Nutrients and Suspended Sediment in Snowmelt Runoff from part of the Upper Mississippi River Basin, Minnesota and Wisconsin, 1997

National Water-Quality Assessment Program

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Mississippi River Basin, Minn
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Water-Resources Investigations Report 00–4165

U.S. Department of the Interior
U.S. Geological Survey

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By James D. Fallon, and Ryan P. McNellis

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National Water-Quality Assessment Program

U.S. Department of the Interior

Bruce Babbitt, Secretary

U.S. Geological Survey

Charles G. Groat, Director

Mounds View, Minnesota, 2000

For additional information write to:
District Chief
U.S. Geological Survey, WRD
2280 Woodale Drive
Mounds View MN 55112

Copies of this report can be purchased from:
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Foreword

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

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

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

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

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

The goals of the NAWQA Program are being achieved through ongoing and proposed investigations of 59 of the Nation's most important river basins and aquifer systems, which are referred to as study units. These study units are distributed throughout the Nation and cover a diversity of hydrogeologic settings. More than two-thirds of the Nation's freshwater use occurs within the 59 study units and more than two-thirds of the people served by public water-supply systems live within their boundaries.

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

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

Robert M. Hirsch
Chief Hydrologist

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Conversion Factors, and Abbreviated Water-Quality Units

Multiply inch-pound unit	By	To obtain metric unit
inch (in.)	2.54	centimeter
ounce avoirdupois	28.35	gram
square mile (mi^2)	259.0	hectare
pounds per square mile per day ($lb/mi^2/d$)	.175	kilograms per square kilometer per day
tons	.907	metric tons

Chemical concentrations of substances are given in metric units of milligram per liter (mg/L). Milligrams per liter express the concentrations of the chemical constituent as a mass (mg) per unit volume (L). One milligram is one-thousandth of a gram.

Nutrients and Suspended Sediment in Snowmelt Runoff from part of the Upper Mississippi River Basin, Minnesota and Wisconsin, 1997

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ABSTRACT

The U.S. Geological Survey sampled snowmelt runoff from 42 stream sites during March and April 1997 in part of the Upper Mississippi River Basin, Minnesota and Wisconsin, to characterize nutrient and suspended-sediment concentrations, yields, and loads. Ancillary data from 12 sites provided data to estimate constituent loads delivered during snowmelt and 1997. The snowmelt period contributed from 1 to 50 percent of 1997 annual loads of total nitrogen, total phosphorus, and suspended sediment at small stream sites, and 17 to 70 percent of annual loads at mainstem river sites. Small streams in agricultural areas transported the greatest proportions of annual loads during snowmelt. Snowmelt from urban streams transported the least proportions of annual loads. Agricultural streams had significantly greater median yields ($p < 0.025$) of dissolved nitrite, nitrate, phosphorus, orthophosphate, total nitrogen, and total phosphorus than forested sites, and significantly greater median yields ($p < 0.025$) of dissolved nitrate and orthophosphate than all other land uses. In forested areas, yields of suspended sediment and all nutrient forms were significantly greater ($p < 0.05$) for streams draining impermeable deposits than permeable deposits.

INTRODUCTION

Water-quality degradation resulting from excessive nutrient and suspended-sediment transport is well known; however, the role of snowmelt runoff in transporting these constituents is less understood. Nutrients and suspended sediment are carried in streams all year, but increased concentrations and loads are associated with certain seasons and land uses. In temperate areas with seasonal snow and ice cover, spring snowmelt transports nutrients and sediment that have accumulated during the winter, adding to relatively constant sources such as ground water and wastewater treatment plants (WWTP). Forested areas may contribute nutrients and suspended sediment from decaying forest litter, wetlands, and eroding stream banks (fig. 1). Agricultural sources include material eroded by wind and water from cultivated fields, feedlots, and ditches (fig. 2). Urban sources include lawns, roads, parking lots, and winter construction activities (fig. 3). The quality of runoff from these land uses may also depend on surficial geologic characteristics or soil materials. For example, fine-grained surficial materials are typically less permeable and can contribute more fine-grained sediment to streams than coarse-grained, permeable deposits. As nutrients and sediment are transported by runoff from these landscapes, constituent loads (or mass of constituents transported by a stream in a specified time) can increase by orders of magnitude because both concentrations of constituents and rates of streamflow increase simultaneously.

During snowmelt runoff, the forms and concentrations of nutrients and suspended sediment carried by a stream vary with streamflow conditions. Immediately preceding snowmelt runoff streamflow is generally low; consequently, principal sources of nutrients may include ground-water discharge and WWTP effluent, in which soluble forms of nitrogen and phosphorus dominate. When snowmelt begins, streamflow and stream energy increase, as do concentrations of suspended sediment (and associated nutrients) (Guy, 1970). During the first few days of snowmelt, streams may carry substantial amounts of fine-grained sediment as a result of mass wasting and freeze-thaw cycles (Guy, 1970). Concentrations of suspended sediment generally peak on the rising limb of the hydrograph, before the streamflow peak, although characteristics of individual basins and runoff events affect this phenomenon (Guy, 1970). Particulate concentrations commonly decrease during the streamflow peak and recession because of decreased availability of source material, dilution by ground water and shallow subsurface flow, and decreased stream energy available for transporting suspended material.

Increases in streamflow and nutrient and suspended sediment loads are apt to be more homogeneous across a region as a result of snowmelt than from rainfall. Snowmelt runoff typi-

Figure 1.--Snowmelt runoff from the forested Trade River Basin in Wisconsin.

Figure 2.--Snow and dirt in snow bank between cultivated field and Buffalo Creek in Minnesota.

Figure 3.--Construction activities, park, and mall parking lot adjacent to Shingle Creek in the Twin Cities metropolitan area, Minnesota.

cally results from warm conditions across a large area of relatively uniform snow pack that has accumulated during the winter. Rainfall runoff typically is less spatially and temporally homogeneous. Consequently, spring snowmelt offers the best opportunity to make comparisons of nutrient and sediment concentrations between many streams sampled simultaneously under high flow conditions.

Background

Little information exists to assess comparable loads and yields (mass transported by stream per unit time divided by the basin drainage area), of nutrients and suspended sediment from snowmelt runoff in streams across the Upper Mississippi River Basin, Minnesota and Wisconsin (fig. 4), although selected areas have been investigated in separate studies. In Twin Cities metropolitan area (TCMA) streams, Oberts (1990) found maximum concentrations of soluble constituents, such as nitrate, occurred during the initial increase on the rising limb of the snowmelt hydrograph; whereas concentrations of particulate constituents peaked later. In the Minnesota River Basin, Payne (1994) noted that maximum concentrations of suspended sediment peaked immediately before the streamflow peak, although these data were for rainfall runoff. Grazyck (1986) noted that loads of suspended sediment, total nitrogen, and total phosphorus were greatest during March through May in the St. Croix River at St. Croix Falls, Wisconsin, based on data from 1974-83. No separate analysis was made of snowmelt-runoff data.

In the spring of 1997, snow covered much of the Upper Mississippi River Basin, setting the stage for spring floods. Four factors contributed to these floods (Minnesota State Climatology Office, 1997): heavy autumn precipitation in 1996, extraordinary winter snowfall, rapid snow-

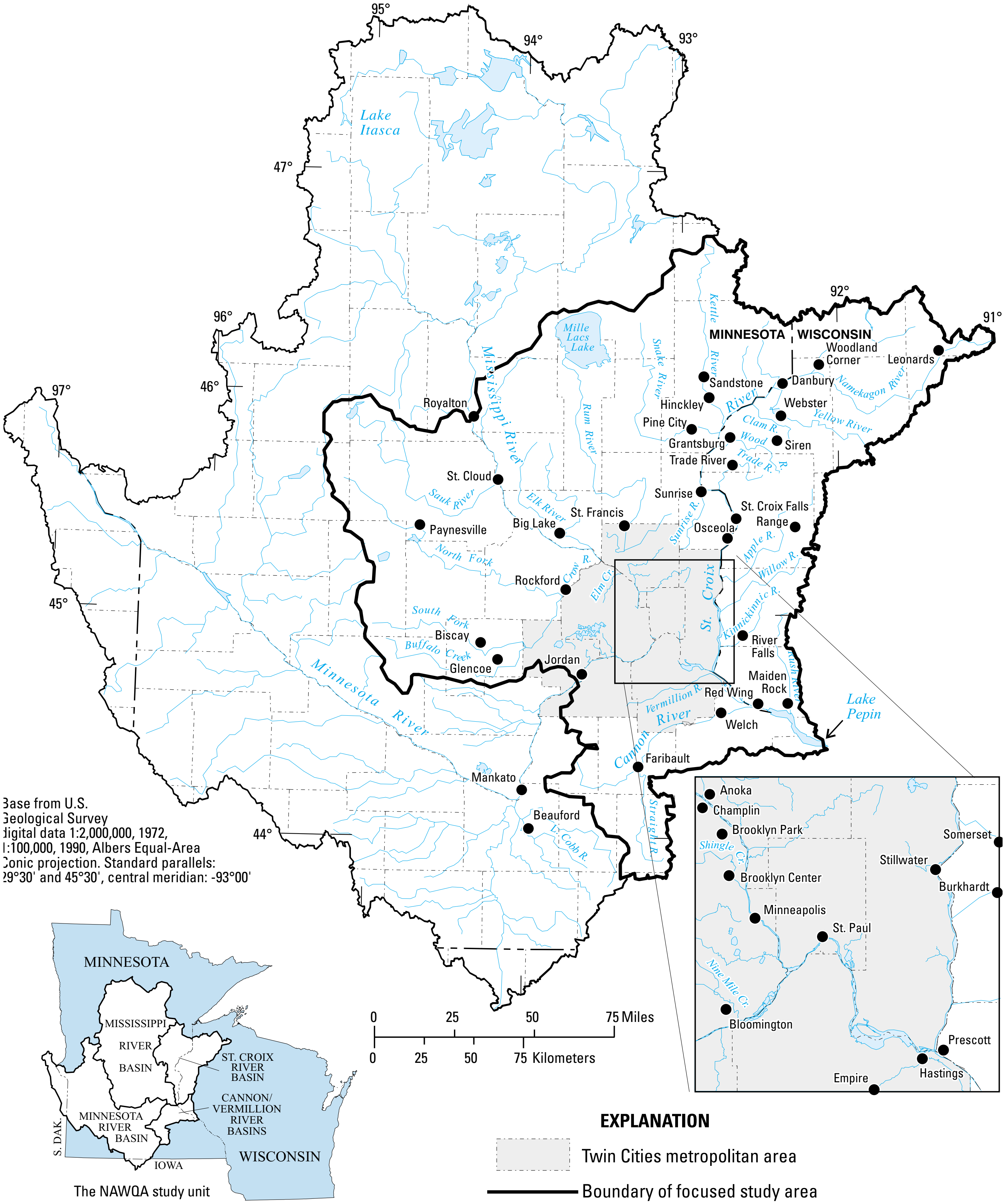

Figure 4.--Location of the Upper Mississippi River Basin study unit and focused study area, Twin Cities metropolitan area, hydrology, selected towns and major cities.

melt conditions, and heavy early spring precipitation. Autumn precipitation in 1996 was in the 95th percentile for most of Minnesota, resulting in above-median streamflows in the fall and winter. Heavy winter snowfall ranged from the 50th to 99th percentile based on 1931-91 records. Water equivalents of the snowpack in February 1997 ranged from 1 in. in the southern Minnesota River Basin to 8 in. in the headwaters of the Minnesota and Mississippi Rivers. Snowpack in the headwaters of the St. Croix River Basin had a water equivalent of 5-7 in. (National Weather Service, 1997). Winter and early spring had few melting days, and an abrupt warming trend occurred the first week of April coinciding with as much as 3.63 in. of rain in parts of the basin on April 5 and 6. These conditions resulted in near record streamflow for many streams. The third to fifth greatest recorded streamflow peaks occurred on the Mississippi River near Anoka and St. Paul, the Minnesota River near Jordan, and the Sauk, Crow, and Snake Rivers. Peak flows were more normal in the extreme southern part of the study unit because of an earlier and more gradual snowmelt.

