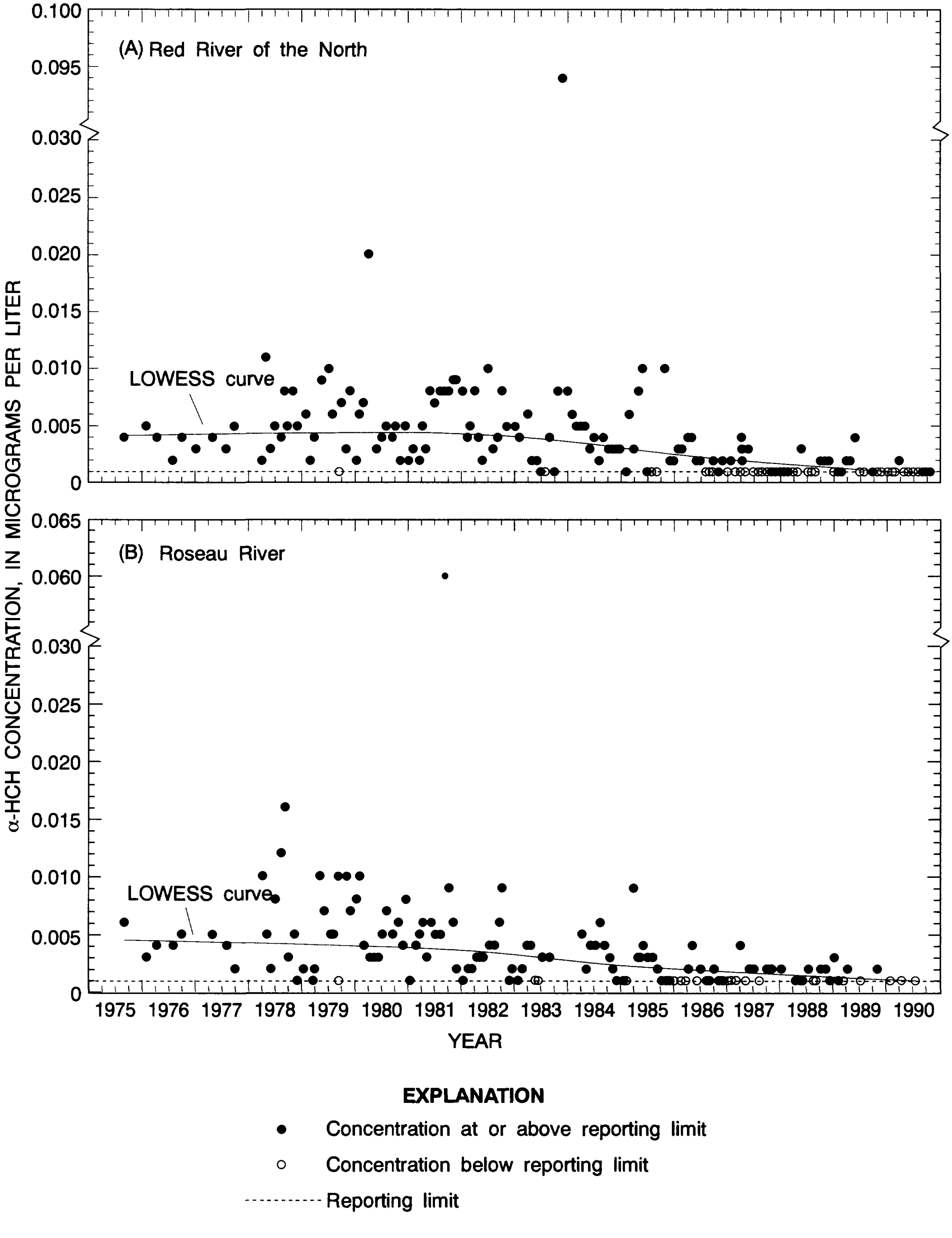


Figure 25.--Concentrations of alpha-hexachlorocyclohexane (α -HCH) versus time for Environment Canada (1975-90) stream sites at the (A) Red River of the North at Emerson, Manitoba and (B) Roseau River at Gardenton, Manitoba.

compound. The MCL for γ-HCH is 0.2 μg/L (U.S. Environmental Protection Agency, 1991; U.S. Environmental Protection Agency, 1993). The U.S. EPA has classified this compound as a possible human carcinogen, and calculated that lifetime exposure to a concentration of 0.2 μg/L is not expected to result in adverse human health effects. However, the assessment for potential human carcinogenicity of γ-HCH is currently under review (U.S. Environmental Protection Agency, 1993). An ambient stream water quality criterion for the protection of human health (based on ingestion of water and aquatic organisms and a 10^{-6} risk level) was set at 0.0186 μg/L (U.S. Environmental Protection Agency, 1980). This value is based on carcinogenic potency and it consists of the γ-HCH concentration estimated to result in an excess cancer risk of 1 in 10^6 over a lifetime exposure. Only one of 309 samples exceeded this criterion. Ambient stream water quality criteria for the protection of aquatic life were set at 2 μg/L for acute toxicity and 0.08 μg/L for chronic toxicity (U.S. Environmental Protection Agency, 1980). None of the samples exceeded either of these criteria.