The lack of information on snowmelt runoff and the deep snowpack of 1997 in the Upper Mississippi River Basin led to a study of nutrients and suspended sediment in snowmelt runoff. The study was part of the U.S. Geological Survey's National Water-Quality Assessment (NAWQA) Program. Goals of the NAWQA Program (Gilliom and others, 1995), which began full implementation in 1991, are to (1) describe the water quality in a large part of the Nation's freshwater streams and aquifers; (2) describe water quality changes over time; and (3) improve the understanding of how physical, ecological, and human factors, including land use, affect water quality. The Upper Mississippi River Basin study unit of NAWQA encompasses the Upper Mississippi River Basin upstream from the outlet of Lake Pepin (fig. 4).

The purposes of the study were to: (1) compare the proportions of total nitrogen, total phosphorus, and suspended-sediment loads contributed during the 1997 snowmelt to annual loads; (2) characterize instantaneous concentrations and yields of nutrients and suspended sediment in streams during increasing streamflow conditions from snowmelt runoff; and (3) compare the concentrations and yields for streams draining different land uses and surficial deposits.

The study was conducted in part of the Upper Mississippi River Basin NAWQA study unit (fig. 4) during March and April 1997. Sampling targeted a smaller focused study area in the southeastern one-third of the study unit (fig. 4) which included all of the St. Croix River Basin, the Mississippi River Basin from Royalton, Minnesota to Lake Pepin, and a part of the Minnesota River Basin. Twenty sites were sampled in the St. Croix River Basin, 3 in the Minnesota River Basin, and 19 along the Mississippi River mainstem and its tributaries (fig. 5). The purpose of this report is to present the results of the study.

Environmental Setting

Land use and land cover, hereinafter referred to as land use, in the Upper Mississippi River Basin study unit and the focused study area ranges from relatively undisturbed second-growth forests and wetlands in the north to intense row crop (mostly corn and soybean) agriculture, dairy farms, and feed lots in the south and west (fig. 5). The seven county TCMA, with a population of 2.3 million people (U.S. Bureau of Census, 1991), overlays this land-use continuum in the southeast part of the focused study area.

Surficial geology is characterized by relatively permeable fluvial deposits of outwash or alluvium, hereinafter referred to as permeable deposits, and by relatively impermeable deposits of glacial tills or lake sediments, hereinafter referred to as impermeable deposits. Permeable deposits are composed of sorted sand and gravel. Impermeable deposits are composed of unsorted mixtures of fine-grained (less than 0.063 millimeters) clay and silt, and coarser-grained sand, gravel, and larger particles; or sorted silts and clays. Soils developed on fine-grained, unsorted impermeable deposits often are more vulnerable to erosion than coarser-grained, sorted permeable deposits (U.S. Department of Agriculture, 1978 and 1979). Distribution of these surficial deposits is complex, but generally, permeable deposits dominate the Wisconsin part of the upper St. Croix River Basin, and the Sunrise, lower Rum, Elk, North Fork Crow, and Vermillion River Basins (fig. 4 and 5). Impermeable deposits compose most of the rest of the focused study area. Land use and land cover, and surficial geology are discussed in more detail in Stark and others (1996).

METHODS

This section summarizes the methods used to select sampling sites, sample, and analyze data. Methods and protocols of the NAWQA Program were used as cited unless noted otherwise.

Site Selection

Twelve sampling sites were part of a regularly sampled network of Upper Mississippi River Basin NAWQA sites, referred to as fixed sites (fig. 5, table 1). At fixed sites, ancillary data from analyses of samples collected monthly or more frequently during 1996-98 were used to interpret results from this study and to estimate nutrient and suspended-sediment loads. Fixed sites were located

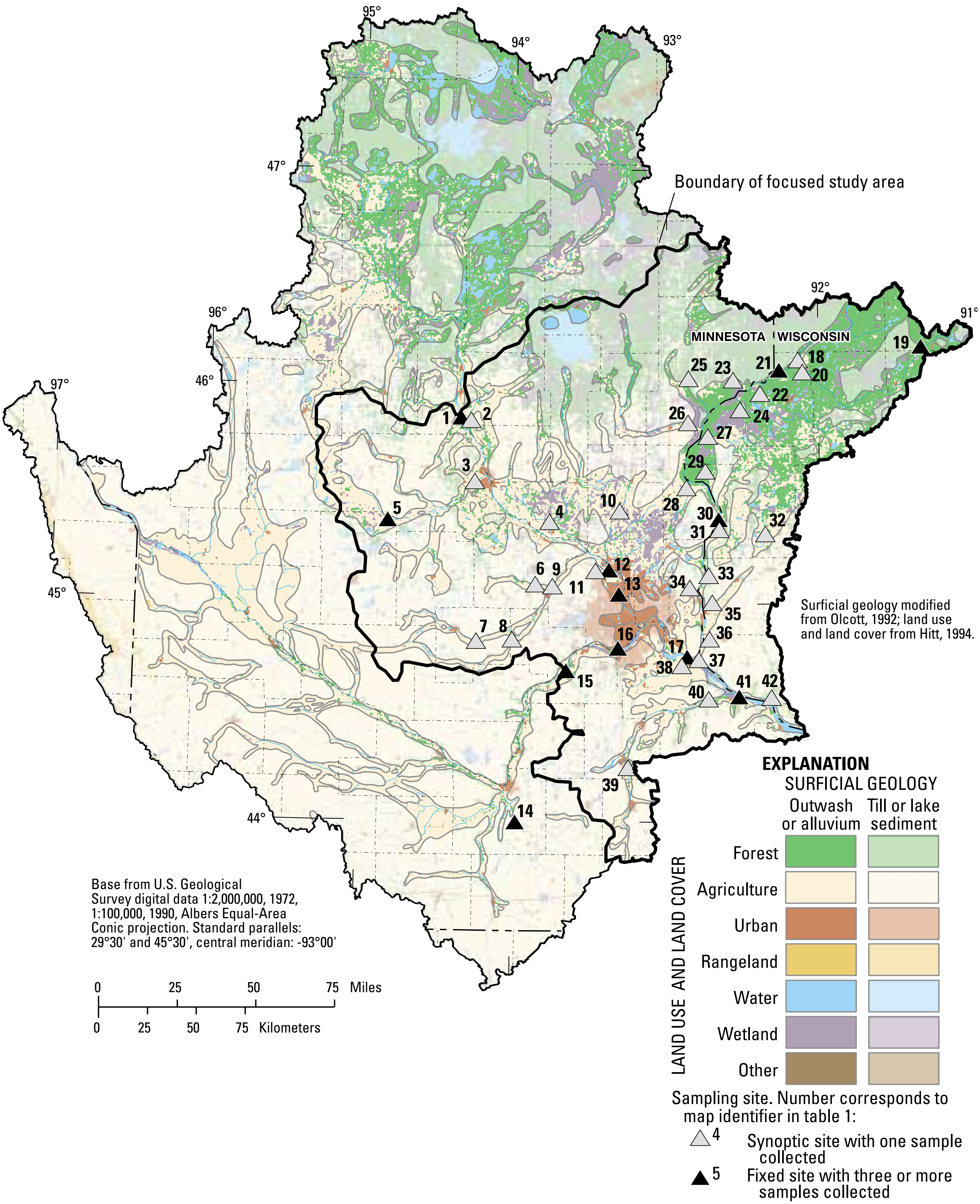

Figure 5.--Surficial geology, land use and land cover, and location of snowmelt runoff sampling sites in the Upper Mississippi River Basin study unit.

Table 1. Site characteristics for streams sampled during 1997 snowmelt runoff in part of the Upper Mississippi River Basin

[Bold text indicates fixed site (figure 5); mi^2, square mile]