Since 1985, atrazine has been analyzed in 64 samples from the Red River at Emerson, Manitoba and 19 samples from the Roseau River at Gardenton, Manitoba. The reporting limit for atrazine was lowered from 0.10 to 0.05 μg/L in 1988. The Red River at Emerson, Manitoba has significantly higher atrazine concentrations (fig. 26A). Higher atrazine concentrations generally occur at the Red River at Emerson, Manitoba during the growing season, June through August (fig 26B). Data are not sufficient to detect seasonal peaks in concentration for the Roseau River at Gardenton, Manitoba (fig. 26C). Atrazine, used almost exclusively for corn, is used in modest amounts in the Red River Basin, particularly in the southern part of the basin. Atrazine is used only sparingly in counties of the Roseau River drainage basin (J.W. Hines, Minnesota Department of Agriculture, written commun., 1992).

Where significant differences in concentrations of any pesticide exist between the Red and Roseau River, concentrations tend to be higher at the Red River at Emerson, Manitoba. This could be expected, given the larger proportion of agricultural land use in the Red River Basin than in the Roseau River drainage basin.

Investigators of two recent county-level studies in Minnesota, coordinated with the Minnesota Board of Water and Soil Resources, have collected stream samples for pesticide analyses. These studies were similar in scale, used similar methods for sample collection, and used the same commercial laboratory for pesticide analyses.

The Kittson County Water Plan Coordinator's office has conducted a two-year (1991-93) study of the Joe River and Two Rivers. Data from the first part of this study are available in an interim report (Money, 1992). Three samplings for base-neutral pesticides (June 24, July 3, and October 21, 1991) showed evidence of a seasonal peak in concentrations of some pesticides, probably related to the timing of application. Linuron was detected at concentrations ranging from 2 to 18 μg/L on the earliest sampling date, but was below the reporting limit at subsequent samplings. Simazine was detected at one site at a concentration of 10 μg/L on June 24, 1991, which exceeds the MCL of 4 μg/L (U.S. Environmental Protection Agency, 1992), but was below its reporting limit at all other sites and sampling dates. Several other herbicides were occasionally detected at sub-microgram per liter concentrations. Cyanazine was detected at two sites on the earliest sampling date. Chlorpyrifos and pendimethalin were detected only later in the season. Acid pesticides were analyzed once (June 24, 1991), and only 2,4-D and picloram were detected.

The Red Lake Watershed District sponsored a cooperative project assessing water quality of the Clearwater River watershed (Holder, 1991). This watershed supports about 14,500 acres of man-made wild-rice paddies, which may have substantial effects on water quality and streamflow in the river basin. Stream and agricultural-runoff sites were sampled with varying frequency, depending on the site, throughout the 1990 growing season. Sites were sampled up to eight times from early May to late October. Of the pesticides sampled, 2,4-D was detected with greatest frequency and at the greatest number of sites. The highest concentrations and frequencies of detection for 2,4-D in stream water samples were measured in early May and during a major runoff event in early June 1990. Concentrations of 2,4-D, when detected, ranged from about 0.5 to 17 μg/L in early May, and from about 2 to 4 μg/L in early June. None of the pesticides were present in the stream at detectable levels during the late October sampling. The higher 2,4-D concentrations detected in this study are considerably greater than concentrations other agencies have detected on larger streams in the Red River Basin. Concentrations of 2,4-D did not approach its MCL of 70 μg/L (U.S. Environmental Protection Agency, 1991). The USEPA has not established an ambient stream-water quality criterion for 2,4-D. However, the National Academy of Sciences' water-quality criterion of 3 μg/L (National Academy of Sciences, 1972) was exceeded frequently in the May and June sampling. Bottom materials were sampled in early May and late October. In early May, 2,4-D was present at five of seven sites and was the only pesticide detected in the sediments. The late October sediment sampling indicated detectable concentrations of 2,4-D, dicamba, MCPA, and bromoxynil. Cyanazine was detected in a

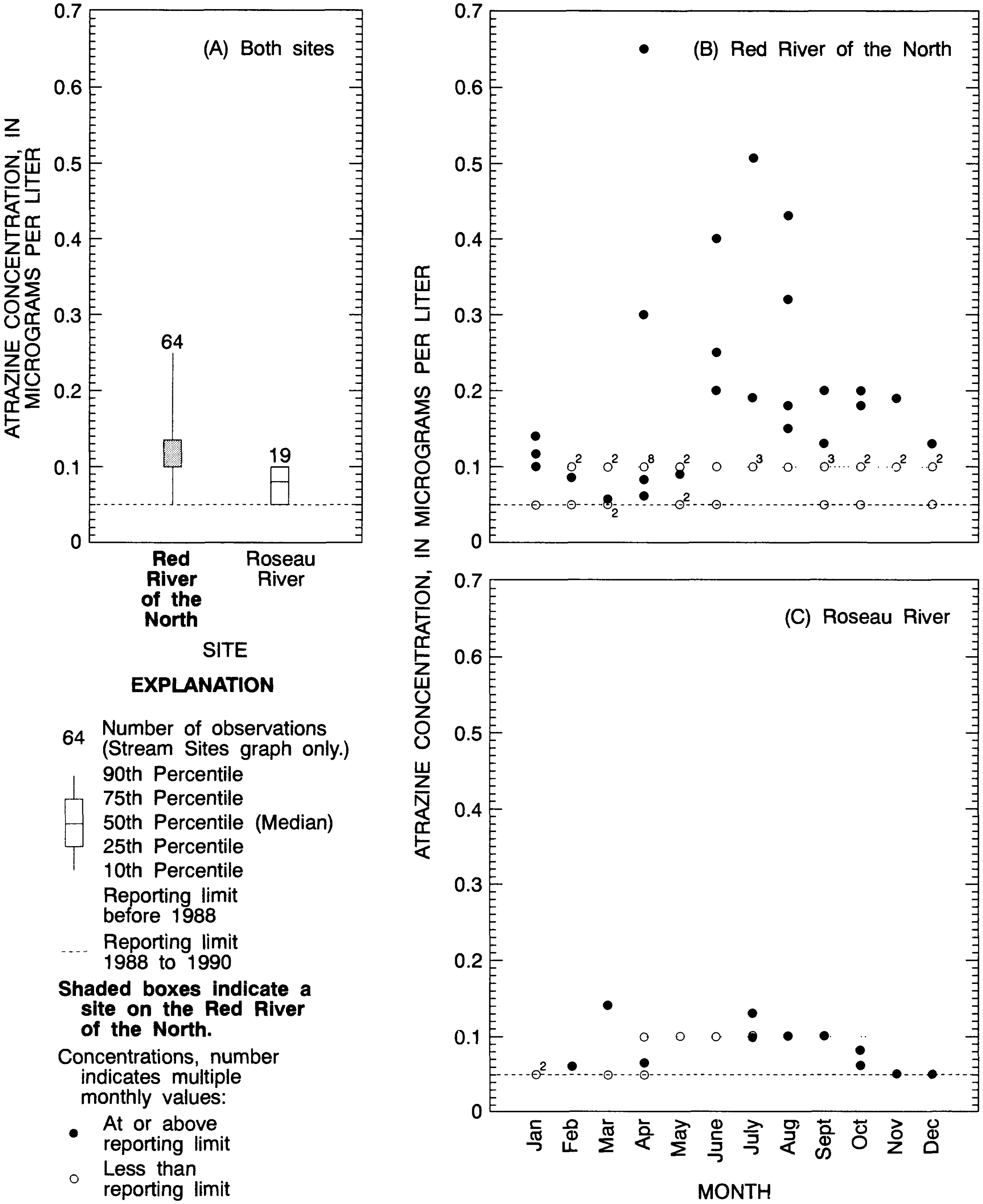


Figure 26.--Atrazine concentrations for Environment Canada stream sites at the Red River of the North at Emerson (1986-1990) and the Roseau River at Gardenton, Manitoba (1988-1990): (A) distribution at both sites, and concentrations by month, (B) Red River of the North, and (C) Roseau River.

runoff sample from a farm field at a concentration of 10 µg/L, which exceeds the USEPA lifetime health advisory limit of 1 µg/L (no MCL has been established for cyanazine).

The majority of pesticide analyses of stream samples in the Red River Basin showed no detectable levels of analytes. Where detected, nearly all of the reported concentrations were below the USEPA MCL or lifetime health advisory limit standards. The exceptions have been noted. It is noteworthy that the highest concentrations of 2,4-D, simazine, and cyanazine were reported at smaller, upstream tributaries and farm-field runoff. The effects of chemical degradation, dilution by other tributaries, and sorption to sediments that are deposited in stream beds may decrease pesticide concentrations at downstream sites on larger streams. This may be an important consideration when studying movement and fate of pesticides in hydrologic systems. By relying solely on measurements at sites that drain large areas, a study may fail to detect the highest pesticide concentrations that may exist in a hydrologic system.

Ground Water

Pesticide data for ground water in NWIS are sparse for the Red River Basin (fig. 27). Three ground-water samples in the North Dakota part of the basin have been analyzed for pesticides (two from the surficial Warwick aquifer and one from the confined Spiritwood aquifer). The sites were sampled in May 1986, and are within 10 km of each other. A total of 14 samples from 9 sites within or very near the Minnesota part of the basin have been analyzed for pesticides during 1980-91. Two sites are from a surficial sand aquifer near the Otter Tail River; the remaining sites are from the Des Moines drift aquifer near the headwaters of the Clearwater River. Of these analyses, only atrazine was detected. Three samples from one well and one sample from another well had detectable atrazine concentrations. These wells are shallow (less than 10 feet deep and less than 6 feet to water) and are in the surficial Des Moines drift aquifer in Clearwater County, Minn. The analytes are shown in table 13.

The MPCA (STORET data base) has analyzed water samples from wells within and very near the Red River Basin (fig. 27). A total of 30 samples from 16 wells in surficial outwash aquifers (well depths 15.5-160 feet) and a total of 30 samples from 26 wells in buried outwash aquifers (well depths 43-364 feet) were sampled from 1978-88. Fifteen of the wells were clustered in a small area in Big Stone County, Minn., south of the basin boundary near the headwaters of the Minnesota River. These wells were sampled in 1987-88 for four triazine herbicides and one thiophosphate insecticide. Four wells near the Otter Tail River headwaters were sampled in 1978 for chlorinated hydrocarbon insecticides and chlorophenoxy acid herbicides. The remaining wells were sampled mainly for chlorinated propenes, chlorinated propanes, tetrachloroethane, dibromoethane, and dichlorobenzene. These compounds are variously used as soil fumigants, herbicides, and solvents in pesticide formulations and other products. None of the samples from the STORET data base yielded reportable quantities of any of the pesticides or fumigants analyzed. Analytes and their reporting limits are shown in table 14.