Map identifier (shown in figure 5)	Site identifier	Site name	Latitude	Longitude	Dominant surficial geology	Land use (percent[1])						Drainage area (mi^2)
						Urban	Agriculture	Forest	Water	Wetland	Other	
1	**05267000**	Mississippi River near Royalton, Minn.	45°51’40”	094°21’30”	Outwash-Alluvium	0.6	25	49	8.6	16	0.9	11,600
2	05268000	Platte River at Royalton, Minn.	45°50’43”	094°17’40”	Outwash-Alluvium	0.4	64	23	1.9	10	0.1	424
3	05270500	Sauk River near St. Cloud, Minn.	45°33’35”	094°14’00”	Outwash-Alluvium	1.1	83	8.4	4.3	2.7	0.1	1,030
4	05275000	Elk River near Big Lake, Minn.	45°20’02”	093°40’00”	Outwash-Alluvium	0.8	75	10	1.3	13	0	549
5	**05276005**	North Fork Crow River above Paynesville, Minn.	45°22’38”	094°47’00”	Outwash-Alluvium	0.3	90	2.1	1.7	5.6	0.1	232
6	05278400	North Fork Crow River near Rockford, Minn.	45°05’44”	093°47’18”	Till plain-Lake sediment	1.2	83	6.3	6.0	3.5	0.1	1,350
7	05278590	South Fork Crow River at Biscay, Minn.	44°50’11”	094°17’16”	Till plain-Lake sediment	2.3	89	0.6	6.0	2.2	0.1	477
8	05278930	Buffalo Creek near Glencoe, Minn.	44°45’50”	094°05’27”	Till plain-Lake sediment	0.7	96	0	1.7	0.9	0.1	373
9	05280000	Crow River at Rockford, Minn.	45°05’12”	093°44’02”	Till plain-Lake sediment	1.4	87	3.7	4.8	2.7	0.1	2,640
10	05286000	Rum River near St. Francis, Minn.	45°19’40”	093°22’20”	Outwash-Alluvium	0.5	47	22	16	14	0.5	1,380
11	05287890	Elm Creek near Champlin, Minn.	45°09’48”	093°26’11”	Till plain-Lake sediment	8.7	84	1.6	2.1	2.8	0.2	85.8
12	**05288500**	Mississippi River near Anoka, Minn.	45°07’36”	093°17’48”	Outwash-Alluvium	1.1	45	34	7.6	12	0.7	19,200
13	**05288705**	Shingle Creek at Queen Ave in Minneapolis, Minn.	45°03’00”	093°18’36”	Outwash-Alluvium	71	20	0.9	4.0	0.7	3.5	28.2
14	**05320270**	Little Cobb River near Beauford, Minn.	43°59’48”	093°54’30”	Till plain-Lake sediment	0.2	94	0.5	0.6	4.0	0	130
15	**05330000**	Minnesota River near Jordan, Minn.	44°41’35”	093°38’30”	Till plain-Lake sediment	0.9	94	1.7	2.2	1.1	0.2	16,200
16	**05330902**	Nine Mile Creek near James Circle at Bloomington, Minn.	44°48’26”	093°18’05”	Till plain-Lake sediment	87	5.7	2.2	3.7	1.7	0	44.6
17	**05331580**	Mississippi River below Lock & Dam #2 at Hastings, Minn.	44°44’48”	092°51’08”	Till plain-Lake sediment	2.5	66	18	5.2	7.1	0.4	37,000
18	05331775	St. Croix River near Woodland Corner, Wis.	46°07’00”	092°07’53”	Outwash-Alluvium	0.2	1.0	86	3.4	9.6	0.2	433
19	**05331833**	Namekagon River at Leonards, Wis.	46°10’18”	091°19’50”	Outwash-Alluvium	0.7	1.8	78	6.3	12	1.0	128
20	05333400	Namekagon River near Woodland Corner, Wis.	46°05’02”	092°06’47”	Outwash-Alluvium	0.4	6.0	76	4.4	13	0.3	1,020
21	**05333500**	St. Croix River near Danbury, Wis.	46°04’28”	092°14’50”	Outwash-Alluvium	0.3	4.9	79	4.0	12	0.3	1,510

Table 1. Site characteristics for streams sampled during 1997 snowmelt runoff in part of the Upper Mississippi River Basin (Continued)

[Bold text indicates fixed site (figure 5); mi^2, square mile]

Map identifier (shown in figure 5)	Site identifier	Site name	Latitude	Longitude	Dominant surficial geology	Land use (percent[1])						Drainage area (mi^2)
						Urban	Agriculture	Forest	Water	Wetland	Other	
22	053350006	Yellow River near Danbury, Wis.	45°58’59”	092°23’05”	Outwash-Alluvium	0.8	23	56	9.0	11	0.6	312
23	05335170	Crooked Creek near Hinckley, Minn.	46°00’42”	092°31’45”	Outwash-Alluvium	0	18	69	1.4	12	0	94.4
24	05335500	Clam River near Webster, Wis.	45°52’52”	092°29’16”	Outwash-Alluvium	0.3	32	55	3.1	9.9	0	358
25	05336700	Kettle River below Sandstone, Minn.	46°06’20”	092°51’50”	Outwash-Alluvium	0.5	27	53	1.7	18	0.1	868
26	05338500	Snake River near Pine City, Minn.	45°50’30”	092°56’00”	Till plain-Lake sediment	0.4	40	42	1.2	16	0	975
27	05338975	Wood River at State Highway 70 near Grantsburg, Wis.	45°46’22”	092°42’29”	Outwash-Alluvium	0.6	44	27	5.0	24	0	160
28	453049-092512101	Sunrise River at Sunrise, Minn.	45°30’49”	092°51’21”	Outwash-Alluvium	2.9	58	8.3	5.3	26	0.1	170
29	05340370	Trade River near Trade River, Wis.	45°35’58”	092°46’02”	Outwash-Alluvium	0.5	47	38	2.6	12	0	133
30	**05340500**	St. Croix River at St. Croix Falls, Wis.	45°24’25”	092°38’49”	Till plain-Lake sediment	0.4	26	56	2.8	14	0.2	6,240
31	053405524	St. Croix River tributary near Osceola, Wis.	45°20’52”	092°40’55”	Till plain-Lake sediment	4.4	65	29	0.4	0	0.7	10
32	05341125	Apple River near Range, Wis.	45°23’45”	092°21’50”	Outwash-Alluvium	0	44	40	5.5	10	0	167
33	05341500	Apple River near Somerset, Wis.	45°09’27”	092°42’59”	Till plain-Lake sediment	0.5	63	24	5.1	7.1	0.1	551
34	05341540	Browns Creek at Stillwater, Minn.	45°04’35”	092°48’21”	Till plain-Lake sediment	6.7	80	5.8	4.3	2.9	0.5	34.1
35	05341740	Willow River at Burkhardt, Wis.	45°01’30”	092°39’23”	Outwash-Alluvium	1.1	89	7.8	0.6	1.1	0	254
36	05342000	Kinnickinnic River near River Falls, Wis.	44°49’50”	092°44’00”	Till plain-Lake sediment	3.6	92	4.6	0.2	0	0	173
37	05344490	St. Croix River at Prescott, Wis.	44°44’57”	092°48’16”	Till plain-Lake sediment	0.9	36.7	46.8	3.2	12.2	0.2	7,690
38	05345000	Vermillion River near Empire, Minn.	44°40’00”	093°03’17”	Outwash-Alluvium	16	76	3.9	1.7	0.5	1.2	129
39	05353800	Straight River near Faribault, Minn.	44°15’29”	093°13’51”	Till plain-Lake sediment	3.5	92	1.5	0.8	2.1	0.2	436
40	05355200	Cannon River at Welch, Minn.	44°33’50”	092°43’55”	Till plain-Lake sediment	2.8	88	4.0	2.7	2.0	0.2	1,340
41	**05355250**	Mississippi River at Red Wing, Minn.	44°36’36”	092°36’36”	Till plain-Lake sediment	2.3	62	22	4.8	7.8	0.4	46,800
42	05355330	Rush River near Maiden Rock, Wis.	44°34’15”	092°19’44”	Till plain-Lake sediment	0.5	88	11	0.1	0	0	225

[1] Percentages associated with each site may not total 100 percent because of rounding.

on either small streams or large mainstem rivers. Fixed sites on small streams, with drainage areas of 28.2 to 232 mi^2, were located downstream of a predominant land use—either forested, agricultural, or urban. Because water quality from these streams is indicative of a predominant land use, they are referred to as indicator sites. Fixed sites on mainstem rivers, including the Mississippi, Minnesota, and St. Croix Rivers, drained large areas (1,510 to 46,800 mi^2). These sites were located at transitional areas of rivers, such as at the transition between forested and agricultural areas or between agricultural and urban areas. Because water quality at these sites represents integrated effects from large areas and sometimes varying land use, they are referred to as integrator sites.

Thirty additional sites, referred to as synoptic sites, were selected to encompass combinations of land use and surficial geology common in the focused study area (figs. 4 and 5). Twenty-four synoptic sites represented the only sampling location on a particular stream. Larger tributaries had multiple sites. Drainage areas upstream of synoptic sites ranged from 10.0 to 7,690 mi^2. To supplement this analysis, data from Elm Creek near Champlin, Minnesota (site 11, fig. 5) were included because samples were collected using similar protocols and were analyzed for similar constituents. Although technically not part of this study, that site is included as one of the 30 synoptic sites.

Percentages of land use (forested, agricultural, urban, wetland, water, or other, which includes rangeland) and surficial geology (permeable or impermeable deposits) were computed for basins upstream of each site. Streams were classified by the predominant land use and surficial geology of each basin. Streams were classified as forested if they drained more than 65 percent forests and wetlands; agricultural if they drained more than 80 percent agricultural area, urban if they were located in the TCMA and drained more than 5 percent urban area, and mixed if they fell between these categories (36-75 percent agricultural, 22-59 percent forest and wetlands, and 0-5 percent urban). No urban sites were located downstream of WWTPs. Ten stream sites were classified as forested, 13 as agricultural, 5 as urban, and 14 as mixed land use. Similarly, streams were classified as draining either permeable or impermeable geologic deposits if they drained more than 50 percent of each respective deposit. Twenty-two stream sites were classified as draining permeable geologic deposits and 20 were classified as draining impermeable deposits. Selected streams draining small basins were sampled to account for combinations of land use and surficial geology that did not exist in larger basins, such as urban or forested areas in permeable deposits. Characteristics of stream sites sampled in this investigation are given in Stark and others (1999).

Field Methods

At fixed sites, samples were collected and processed using NAWQA protocols (Shelton, 1994). Additional samples were collected at these sites before and after the increasing streamflow of snowmelt runoff so that concentrations and yields associated with increasing streamflow conditions could be compared to concentrations and yields associated with other streamflow conditions during snowmelt.

At the 30 synoptic sites, samples were collected and processed using modified equipment and protocols to shorten sampling times and increase sampling coverage. Modifications included: reducing the number of equal-width-increment sampling transects from 10-20 to 3-5; collecting suspended-sediment samples separate from nutrients; and splitting composite samples for total nutrients by mixing and pouring from 3-liter polypropylene bottles instead of using cone splitters. When two or more sites were sampled with the same equipment on the same day, equipment was triple rinsed with both deionized water after sampling and rinsed with native water from each subsequent site prior to sampling. Equipment was cleaned according to NAWQA protocols at the end of each day (Shelton, 1994).

Nutrient samples were chilled and shipped on ice within 48 hours to the USGS National Water-Quality Laboratory in Arvada, Colorado. Analyses included dissolved nitrite nitrogen, dissolved nitrite plus nitrate nitrogen, dissolved ammonia plus organic nitrogen, total ammonia plus organic nitrogen, total phosphorus, dissolved phosphorus, and dissolved orthophosphate. Sediment samples were shipped to a USGS sediment laboratory in Iowa City, Iowa, for analysis of total suspended-sediment concentration and percentage suspended-sediment material that is either fine-grained (less than 0.063 millimeters) or sand sized (0.063 to 2.0 millimeters).

Stream mixing was assessed by taking measurements of water temperature, pH, specific conductance, and dissolved oxygen and comparing results across the stream. Stream stage was measured before and after sampling to document changing stage conditions. Streamflow was measured at sites lacking current stage-discharge relations or obtained from stage-discharge relations where available. Barometric pressure was recorded to calibrate dissolved oxygen meters and to calculate the percent saturation of dissolved oxygen in streams.

Data Analysis

Total nitrogen was calculated as the sum of total ammonia plus organic nitrogen and dissolved nitrite plus nitrate nitrogen, for use in determining concentrations, yields, and loads. Particulate nitrogen was calculated as total ammonia and organic nitrogen minus dissolved ammonia and organic nitrogen. Particulate phosphorus was calculated as the difference between total phosphorus and dissolved phosphorus.

Nutrient and suspended-sediment loads at the fixed sites were determined using the U.S. Geological Survey's ESTIMATOR program (T. Cohn and E. Gilroy, U.S. Geological Survey, written commun., 1993; Cohn and others, 1989: Cohn and others, 1992a; Cohn and others, 1992b) by summing the daily-mean loads of the annual or snowmelt periods. ESTIMATOR computes a logarithm-linear model that uses a minimum-variance, unbiased estimator to minimize error from the retransformation bias associated with logarithm-linear regression models and uses an adjusted maximum likelihood estimator to compensate for censored values below method reporting limits. The regression equations used in ESTIMATOR contained some or all of the following terms based on a statistical significance of $p < 0.05$: a constant; logarithm of flow, logarithm of flow squared, and square root of flow fits to discharge; fractional time fits for temporal trends; sine and cosine fits to accommodate seasonality. Models were calibrated with daily-mean streamflow data and with sediment and nutrient sample analyses from fixed sites during 1996-98 (Mitton and others, 1997, 1998, and 1999).

Because the accuracy of load calculations depends on many factors, including range of concentrations and streamflow, number of samples, and climatological conditions, the accuracy of the model should be considered for each site and load estimate. For these reasons, error estimates are presented as confidence intervals along with load estimates in table 2.

Confidence intervals for the 95th percentile were computed by multiplying the standard error of prediction by 1.96 (two standard deviations) from the standard normal distribution curve. The standard error of prediction was included in the ESTIMATOR output as the daily mean per month and as the daily mean per year. The 95th percentile for the annual loads was calculated from the daily mean per year standard error of prediction. For the snowmelt loads the 95th percent confidence interval was calculated from the daily standard error of prediction from monthly data and was used in the same manner that the monthly mean daily loads were used to compute snowmelt loads. In the case of total nitrogen, the standard errors of prediction were calculated by taking the square root of the sum of the standard error of predictions squared for total nitrite plus nitrate nitrogen and total organic plus ammonia nitrogen standard errors of prediction.

Annual loads were calculated for the 1997 calendar year for the 12 fixed sites. Loads contributed by snowmelt were based on the individual snowmelt hydrograph for each fixed site. The snowmelt part of the hydrograph was defined as the period from the initial increase in streamflow after winter through peak flow and part of the recession. The end of the recession was considered to occur when the decrease in daily mean streamflow was less than 20 percent of the maximum decrease in daily mean streamflow for any three consecutive days during the recession. Snowmelt hydrographs and periods used for computing constituent loads are shown in figure 6. This method worked well for 11 of 12 fixed sites. However, at the Namekagon River at Leonards, Wisconsin, the slope of the streamflow recession was so flat that the snowmelt period defined using these methods would have been much shorter than other sites. To make results more comparable, the second local maximum daily decrease was used in place of the first maximum to effectively lengthen the snowmelt period. The lengths of the snowmelt periods vary because of different basin sizes and characteristics, snowpack conditions, precipitation during snowmelt, daily temperature, land use, and surficial geology.

For samples collected at all 42 sites during increasing streamflow conditions, instantaneous yields of selected constituents were calculated as the product of the constituent concentration and the instantaneous streamflow at the time of sampling divided by the drainage area of the stream. For convenience, these yields are reported in pounds per square mile per day ($lb/mi^2/d$).

In some streams, such as mainstem river sites, the contribution of water stored in pools and reservoirs upstream of dams could confound the effects of snowmelt runoff on water quality by contributing substantial amounts of water from non-snowmelt origin. However, samples collected from mainstem rivers for comparisons of instantaneous concentrations were collected near the peaks of streamflow hydrographs (fig. 5). Consequently, the large volumes of water transported during streamflow rises from snowmelt runoff would likely have flushed most water that was stored in pools and reservoirs prior to snowmelt.

Concentrations of suspended sediment and nutrients can vary substantially during the rising part of the hydrograph. Consequently, individual comparisons of instantaneous concentrations and yields between sites were not made. Instead, sites were grouped by land use and surficial geology (permeable or impermeable deposits) for statistical analysis to minimize the

Table 2. Summary statistics of load computations for total nitrogen, total phosphorus, and suspended sediment during 1997 and 1997 snowmelt runoff

[mi^2, square mile; Ave., Avenue; Cir., Circle; L&D, Lock and Dam; St., Saint]

Site type and name	Map identifier (figure 5)	Principal land use and land cover	1997 annual statistics			1997 snowmelt statistics			
			Load (tons)	95th-percentile confidence interval (percent)	Yield (tons per mi^2)	Load (tons)	95th-percentile confidence interval (percent)	Yield (tons per mi^2)	Percent of annual load contributed during snowmelt
			Total nitrogen						
Indicator (small stream) sites									
North Fork Crow River above Paynesville, Minn.	5	Ag	347	25	1.49	142	27	0.61	41
Shingle Creek at Queen Ave. in Minneapolis, Minn.	13	Urban	26	17	0.93	3.4	17	0.12	13
Little Cobb River near Beauford, Minn.	14	Ag	1,000	42	7.72	507	50	3.90	50
9-Mile Creek near James Cir. at Bloomington, Minn.	16	Urban	45	26	1.00	2.3	21	0.05	5
Namekagon River at Leonards, Wis.	19	Forest	55	9	0.43	9.5	11	0.07	17
Integrator (mainstem river) sites									
Mississippi River near Royalton, Minn.	1	Forest	6,830	12	0.59	1,950	15	0.17	29
Mississippi River near Anoka, Minn.	12	Mixed	19,200	22	1.00	7,440	27	0.37	39
Minnesota River near Jordan, Minn.	15	Ag	85,900	63	5.29	37,000	74	2.28	43
Mississippi River below L&D 2 at Hastings, Minn.	17	Mixed	97,800	27	2.64	47,800	33	1.29	49
St. Croix River near Danbury, Minn.	21	Forest	641	12	0.43	110	13	0.07	17
St. Croix River at St. Croix Falls, Minn.	30	Forest	3,660	16	0.61	1,440	18	0.24	39
Mississippi River at Red Wing, Minn.	41	Mixed	99,000	25	2.12	47,500	31	1.02	48
			Total phosphorus						
Indicator (small stream) sites									
North Fork Crow River above Paynesville, Minn.	5	Ag	26	43	0.11	13	53	0.05	48
Shingle Creek at Queen Ave. in Minneapolis, Minn.	13	Urban	2.3	25	0.08	0.2	42	0.01	8
Little Cobb River near Beauford, Minn.	14	Ag	18	35	0.14	7.7	55	0.06	43
9-Mile Creek near James Cir. at Bloomington, Minn.	16	Urban	4.1	31	0.09	0.2	35	<0.01	4
Integrator (mainstem river) sites									
Mississippi River near Anoka, Minn.	12	Mixed	1,060	22	0.06	381	45	0.02	36
Minnesota River near Jordan, Minn.	15	Ag	3,150	32	0.19	1,700	45	0.10	54
Mississippi River below L&D 2 at Hastings, Minn.	17	Mixed	5,170	18	0.14	2,530	34	0.07	49
Mississippi River at Red Wing, Minn.	41	Mixed	4,580	15	0.10	1,810	28	0.04	40

Table 2. Summary statistics of load computations for total nitrogen, total phosphorus, and suspended sediment during 1997 and 1997 snowmelt runoff (Continued)

[mi^2, square mile; Ave., Avenue; Cir., Circle; L&D, Lock and Dam; St., Saint]

Site type and name	Map identifier (figure 5)	Principal land use and land cover	1997 annual statistics: Load (tons)	1997 annual statistics: 95th-percentile confidence interval (percent)	1997 annual statistics: Yield (tons per mi^2)	1997 snowmelt statistics: Load (tons)	1997 snowmelt statistics: 95th-percentile confidence interval (percent)	1997 snowmelt statistics: Yield (tons per mi^2)	Percent of annual load contributed during snowmelt
Suspended sediment									
Indicator (small stream) sites									
North Fork Crow River above Paynesville, Minn.	5	Ag	6,130	36	26.4	1,620	73	6.99	26
Shingle Creek at Queen Ave. in Minneapolis, Minn.	13	Urban	903	32	32.2	99	55	3.55	11
Little Cobb River near Beauford, Minn.	14	Ag	13,900	35	107	6,020	54	46.3	43
9-Mile Creek nr James Cir. at Bloomington, Minn.	16	Urban	7,060	120	157	65	77	1.45	1
Namekagon River at Leonards, Wis.	19	Forest	567	21	4.43	106	39	0.83	19
Integrator (mainstem river) sites									
Mississippi River near Royalton, Minn.	1	Forest	135,000	35	11.6	64,000	64	5.50	47
Mississippi River near Anoka, Minn.	12	Mixed	325,000	45	16.9	172,000	75	8.95	53
Minnesota River near Jordan, Minn.	15	Ag	2,130,000	21	131	805,000	39	49.6	38
Mississippi River below L&D 2 at Hastings, Minn.	17	Mixed	2,650,000	39	71.5	1,280,000	55	34.6	48
St. Croix River near Danbury, Minn.	21	Forest	8,820	20	5.86	2,070	40	1.38	23
St. Croix River at St. Croix Falls, Minn.	30	Forest	102,000	43	17.0	71,100	52	11.9	70
Mississippi River at Red Wing, Minn.	41	Mixed	2,400,000	48	51.2	1,050,000	81	22.4	44