The MDH (Minnesota Department of Health) conducted a statewide survey of community well-water systems from 1986-91 that focused on pesticide contamination (T. Klaseus, Minnesota Department of Health, written commun., 1992). Atrazine was the most widely detected of those pesticides analyzed throughout Minnesota. Very few of the samples from within the Red River Basin yielded detectable quantities of atrazine. Atrazine detections were generally limited to the extreme southern and southeastern portions of the drainage basin, in an area characterized by morainal topography with sandy, permeable surficial aquifers where corn, a crop on which atrazine commonly is applied, is grown. Where detected in the basin, atrazine concentrations ranged from 0.01to 0.23 µg/L, and were lower than the range of concentrations reported in other regions of the state (some sites in other regions of the state yielded concentrations of several µg/L). Table 15 shows the analytes and their reporting limits for this survey.

Another MDH survey (Klaseus and Hines, 1989) showed similar results. A total of 21 private wells within or very near the basin boundary (in Polk, Norman, Clay, and Otter Tail Counties) were analyzed for pesticides. The authors did not report pesticide results for individual wells; however, pesticide detections were summarized for wells in a five county area. Fifteen wells, four of which were within or near the Red River Basin in eastern Otter Tail County, had pesticide detections. All 15 of these wells had detections of atrazine (0.02-0.48 µg/L); one well had a detection of alachlor (0.16 µg/L); and one well had a detection of picloram (0.03 µg/L). Sites in the Red River Valley Lake Plain showed no detectable levels of any of the pesticides analyzed. Table 16 lists the pesticides analyzed for this study.

The MDH and the MDA (Minnesota Department of Agriculture) jointly prepared a report describing surveys of selected pesticides in Minnesota wells, conducted from July 1985 to June 1987 (Klaseus, Buzicky, and Schneider, 1988); the analytes, reporting limits, and number of detections are shown in table 16. Data from the MDH survey show reportable levels of pesticides at a very low

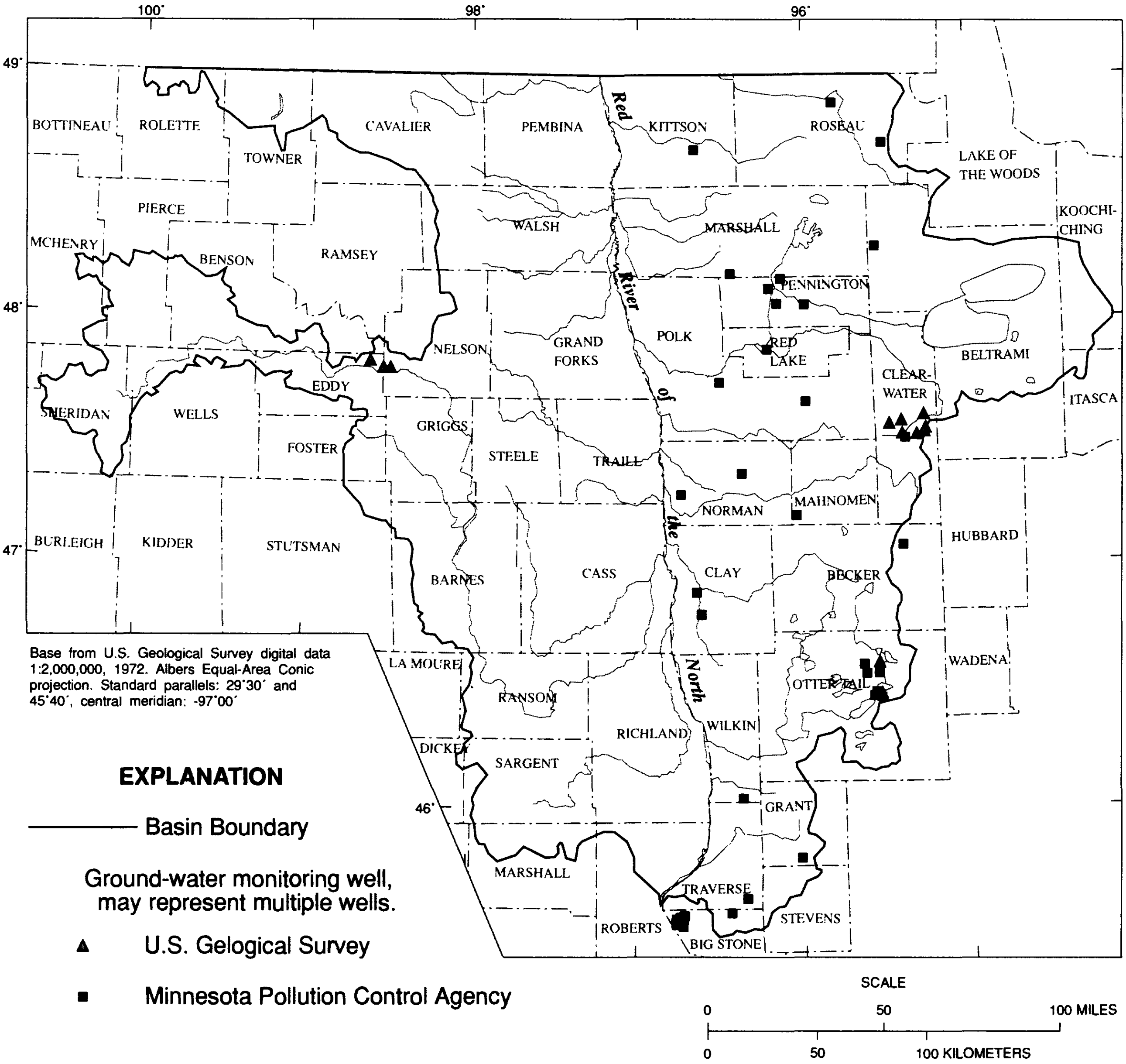


Figure 27.--Distribution of water wells sampled for pesticide concentrations in or near the Red River of the North Basin.

percentage of wells within the Red River Basin, especially within the Red River Valley Lake Plain. In central and eastern Otter Tail County, several wells yielded reportable levels of pesticides. Similarly, the MDA data showed no wells with pesticide detections in the Red River Valley Lake Plain, and a few wells with pesticide detections near the southeastern margin of the drainage basin.