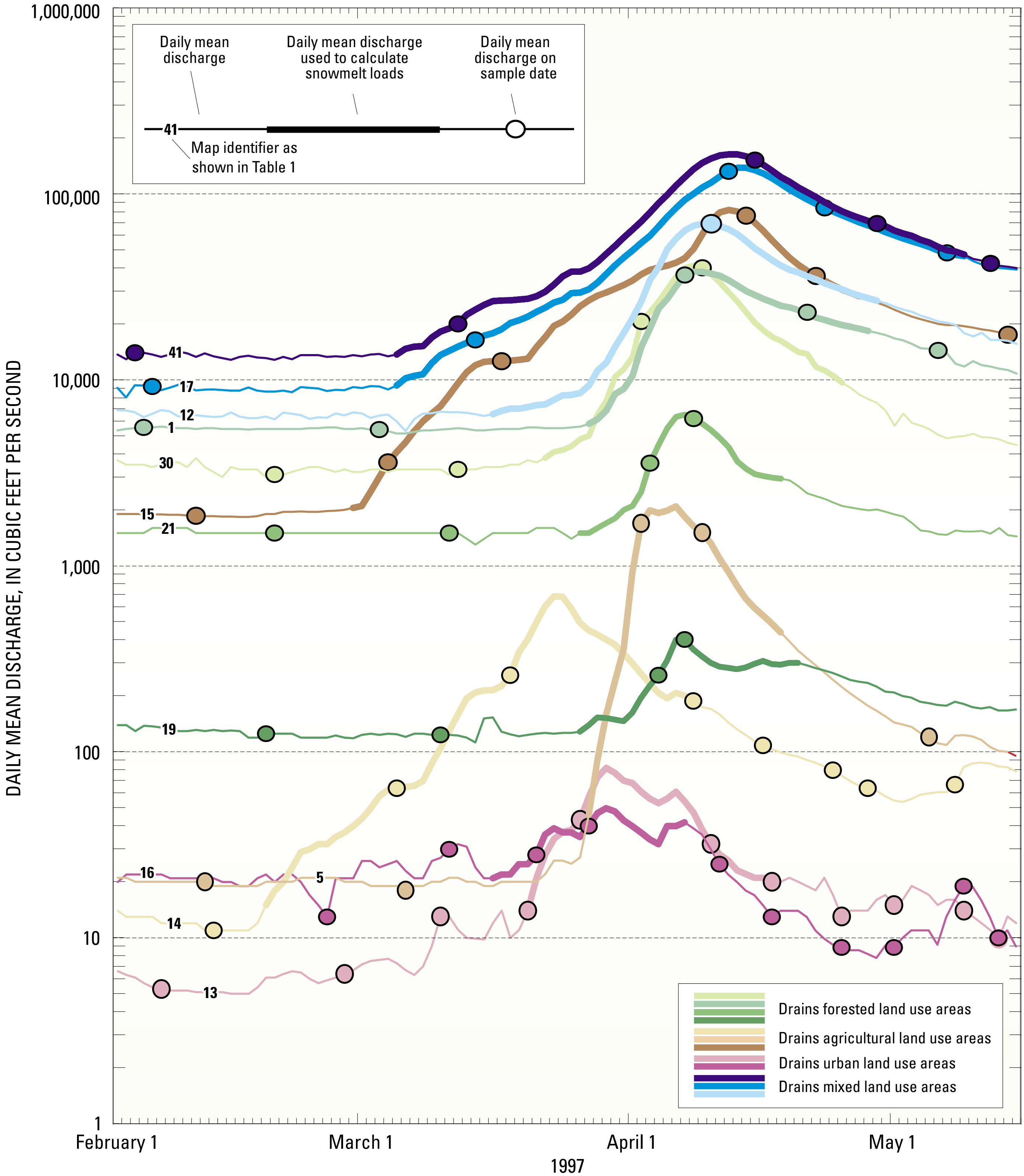

Figure 6.--Daily mean discharge, periods used to compute snowmelt loads, and sampling dates during the 1997 snowmelt period at fixed sites in part of the Upper Mississippi River Basin study unit.

bias introduced by variability among individual samples.

Comparisons of instantaneous yields for streams draining different categories of land use or surficial geology were made using the non-parametric, Kruskal-Wallis, one-way analysis of variance (ANOVA) of the medians, because the data were not normally distributed and because sample sizes were small and variable (5 to 14 samples per site). For comparisons between the four land-use categories, a multiple-stage test was performed on the Kruskal-Wallis statistics (Helsel and Hirsch, 1992). Results were considered statistically significant between the four land-use categories for $p < 0.05$ during the first step of the test and $p < 0.025$ for the final step between any two categories (Helsel and Hirsch, 1992). Within both the forested and mixed land-use categories, comparisons for yields for streams draining permeable and impermeable deposits were considered significantly different for $p < 0.05$. Comparisons for yields for streams draining permeable and impermeable deposits in agricultural and urban areas were not possible because there were not enough agricultural and urban streams with both types of deposits for valid statistical analyses. Only samples collected during increasing stream stages were used for comparisons to minimize the variability in concentrations that occur over the hydrograph.

LOADS OF NUTRIENTS AND SUSPENDED SEDIMENT AT FIXED SITES

At fixed sites, from 1 to 70 percent of 1997 annual loads of total nitrogen, total phosphorus, and suspended sediment were transported during the snowmelt period. Agricultural streams generally transported the greatest proportions of loads during snowmelt.

Total Nitrogen

At indicator sites, total nitrogen loads ranged from 26 to 1,000 tons in 1997 (table 2). Snowmelt loads ranged from 2.3 to 507 tons, composing 5 to 50 percent of respective annual loads (table 2). Snowmelt from urban streams transported the least proportions of annual loads (table 2). Relatively large amounts of impervious surfaces in urban areas reduce vegetation and soil cover compared to other land covers, which limit nutrient sources more than in agricultural or forested areas. Furthermore, nutrient accumulation during winter may be limited by more frequent small runoff events resulting from sun-warmed impervious surfaces and application of road de-icers compared to other land uses. These small runoff peaks are evident at Shingle and Nine Mile Creeks (sites 13 and 16, respectively, fig. 5) in late February and early March (fig. 6) prior to the large snowmelt event. Furthermore, the largest annual streamflow peak occurred during summer in these streams whereas snowmelt produced the largest annual peaks in other streams, indicating that annual snowmelt peaks are reduced in urban basins, or that rainfall peaks are increased, or both. Agricultural streams transported 2–10 times more total nitrogen during snowmelt, in terms of percent of annual load, than streams in other land uses. Agricultural streams in the study unit have greater sources of nutrients available as a result of commercial fertilizer or livestock manure application (Kroening, 1998). Manure is often spread on snow covered or exposed fields that are vulnerable to erosion. Proportions of loads delivered during snowmelt at the forested site were intermediate between urban and agricultural sites, perhaps because forested basins have more nitrogen sources and winter accumulation than urban streams yet fewer nutrient sources or more vegetative cover to protect soils than agricultural basins.

At integrator sites, total nitrogen loads ranged from 641 to 99,000 tons in 1997 (table 2). Snowmelt loads ranged from 110 to 47,800 tons, accounting for 17 to 49 percent of the respective annual loads (table 2). Streams draining substantial amounts of agricultural land had the larger proportions; whereas, forested sites had smaller proportions.

Total Phosphorous

Total phosphorus loads were not estimated for forested sites because many samples had concentrations below the method reporting limit. At indicator sites, total phosphorous loads ranged from 2.3 to 26 tons in 1997 (table 2). Snowmelt loads ranged from 0.2–13 tons, composing 4–48 percent of annual loads (table 2). Results were similar to those of total nitrogen. In urban streams, the proportion of annual loads from snowmelt was small—from 4 to 8 percent (table 2). These loads are slightly smaller, but comparable to those of Oberts (1982), who found that snowmelt contributed 8–20 percent of the annual phosphorus loads in small streams of the TCMA. Agricultural streams had the greatest proportions of loads delivered by snowmelt—almost one-half of the annual load. Five to 12 times more of the annual total phosphorus load, in terms of percent of annual load, was delivered during snowmelt in agricultural streams than in urban streams.

Annual loads at mainstem integrator sites ranged from 1,060 to 5,170 tons (table 2). Snowmelt loads ranged from 381 to 2,530 tons, composing 36–54 percent of annual loads (table 2). Results were similar to those of total nitrogen. Although estimates of phosphorus loads were not made for forested sites, it is apparent from the magnitude of total phosphorus concentrations and streamflow that annual loads would have been less than those of other sites.

Suspended Sediment

At indicator sites, annual loads of suspended sediment ranged from 567 to 13,900 tons in 1997 (table 2). Snowmelt loads ranged from 65 to 6,020 tons, composing 1–43 percent of the annual loads (table 2). Like nutrients, proportions of sediment flushed during the snowmelt period were least at urban sites and greatest at agricultural sites.

At integrator sites, annual loads ranged from 8,820 tons to 2.65 million tons (table 2). Snowmelt loads ranged from 2,070 tons to 1.28 million tons, accounting for 23 to 70 percent of annual loads (table 2). The proportion of suspended sediment delivered during snowmelt was greatest at one of the forested sites (St. Croix River near St. Croix Falls, Wisconsin, site 30, fig. 5).

These results indicate that during 1997, proportionately more of the annual loads of nutrients and suspended sediment at agricultural and forested streams were delivered during the snowmelt period than during other periods. At some sites, the snowmelt period delivered the majority of the annual load. Accordingly, the snowmelt period should be considered in strategies aimed at reducing loads of these constituents to streams.

INSTANTANEOUS CONCENTRATIONS AND YIELDS OF NUTRIENTS AND SUSPENDED SEDIMENT

Samples were collected from all sites during snowmelt runoff under increasing streamflow conditions when constituent concentrations were expected to be greatest. Nutrient analyses were unavailable for the Vermillion River near Empire, Minnesota. Instantaneous concentrations and yields for streams draining representative combinations of land use and surficial geology were determined to assess those combinations that contribute nutrient and suspended sediment during snowmelt.

Comparisons of Concentrations in Increasing Streamflow with Other Streamflow Conditions

To test the assumption that streams sampled during rising streamflow conditions would have the greatest concentrations, additional samples were collected at fixed sites before and after increasing streamflow (fig. 6). Eighty-seven percent of the concentrations of nutrients and suspended sediments were greatest in samples collected during increasing streamflow. This suggests that at sites where one sample was collected during increasing streamflow, concentrations are among the greatest that occurred there.

Exceptions occurred at two agricultural streams (North Fork Crow River above Paynesville, Minnesota, and Little Cobb River near Beauford, Minnesota; sites 5 and 14, respectively, fig. 5) and a forested stream (St. Croix River near Danbury, Wisconsin; site 21, fig. 5). In these streams, concentrations of dissolved nitrate and total nitrogen (composed mostly of dissolved nitrate) were greatest during streamflow recession. Other analyses (Mitton and others, 1997, 1998, and 1999) of water from these sites indicate these streams commonly have high concentrations of nitrate during base flow. This may indicate a substantial ground-water contribution during the streamflow recession, perhaps related to the sandy, permeable soils of the North Fork Crow River Basin and shallow drain tiles in the Little Cobb River Basin. Suspended-sediment concentrations also were greatest during the recession in the Little Cobb River—perhaps because the sample collected during increasing streamflow was collected early, before sediment concentrations had increased substantially. Finally, in samples from the St. Croix River near Danbury, Wisconsin, differences between concentrations of dissolved ammonia plus organic nitrogen collected during increasing streamflow and those collected during the recession were within the analytical variability of the method (Maloney and others, 1994; U.S. Geological Survey, 1999).

Nitrogen in Increasing Streamflow

During increasing streamflow conditions of snowmelt runoff, total nitrogen concentrations ranged from 0.52 to 7.70 mg/L. The median concentration was 2.02 mg/L. Concentrations generally were greater in the southern and western parts of the focused study area (fig. 7a), where basins have greater proportions of agricultural land use (fig. 5).

Principal nitrogen forms were dissolved nitrate, dissolved organic nitrogen, or particulate nitrogen. Dissolved nitrate concentrations ranged from 0.1 to 6.0 mg/L and composed 32–94 percent of total nitrogen. Dissolved nitrate was the principal nitrogen form in streams across most of the focused study area, it composed more than one-half of total nitrogen in all sampled agricultural streams in the southern and western parts of the focused study area. In contrast, nine forested streams of the Upper Mississippi and St. Croix Rivers contained dissolved organic nitrogen as the predominant nitrogen form, composing 31–52 percent of total nitrogen. Concentrations ranged from 0.15 to 0.88 mg/L. Particulate nitrogen was the most common form in four other streams in the St. Croix River Basin, with concentrations ranging from 0.1 to 0.88 mg/L.

Dissolved ammonia and nitrite nitrogen formed lesser amounts of total nitrogen. Dissolved ammonia

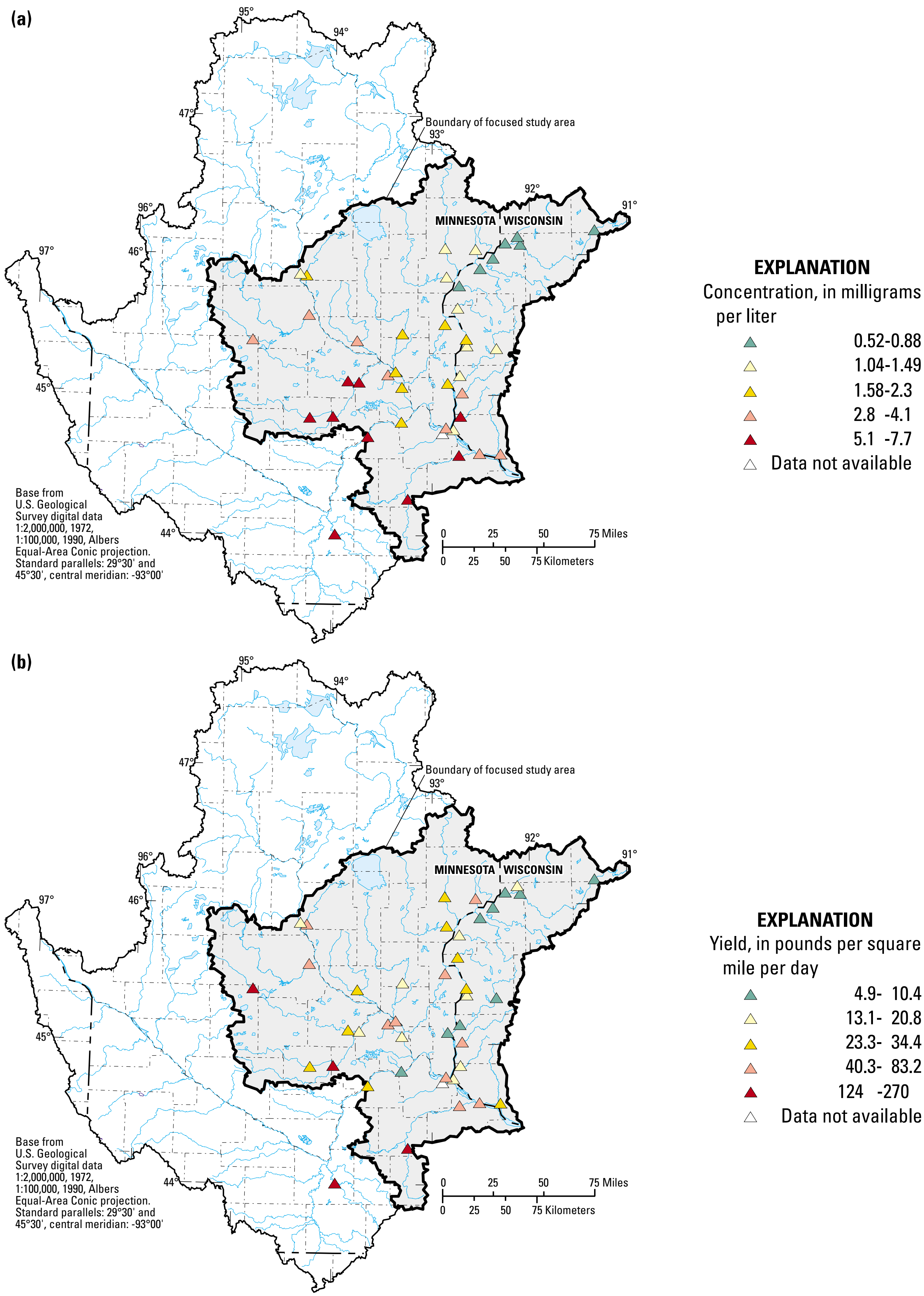

Figure 7.--Instantaneous (a) concentrations and (b) yields of total nitrogen at sites sampled during 1997 snowmelt runoff in part of the Upper Mississippi River Basin study unit.

concentrations ranged from less than 0.15 to 0.92 mg/L (0.3–26 percent of total nitrogen concentrations). Dissolved nitrite concentrations ranged from less than 0.01 to 0.12 mg/L. No samples had concentrations of dissolved un-ionized ammonia, nitrite, nitrate, or nitrite plus nitrate, that exceeded state water-quality standards for aquatic health (Minnesota Pollution Control Agency, 1999, Wisconsin Department of Natural Resources, 1997, 1998, and 1999).

Instantaneous yields of total nitrogen ranged from 4.9 to 270 lb/mi^2/d, with a median of 24.8 lb/mi^2/d. Yields generally were greatest for streams west of the Mississippi River (fig. 7b). However, the yield for one stream in the St. Croix River Basin, Crooked Creek near Hinckley, Minnesota (site 23, fig. 5), ranked in the upper quartile of total nitrogen yields (54 lb/mi^2/d).

Phosphorus in Increasing Streamflow

Total phosphorus concentrations ranged from less than 0.03 to 0.57 mg/L. The median concentration was 0.18 mg/L. Like nitrogen, total phosphorus concentrations generally were greater in streams west of the Mississippi River (fig. 8a), where the greatest proportions of agricultural lands in the focused study area are located (fig. 5).

Particulate phosphorus was the predominant form of phosphorus in more than one-half of the streams sampled, regardless of land use. Concentrations ranged from less than 0.01 to 0.29 mg/L, composing 18–92 percent of total phosphorus. Dissolved phosphorus concentrations ranged from less 0.01 to 0.4 mg/L and composed 8–81 percent of total phosphorus. Dissolved phosphorus was the principal phosphorus form at 13 agricultural streams in the southern and western parts of the focused study area. At six of these sites, dissolved orthophosphate, a component of dissolved phosphorus, was the predominant form of total phosphorus. Dissolved orthophosphate concentrations ranged from less than 0.01 to 0.36 mg/L.

Yields of total phosphorus ranged from less than 0.3 to 19.8 lb/mi^2/d, with a median of 2.4 lb/mi^2/d. The greatest yields were found west of the Mississippi River (fig. 8b), although above-median yields also were found for forested streams of the Upper St. Croix River Basin.

Suspended Sediment in Increasing Streamflow

Suspended-sediment concentrations ranged from 6.2 to 249 mg/L. The greatest concentrations occurred in streams west of the Mississippi River, although some streams in the Upper St. Croix River also had concentrations above the median of 56 mg/L (fig. 9a).

Fractions of fine-grained sediment and sand-sized suspended sediment were determined for 38 sites. Fine-grained sediment is commonly associated with water-quality degradation. The median percentage of fine-grained sediment was 31 percent; indicating most of the sediment transported was sand sized. However, the percentage of fine-grained sediment was highly variable, ranging from 16 to 95 percent.

Instantaneous yields of suspended sediment ranged from 35.3 to 7,880 lb/mi^2/d, with a median of 619 lb/mi^2/d. In contrast to nutrient yields, many of the greatest sediment yields occurred for forested streams draining the Upper St. Croix River, as well as streams west of the Mississippi River (fig. 9b). Fine-grained suspended-sediment yields ranged from 25 to 3,100 lb/mi^2/d. The distribution of sites containing the greatest yields of fine-grained suspended sediment was similar to that of suspended sediment.

EFFECTS OF LAND USE AND SURFICIAL GEOLOGY ON YIELDS

Yields are important for identifying basins that are contributing the greatest mass of constituent per unit area. The greatest instantaneous yields of nutrients and suspended sediment during snowmelt runoff generally occurred for streams west of the Mississippi River that drain basins with intense agricultural land use. However, combinations of land use and surficial geology containing lesser amounts of agriculture also contribute substantial yields and favor the transport of certain forms of nitrogen and phosphorus.

Land Use

Of the land uses in the focused study area, the forests and wetlands in the northern part are least disturbed by human activities. Streams draining these forested areas offer the best background conditions to compare to other sites, even though most represent different ecoregions (Northern Lakes and Forests, and North Central Hardwood Forests) than other land uses (North Central Hardwood Forests, Western Cornbelt Plains, and Driftless Area) (Omernik and Gallant, 1988). Other differences also exist. Forested areas generally contain more lakes and wetlands than the southern part of the focused study area, because lakes and wetlands were less extensive or were drained in the southern part. The southern part of the focused study area generally has more topographical relief and agricultural land use. Because forested areas are relatively undisturbed, differences in water-quality constituents, such as nutrient and sediment yields, may be more sensitive to disturbances.