Atrazine was the most frequently detected pesticide in these statewide surveys. Statewide, atrazine was detected in 85 of 200 private wells (Klaseus and Hines, 1989) and in 154 of 500 selected wells (Klaseus, Buzicky and Schneider, 1988). Alachlor was the second most frequently detected pesticide in Minnesota wells in both of these studies. Fifteen of 200 wells (Klaseus and Hines, 1989) and 16 of 500 wells (Klaseus, Buzicky, and Schneider, 1988) had detectable levels of alachlor. Other pesticides were detected with much less frequency (table 16). These surveys were generally targeted toward agricultural lands, and toward areas where ground water was thought to be susceptible to contamination because of permeable soils. Pesticides were detected relatively infrequently in wells in

Table 13.--Summary of U.S. Geological Survey pesticide data for ground-water samples in the Red River of the North Basin, 1979-90.

[µg/L, micrograms per liter; <, less than; ND, detection limit not reported in data base, concentration reported as 0 µg/L]

Chemical	Minimum reported concentration (µg/L)	Maximum reported concentration (µg/L)	Number of observations	Number of observations greater than reporting limit
Alachlor	<0.1	<0.1	10	0
Aldrin	ND	ND	2	0
Ametryne	ND	<.1	15	0
Atrazine	ND	2.9	15	4
Chlordane	ND	ND	2	0
DDD	ND	ND	2	0
DDE	ND	ND	2	0
DDT	ND	ND	2	0
1,2-dibromoethane	<3.0	<3.0	2	0
1,2-dichloropropane	<3.0	<3.0	2	0
1,3-dichloropropene	<3.0	<3.0	2	0
cis-1,3-dichloropropene	<3.0	<3.0	2	0
trans-1,3-dichloropropene	<3.0	<3.0	2	0
Dieldrin	ND	ND	2	0
Endosulfan	ND	ND	2	0
Endrin	ND	ND	2	0
Heptachlor	ND	ND	2	0
Heptachlor epoxide	ND	ND	2	0
Lindane	ND	ND	2	0
Methoxychlor	ND	ND	2	0
Mirex	ND	ND	2	0
Prometone	ND	<.1	15	0
Propazine	ND	<.1	15	0
Simazine	ND	<.1	15	0
Trifluralin	<.1	<.1	10	0
Toxaphene	ND	ND	2	0

Table 14.--Minnesota Pollution Control Agency pesticide concentration data for ground-water samples collected in and near the Red River of the North Basin

[µg/L, micrograms per liter; <, less than]

Chemical	Reported concentration (µg/L)	Number of observations
Alachlor	<0.16	26
2,4-D	<.1	4
DDT	<.01	4
1,2-dibromoethane	<.5	31
1,2-dichlorobenzene	<1.0	31
1,3-dichloropropane	<3.0	24
cis-1,3-dichloropropene	<.2	31
trans-1,3-dichloropropene	<.2	31
1,1-dichloropropene	<.2	31
EPN	<.24	26
Metribuzin	<.17	26
Metolachlor	<.56	26
Silvex	<.02	4
Simazine	<.49	26
2,4,5-T	<.1	4
1,1,1,2-tetrachloroethane	<.2	31
1,1,2,2-tetrachloroethane	<2.0	31
1,2,3-trichloropropane	<2.0	24
Toxaphene	<.1	4

Table 15.--Pesticides and their reporting limits for Minnesota Department of Health community well water system survey, 1986-91 (T. Klaseus, Minn. Department of Health, written commun., 1992, and J. Walsh, Minnesota Department of Health, oral commun., 1993)

[µg/L, micrograms per liter]

Pesticide	Reporting limit (µg/L)
Alachlor	0.02
Atrazine	.02
Butylate	.02
Chlorpyrifos	.01
Cyanazine	.1
Diallate	.05
EPTC	.01
Fonofos	.01
Linuron	.5
Methyl parathion	.01
Metolachlor	.1
Metribuzin	.05
Phorate	.05
Propachlor	.01
Simazine	.05
Trifluralin	.05

Table 16.--Pesticides and reporting limits for ground water pesticide surveys in Minnesota by (A) Minnesota Department of Health (Klauseus and Hines, 1989), (B) Minnesota Department of Agriculture (Klaseus, Buzicky, and Schneider, 1988), and (C) Minnesota Department of Health (Klaseus, Buzicky, and Schneider, 1988).