During snowmelt, particulate nutrients were the principal nutrient forms in the 10 streams draining forested areas. Particulate- and dis-

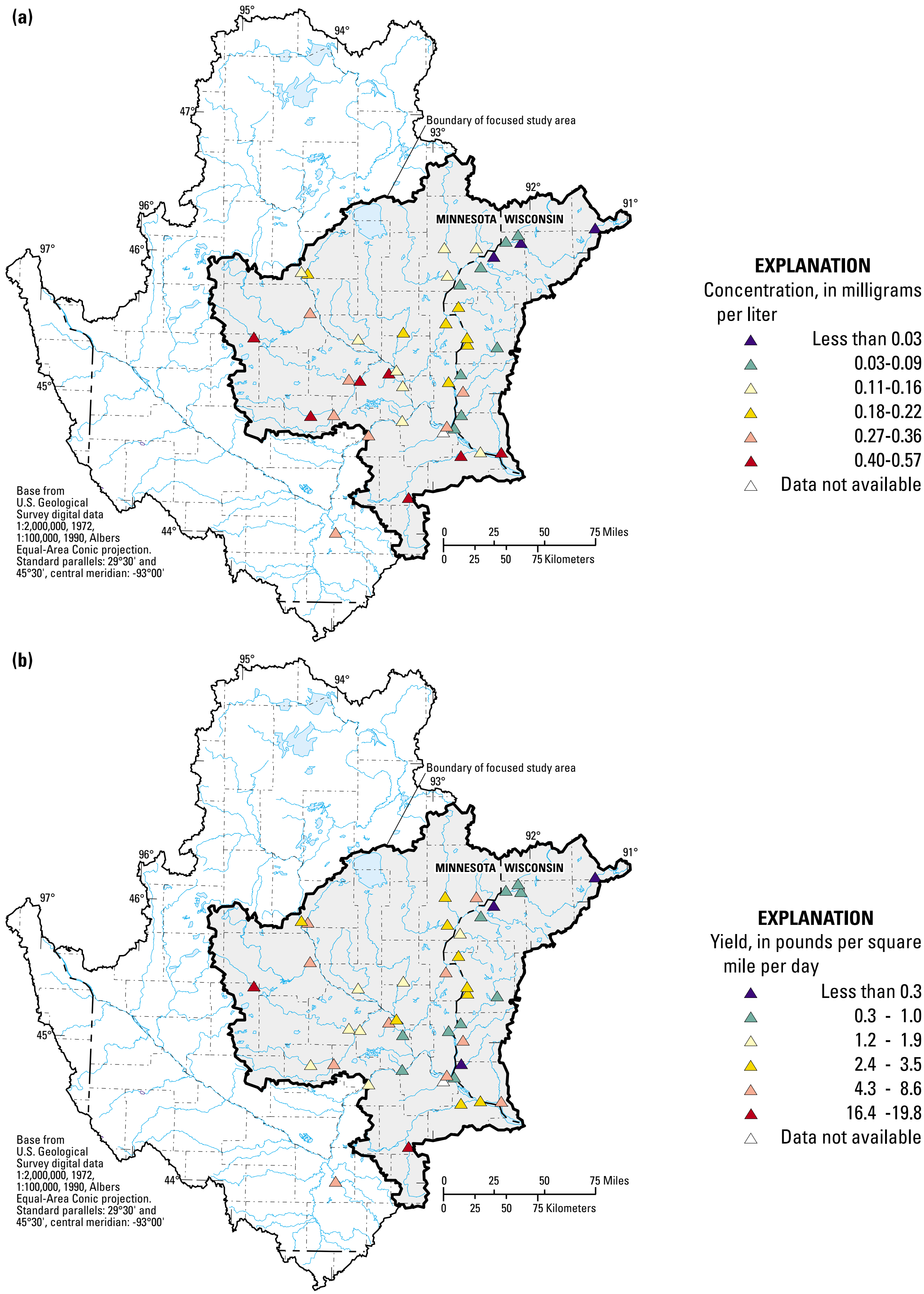

Figure 8.--Instantaneous (a) concentrations and (b) yields of total phosphorus at sites sampled during 1997 snowmelt runoff in part of the Upper Mississippi River Basin study unit.

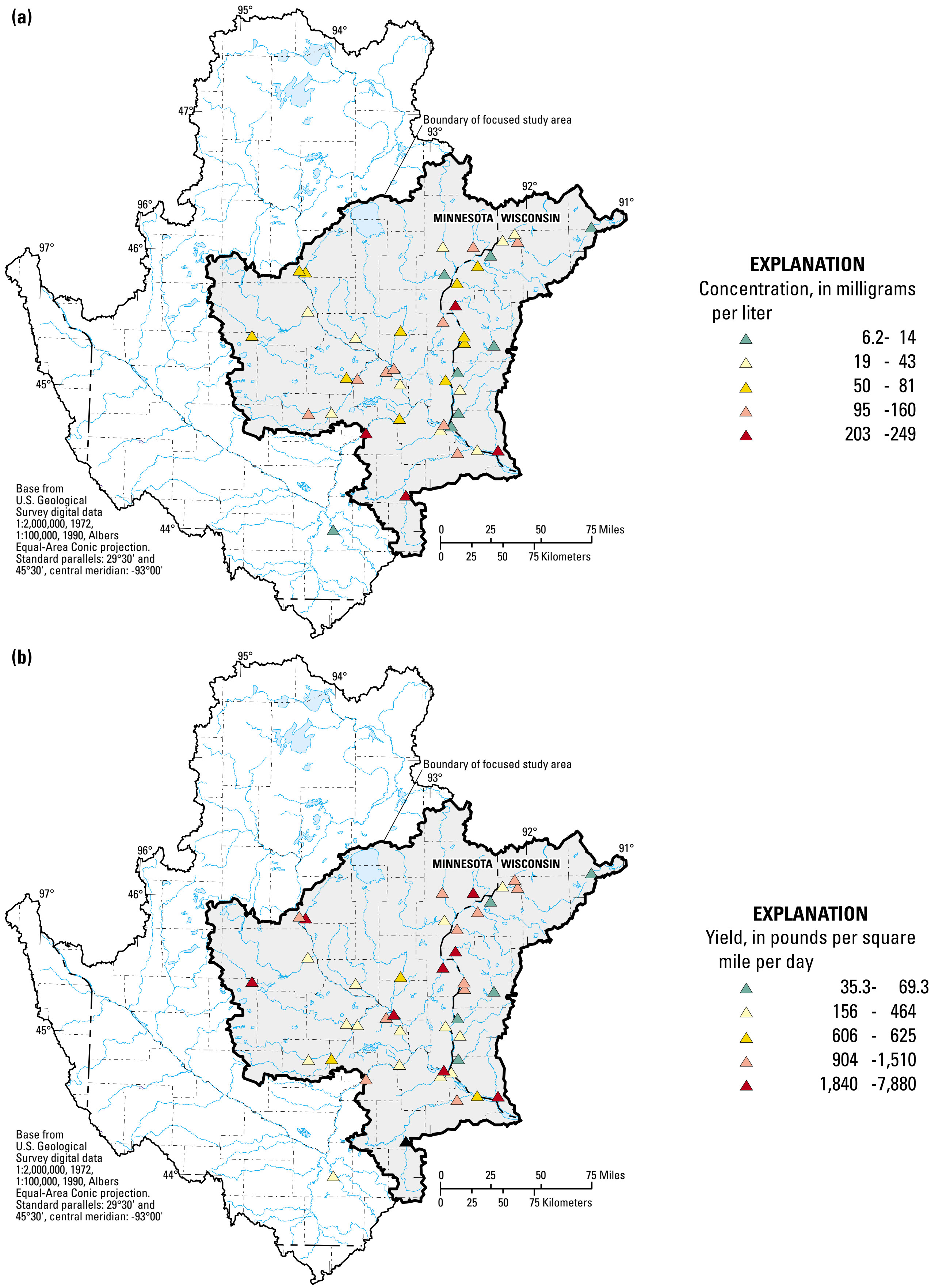

Figure 9.--Instantaneous (a) concentrations and (b) yields of suspended sediment at sites sampled during 1997 snowmelt runoff in part of the Upper Mississippi River Basin study unit.

solved organic nitrogen were the principal nitrogen forms at eight sites. Particulate phosphorus was the principal phosphorus form at all ten sites. Kroening and Andrews (1997) also found that total organic plus ammonia nitrogen, composed mostly of dissolved organic and particulate nitrogen, constituted more than 70 percent of the median annual loads of total nitrogen in rivers draining forested parts of the focused study area. Organic nitrogen and particulate phosphorus may be transported from naturally occurring organic material that has accumulated in forest soils and wetlands as a result of very slow nitrification and denitrification processes during low temperatures in the winter (Wetzel, 1983). In a study of forested streams, Likens and Borman (1995) found that most particulate matter was transported during runoff.

In contrast, dissolved nitrate was the principal nitrogen form in all 13 agriculture streams during snowmelt, and dissolved phosphorus was the predominant phosphorus form in 11 streams. Kroening and Andrews (1997) also found that nitrate composed more than 80 percent of median total nitrogen loads annually in agricultural streams of the focused study area. The predominance of these nutrient forms in agricultural streams indicates these constituents likely result from agricultural practices and fertilizer application.

Agricultural streams had significantly greater median yields ($p < 0.025$) of nutrients (dissolved nitrite, nitrate, phosphorus, orthophosphate, and total nitrogen and total phosphorus) than forested streams. The comparison for dissolved nitrate is shown in fig. 10. Agricultural streams also had significantly greater median yields ($p < 0.025$) of dissolved nitrate and orthophosphate than streams draining other land uses. Median yields of other nitrogen forms, including dissolved and total ammonia plus organic nitrogen and particulate nitrogen, were greater at agricultural sites than forested, but not significantly ($p > 0.025$). This suggests that naturally occurring organic material in forests and wetlands contribute loads of particulate and organic nitrogen comparable to agricultural areas.

Suspended-sediment and fine-grained sediment yields were similar for agricultural and forested streams. This suggests that forested basins are as vulnerable to erosion as agricultural streams during snowmelt even though agricultural areas generally have more exposed soil, or that other factors, such as surficial geology, have a greater effect than land use on sediment yield. In any land use, substantial sediment load may originate from bank erosion and instream sources, which greater streamflow may resuspend. Payne (1994) attributed suspended sediment gains in selected stream reaches of the Minnesota River Basin during snowmelt to scouring of previously deposited sediment and bank and bed erosion, considering the lack of substantial inflows between sampling points.