[µg/L, micrograms per liter; --, not analyzed; *, pesticide degradation product; numbers in parentheses denote number of wells having at least one sample above the respective reporting limit for the analyte. Total number of wells for each study are (A) 200, (B) 100, (C) 400]

Chemical	Reporting limit (A) (µg/L)	Reporting limit (B) (µg/L)	Reporting limit (C) (µg/L)
Alachlor	0.05 (15)	0.16 (8)	0.05 (8)
Aldicarb	.5	.5 (2)	.5
Aldicarb sulfone *	--	.5	--
Aldicarb sulfoxide *	--	.5	--
Atrazine	.02 (85)	.05 (47)	.01 (107)
Butylate	.01	.79	.01
Carbaryl	.05	.5	.05
Carbofuran	.05	.5	.05
3-hydroxy-carbofuran *	--	.5	--
Chloramben	.05	1.6	.05
Chlorpyrifos	.05	.24	.05
Cyanazine	.5 (1)	.12 (3)	.5 (1)
2,4-D	.04 (1)	.21	.04 (7)
Diallate	.12	--	.12
Dicamba	.04 (2)	.18 (1)	.04 (3)
Dimethoate	.2	--	.2
Disulfoton	.45	.82	.45
EPTC	.01	.24	.01 (1)
Fonofos	.03	.16	.03
Linuron	.4	.17	.4
MCPA	.05	.27	.05 (2)
Methyl parathion	.02	.10	.02
Metolachlor	.13 (4)	.56	.13 (2)
Metribuzin	.02 (1)	.17 (4)	.02 (2)
PCNB	.02	--	.02
Pentachlorophenol	--	.28 (3)	--
Phorate	.1	.49	.1
Phosphamidon	--	.70	--
Picloram	.04 (3)	1.80	.04 (3)
Propachlor	.2	(2)	.08
Simazine	.3	.08 (1)	.3
2,4,5-T	.04	--	.04 (1)
2,4,5-TP	.05	--	.05
Terbufos	.2	--	.2
Trifluralin	.03	.21	.03

the Red River Basin, which is probably due to the lower rate of atrazine use and the less permeable soils in the Red River Valley Lake Plain.

An important factor in determining susceptibility of aquifers to contamination by pesticides is the permeability of the overlying soil. The low-permeability soils at the surface of most of the Red River Valley ecoregion are not conducive to downward movement of pesticides. It is possible that these chemicals are flushed through surface waters, or they degrade in the soil before reaching buried aquifers in appreciable concentrations. While the Red River Valley ecoregion is an area of extensive agricultural chemical use, the available data, although limited, indicate that aquifers in the region are not highly susceptible to contamination.

The sandy, glacial deposits in upland areas nearer the drainage basin boundary contain aquifers that appear to be more susceptible to pesticide contamination, although the pesticide concentrations are quite low compared to some aquifers in other parts of Minnesota.

Fish Tissues

The U.S. Fish and Wildlife Service has operated the National Pesticide Monitoring Program (NPMP; renamed the National Contaminant Biomonitoring Program (NCBP)) since 1967. Numerous freshwater fish species from stream sites around the Nation, including the Red River at Noyes, Minn., have been sampled periodically and analyzed for organochlorine chemicals. Analytes include DDT and its metabolites DDE and DDD, dieldrin, endrin, heptachlor, chlordane and oxychlordane, nonachlor, toxaphene, α-HCH and β-HCH, hexachlorobenzene, methoxychlor, mirex, DCPA, and pentachloroanisole. Not all of these chemicals were analyzed throughout this program. Also, fish species sampled varied among collection periods within sites, and among sites. Results of the NPMP/NCBP have been presented by Henderson and others (1969), Henderson and others (1971), Schmitt and others (1981), Schmitt and others (1983), Schmitt and others (1985), and Schmitt and others (1990). Data from this program's 1986 samplings are not published, but were made available by the U.S. Fish & Wildlife Service (S.L. Smith, written commun., 1992).

Analytical methods for trace organochlorine chemicals have improved remarkably over the period of the program. In this report, semi-quantitative descriptions of chemicals that were detected are given. The original references contain information on quality assurance procedures, statistical tests used to analyze national and local trends, as well as the raw analytical data for composited fish samples.

Although analytical methods improved with time, it appears that a clear trend in the DDT data exists. In the early years of the NPMP, the parent compound DDT was frequently detected at roughly the same concentrations to those of the principal metabolites, DDE and DDD (DDE was usually the predominant metabolite). After the 1972 ban on DDT, concentrations in fish decreased rapidly. From the early 1970s to the mid 1980s, DDE and DDD concentrations in fish from the Red River slowly decreased from the tenths of μg/g (micrograms per gram) range to the hundredths of μg/g range, while the parent DDT quickly decreased from tenths of μg/g to less than, or occasionally equal to the 0.01 μg/g detection limit (fig. 28).

In 1986 (the last year for which data are available), low levels of DDE and DDD were detected in fish from the Red River even fourteen years after the ban on DDT use in the United States. It is possible that these metabolites persist in soils and stream sediments, and are eroded into streams, or cycled into the food chain by benthic organisms. It is also possible that the levels of DDT metabolites in the Red

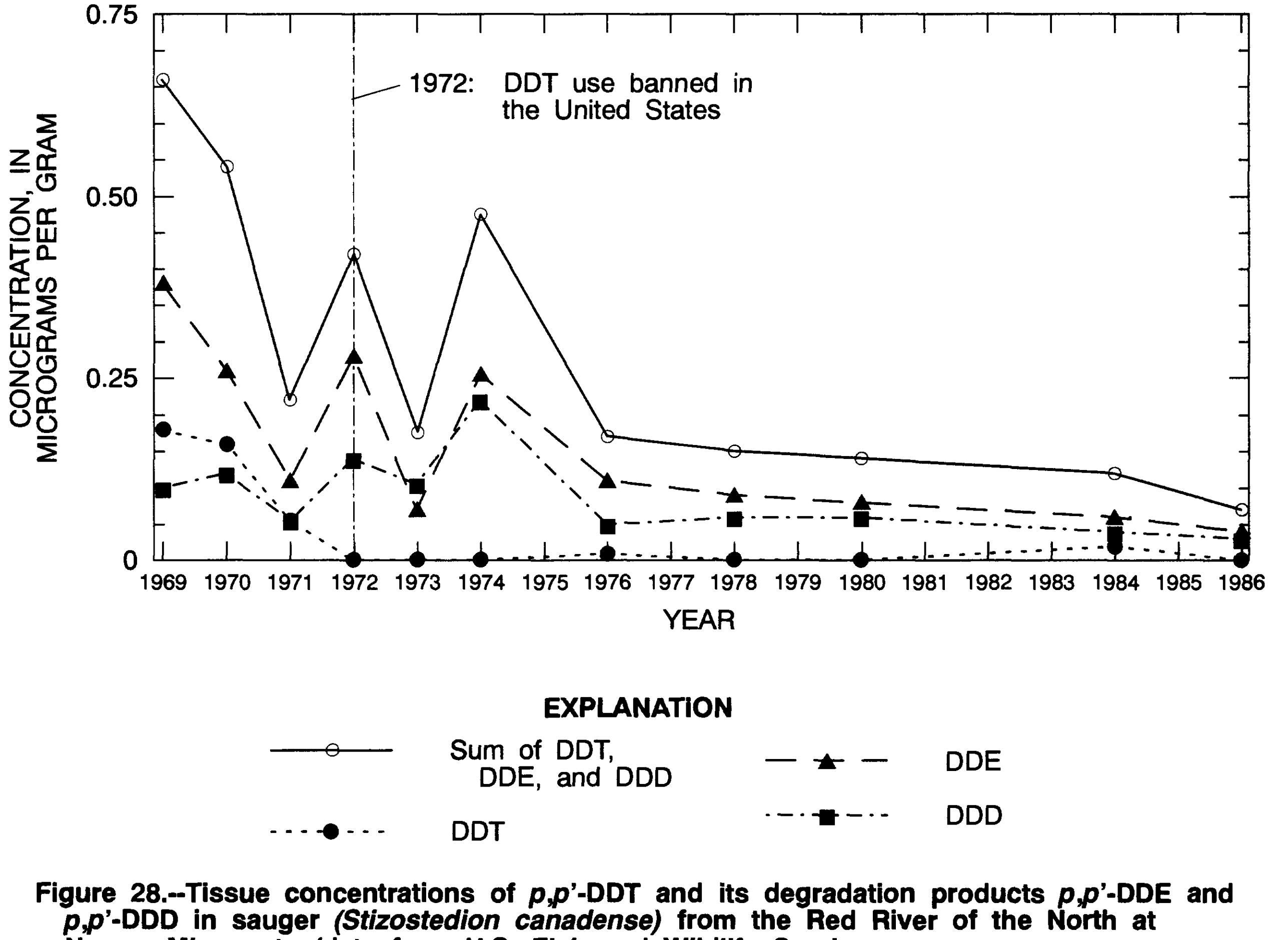


Figure 28.--Tissue concentrations of *p,p'*-DDT and its degradation products *p,p'*-DDE and *p,p'*-DDD in sauger *(Stizostedion canadense)* from the Red River of the North at Noyes, Minnesota (data from U.S. Fish and Wildlife Service National Contaminant Biomonitoring Program).

River Basin are supported by long-range atmospheric transport from countries that continue to use DDT. Supporting this hypothesis are recent measurements of DDT and its metabolites in air, water, and (or) biota from very remote locations such as the Canadian Arctic (Bidleman and others, 1990) and the South Atlantic and Antarctic Oceans (Weber and Montone, 1990).

Other pesticides detected by the NPMP in Red River fish in the late 1960s and early 1970s include dieldrin, HCH, and infrequent, low-level detections of endrin. In one laboratory cross-check sample, heptachlor and chlordane were also detected. Similarly, low concentrations (hundredths of µg/g) were occasionally detected for these compounds from the mid 1970s to mid 1980s. Toxaphene, noticeably absent in the early 1970s, began to appear in detectable quantities in the mid 1970s in the tenths of µg/g range, and also appeared in the mid 1980s samples. Nonachlor residues have been detected at the 0.01 µg/g detection limit in some samples from 1984 and 1986. Mirex was analyzed since 1980, and DCPA was analyzed since 1976, but neither was detected in any tissue samples from the Red River.

Agricultural statistics for North Dakota (McMullen and others, 1990) indicate that mirex and DCPA were not used in the State when surveys were made in 1978, 1984, and 1989. Minnesota statistics show very minor usage of DCPA in a 1990 survey.

Summary

This report is part of a series planned as part of the National Water Quality Assessment Program (NAWQA). Focusing on the Red River Basin. This report is a review of data collected during 1970-90. Plant nutrients (phosphorus and nitrogen), suspended sediment, and pesticides are the topics covered in this review of existing information.

Water quality data have been collected by several agencies for many different purposes throughout the Red River Basin. Although the coverage of the data varies considerably across the basin, especially across state lines, it does provide some insight into the distribution of agriculture-related chemicals, and analysis of existing data suggests where additional data collection is needed. Subsequent sampling could be conducted in several areas because available data are inadequate, or additional sampling and analysis could document the cause of high concentrations of specific constituents and compounds.

Agriculture is the primary land use in this basin. Although nutrient concentrations may be high in agricultural areas, they generally do not exceed water quality standards. The 10 mg/L drinking water standard for nitrate rarely was exceeded at any of the surface water sites or in water wells, except in localized areas. The highest nitrogen concentrations usually were found in the Red River. The composition of that nitrogen often was difficult to determine from the data, but appeared to be mostly organic nitrogen with some nitrate and rarely any nitrite nitrogen. Concentrations of ammonia nitrogen were negligible except during mid-winter (usually January), when concentrations could exceed 1.0 mg/L. Stream nutrient concentrations generally were highest at sites on the Red River downstream from the urban areas of Fargo, N. Dak. and Moorhead, Minn.