Median yields of nutrients and suspended sediment for urban streams were significantly less ($p < 0.025$) than agricultural streams, generally less than mixed land use streams, and similar to forested streams. The comparisons for dissolved phosphorus are shown in fig. 10. Urban land cover

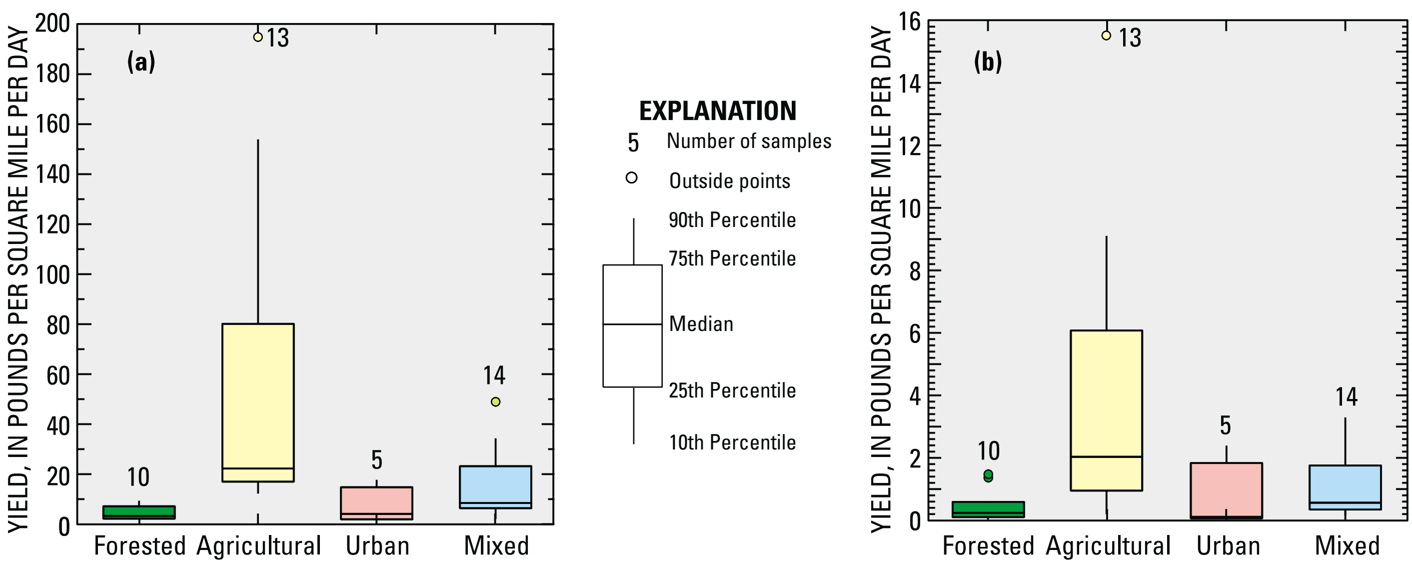

Figure 10.--Instananeous yields of (a) dissolved nitrate nitrogen and (b) dissolved phosphorus for streams draining forested, agricultural, urban, and mixed land uses and land covers, during 1997 snowmelt runoff in part of the Upper Mississippi River Basin Study unit.

generally has less nutrient and suspended sediment sources than agricultural and forested areas during snowmelt. Natural sources of organic nutrients and particulate matter such as wetlands are often drained or filled and vegetative mass is reduced. Urban areas have lower application rates of nutrients, and less exposed soil subject to erosion, than agricultural areas. Also, urban areas tend have more frequent and smaller snowmelt runoff events than other land covers because of application of deicers and warmer temperatures resulting from the thermal heat sink of an urban area, as evident at Shingle and Nine Mile Creeks (fig. 6). The greater frequency of winter runoff events in urban streams also may limit nutrient accumulation. Consequently, although urbanization has been cited as a cause of increased nutrient yields (Wetzel, 1983), in this study nutrient yields from urban areas without WWTPs were not significantly greater than forested areas during snowmelt runoff. However, annual yields of total nitrogen and suspended sediment for urban streams were greater than forested streams (table 2). Urban sources of nutrients and sediment may be more substantial during other seasons when fertilizer application, leaf litter, storm runoff, and storm sewer drainage activities increase. Consequently, limiting nutrients and suspended sediment during the growing season may be more effective than during snowmelt.

Surficial Geology

Significant differences ($p < 0.05$) in water quality were observed among streams draining permeable and impermeable deposits in forested areas. Median yields of total nitrogen and total phosphorus were greater for forested streams draining mostly impermeable deposits than for mostly permeable deposits (fig. 11). Median yields of suspended sediment and every nitrogen and phosphorus form analyzed also were significantly greater ($p < 0.05$) for streams draining impermeable deposits. Median yields were greater in basins draining impermeable deposits, probably because soils in these basins are more vulnerable to erosion (U.S. Department of Agriculture, 1978 and 1979) and water-quality degradation, and contribute greater yields to downstream lakes and rivers, especially during runoff. While percentages of agricultural land in basins draining mostly permeable or mostly impermeable deposits could be a contributing factor, differences in the amounts of agricultural land were not statistically significant ($p > 0.05$). In forested areas, the type of surficial geology may be important to consider in strategies to reduce loads during snowmelt runoff.

In streams draining mixed land use, yields of dissolved nitrite and total nitrogen were significantly greater ($p < 0.05$) in streams draining impermeable deposits than streams draining permeable deposits. These differences may be due to variable amounts of agricultural land use in these basins.

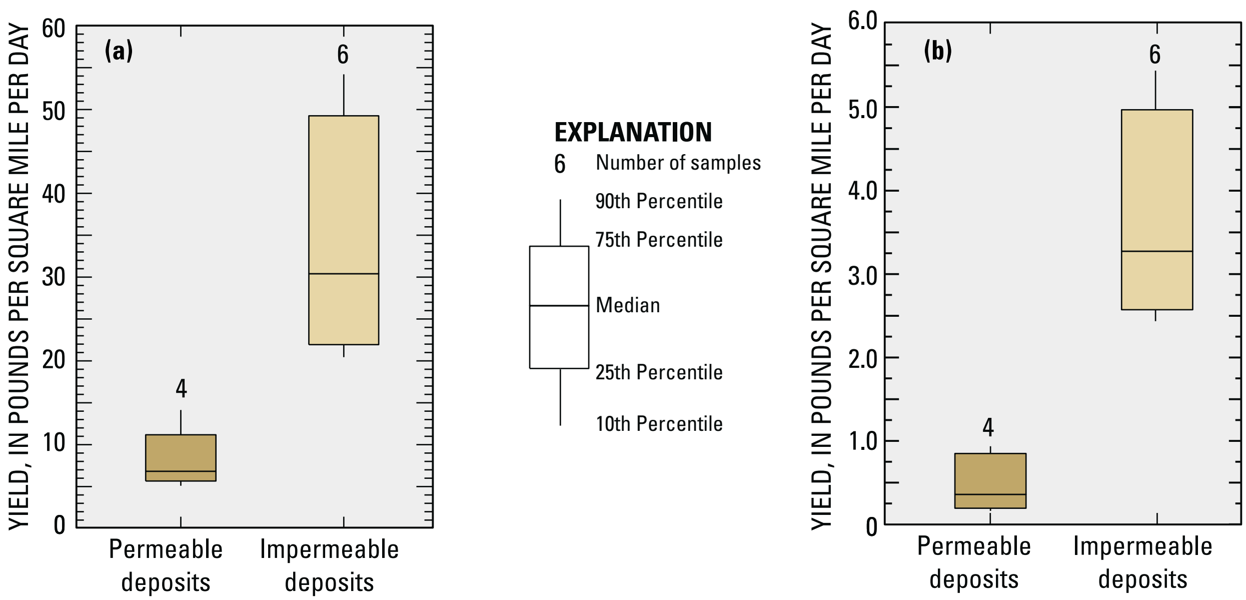

Figure 11.--Instananeous yields of (a) total nitrogen and (b) total phosphorus in permeable and impermeable deposits for streams draining forested basins, during 1997 snowmelt runoff in part of the Upper Mississippi River Basin Study unit.

SUMMARY

The USGS sampled snowmelt runoff from 42 stream sites in part of the Upper Mississippi River Basin, Minnesota and Wisconsin, to characterize nutrient and suspended-sediment concentrations, yields, and loads. Streams sampled drained combinations of land use and surficial geology common in the focused study area of the Upper Mississippi River Basin NAWQA study unit. Streams were classified by the predominant land use (forested, agricultural, urban, or mixed) and the predominant type of surficial geologic deposit (permeable or impermeable). Drainage areas ranged from 10 to 46,800 mi^2. Streams were sampled during March and April 1997, when melting of the snowpack combined with rainfall to produce near-record streamflow. Samples were collected during increasing streamflow conditions when concentrations were greatest. Ancillary data from 12 sites provided comparative concentrations from before and after streamflow increases and provided data to estimate constituent loads delivered during snowmelt and 1997.

The snowmelt period contributed from 1 to 50 percent of 1997 annual loads of total nitrogen, total phosphorus, and suspended sediment at small stream sites, and 17–70 percent of annual loads at mainstem river sites. Small streams draining agricultural areas transported the greatest proportions of annual loads during snowmelt. Agricultural areas have greater sources of nitrogen, phosphorus, and suspended sediment available as a result of commercial fertilizer or livestock manure application. Manure is often spread on snow-covered or exposed soils that are vulnerable to erosion. Snowmelt from urban streams transported the least proportions of annual loads. Impervious surfaces in urban areas reduce vegetation and soil cover, which limit nutrient and suspended-sediment sources. Furthermore, nutrient accumulation during winter may be limited by more frequent small runoff events resulting from sun-warmed impervious surfaces and application of road de-icers. Proportions of the annual loads of total nitrogen and suspended sediment from snowmelt at the forested site were between urban and agricultural sites. Forested basins may have more nutrient and sediment sources and winter accumulation than urban streams, yet less sources or more vegetative cover to protect soils than agricultural basins.

In snowmelt runoff samples, total nitrogen, total phosphorus, and suspended sediment concentrations and instantaneous yields were greatest for streams draining agricultural areas, especially those west of the Mississippi River. Dissolved nitrate was the principal nitrogen form for all agricultural streams, likely the result agricultural practices and fertilizer application. Dissolved organic nitrogen and particulate nitrogen were the principal nitrogen forms for forested streams, as these constituents are transported from naturally occurring organic material that has accumulated in forest soils and wetlands. No nitrogen concentrations (including dissolved un-ioinized ammonia, nitrite, nitrate, or nitrite plus nitrate) exceeded applicable Minnesota or Wisconsin water-quality standards for human or aquatic health. Dissolved phosphorus, mostly orthophosphate, was the principal phosphorus form for agricultural streams.

Median instantaneous yields of nutrients for agricultural streams were greater than for streams draining other land uses. Agricultural streams had significantly greater median yields ($p < 0.025$) of dissolved nitrite, nitrate, phosphorus, orthophosphate, total nitrogen, and total phosphorus than forested sites, and significantly greater median yields ($p < 0.025$) of dissolved nitrate and orthophosphate than all other land uses. Suspended-sediment and fine-grained sediment yields were similar for agricultural and forested streams, suggesting that forested basins are as vulnerable to erosion as agricultural streams during snowmelt.

In forested areas, yields of suspended sediment and all nutrient forms were significantly greater ($p < 0.05$) for streams draining impermeable deposits than permeable deposits. Soils developed on impermeable deposits in these basins are more vulnerable to erosion and water-quality degradation, and contribute greater yields to downstream lakes and rivers, especially during runoff.

In agricultural and forested streams, the snowmelt period can deliver greater proportions of annual loads of nutrients and suspended sediment than other equivalent periods, and occasionally, the majority of the annual load. Consequently, the snowmelt period should be considered in strategies aimed at reducing loads of nutrients and suspended sediment to streams. For forested areas, the type of surficial geology may be important to consider in strategies to reduce loads during snowmelt runoff. For urban areas, limiting nutrients and suspended sediment during the growing season runoff may be more effective than during snowmelt.

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