Certain tributary streams can carry high concentrations of nitrogen that occasionally exceeded concentrations in the Red River. Some streams draining the corn and soybean areas in the southern part of the basin had high nitrogen and nitrate concentrations. The Pembina River, which drains the northwestern part of the basin, had a large range in nitrogen concentrations and often exceeded those in the Red River.

Phosphorus concentrations were distributed throughout the basin in a pattern similar to that of nitrogen. The highest concentrations tended to occur in the Red River. Tributary streams, especially the Pembina River, occasionally had peak concentrations of phosphorus that exceeded those in the Red River. The phosphorus data indicate effects of point sources, including discharges from the Fargo-Moorhead area into the Red River and from Hallock into Two Rivers.

Nutrient loading typically was more a function of streamflow than of concentration. The largest nutrient loads were carried by the Red River, with substantial additions from the Red Lake and Sheyenne Rivers. Increased nutrient loading downstream from the Fargo-Moorhead area appeared to come from urban and industrial sources.

Discussion of nutrient concentrations in ground water generally was restricted to nitrate, because fewer other data were available and coverage of the basin was inadequate for phosphorus and other forms of nitrogen. Median nitrate (as nitrogen) concentrations were less than 1.0 mg/L for all counties in the basin except Otter Tail County in Minnesota. Nitrate concentrations also were elevated in wells in Becker County. Of 31 wells sampled in Otter Tail County by the U.S. Geological Survey, half had more than 3.0 mg/L nitrate in the water. This could result from sampling in Otter Tail and Becker Counties that focused on contaminated aquifers, but probably is caused by irrigation water leaching nitrogen fertilizers from porous soils into aquifers susceptible to contamination. Nitrate concentrations in some counties occasionally exceeded the MCL of 10 mg/L. Shallow ground water was much more likely to have elevated nitrate concentrations than deeper ground water. This indicates that shallow ground water is more susceptible to contamination from surface sources.

Suspended-sediment concentrations were evaluated for this report, but the coverage throughout the basin was sparse. Although suspended solids concentrations were available for many more sites, the data were incompatible with suspended-sediment concentrations. That is because samples for suspended solids concentration often were collected and analyzed using methods that would miss larger particles, and often would underestimate material suspended in the water. Suspended-sediment concentrations generally were highest on the Red River. Median concentrations at most sites were much less than 100 mg/L. The Red River at Emerson, Manitoba and three sites on the Pembina River were the only sites that had median sediment concentrations greater than 100 mg/L. About 10 percent of the sediment concentrations at each of three sites on the Pembina River were higher than 2,000 mg/L.

Pesticide data that are available within large national data bases (STORET and NWIS) are mainly limited to the period from the mid 1960s to the early 1980s. More recent data were available from several sources such as small, county-level studies and statewide surveys of drinking water wells, and Environment Canada's ENVIRODAT data base.

Most of the pesticide analyses summarized show no quantities of pesticides above reporting limits. When detected, reported concentrations nearly always met water quality standards.

The only pesticides detected in a relatively large fraction of surface water samples are 2,4-D (present in 43 percent of USGS samples and 38 percent of Environment Canada samples),
α–HCH (present in 80 percent of Environment Canada samples), γ-HCH (present in 39 percent of Environment Canada samples), and atrazine (present in 42 percent of Environment Canada samples). These pesticides were measured over fairly long time spans (approximately 15 years for some pesticides), and are from sites having large drainage areas. Concentrations of these pesticides generally were low, rarely approaching water-quality or drinking-water standards. A few county-level studies have measured pesticide concentrations at sites in smaller watersheds, but during relatively short periods of time (a few months to one or two years). The highest concentrations (sometimes exceeding drinking water standards), and the only detections for some pesticides out of all data sources, were sometimes observed in these studies. One study showed higher concentrations of 2,4-D at upstream sites in a river basin, and no detectable levels of 2,4-D at the outlet from that basin. This observation may indicate that reliance solely on downstream sites (those that drain large areas) may fail to show impaired water-quality conditions, if they should exist, and may fail to account for the environmental fate of pesticides used within a drainage basin.

Analyses of pesticides in ground water are quite limited in number and geographic distribution, especially in the North Dakota part of the basin. Available data show that very few wells are contaminated with pesticides. Wells in which pesticides were detected are mainly limited to aquifers in sandy glacial deposits that underlie agricultural lands in the extreme southern and southeastern parts of the basin. The low-permeability soils of the Red River Valley are not conducive to downward movement of pesticides into aquifers. Atrazine is the most commonly detected pesticide in ground water in the Red River Basin and throughout Minnesota. Atrazine use is greater in the southern part of the Red River Basin, where corn is grown in significant amounts.

Selected organochlorine pesticides in fish tissue have been periodically analyzed in samples from the Red River at Noyes, Minn. since 1967. Following the 1972 ban on DDT, concentrations of DDT in fish quickly decreased to near or below the reporting limits. Concentrations of the principal metabolites of DDT (DDE and DDD) in fish decreased more slowly. Low levels of these compounds continued to be detected in fish fourteen years after DDT was banned in the United States. While these compounds may have persisted in the Red River Basin from past DDT use, atmospheric transport from countries that continue to use DDT is also a likely source of these compounds.

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