Isotopic and Chemical Composition of Inorganic and Organic Water-Quality Samples from the Mississippi River Basin, 1997–98

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CONVERSION FACTORS AND ABBREVIATIONS

Multiply	By	To obtain
cubic meters per second	3.531×10^{1}	cubic foot per second
metric ton	2.205×10^{3}	pound
kilogram	2.2046	pound
square kilometer	3.861×10^{-1}	square mile
hectare	2.471	acre
micron	2.0×10^{-6}	meters
liter	2.642×10^{-1}	gallon

Abbreviations

NASQAN - National Stream Quality Accounting Network
NAWQA - National Water Quality Assessment
microgram per liter (µg/L)
microsiemens per centimeter at 25 degrees Celsius (µS/cm)
milligram per liter (mg/L)
milliliter (ml)
degrees, minutes, second (ddmmss)
cubic meters per second (m^3/s)
square kilometer (km^2)

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Abstract

Nitrate (NO_3) and other nutrients discharged by the Mississippi River combined with seasonal stratification of the water column are known to cause a zone of depleted dissolved oxygen (hypoxic zone) in the Gulf of Mexico each summer. About 120 water and suspended sediment samples collected in 1997 and 1998 from 24 locations in the Mississippi River Basin were analyzed for the isotope ratios $\delta^{15}N$ and $\delta^{18}O$ of dissolved NO_3, and $\delta^{15}N$ and $\delta^{13}C$ of suspended particulate organic material (POM). Sampling stations include both large rivers (drainage areas more than 30,000 square kilometers) that integrate the effects of many land uses, and smaller streams (drainage areas less than 2,500 square kilometers) that have relatively uniform land use within their drainage areas. The data are used to determine sources and transformations of NO_3 in the Mississippi River.

Results of this study demonstrate that much of the NO_3 in the Mississippi River originates in the agriculturally dominated basins of the upper midwestern United States and is transported without significant transformation or other loss to the Gulf of Mexico. Results from major tributaries that drain into the Mississippi River suggest that NO_3 is not significantly altered by denitrification in its journey, ultimately, to the Gulf of Mexico. The spatial variability of isotope ratios among the smaller streams appears to be related to the dominant nitrogen source in the basins. There are some distinct isotope differences among land-use types. For example, for both NO_3 and POM, the majority of $\delta^{15}N$ isotope ratio values from basins dominated by urban and undeveloped land are less than +5 per mil, whereas the majority of values from basins dominated by row crops and row crops and/or livestock production are greater than +5 per mil. Also, the median $\delta^{18}O$ of NO_3 isotope ratio value (+14.0 per mil) from undeveloped basins is more than 6 per mil higher than the median value (+7.3 per mil) from the row crop dominated basins and 5 per mil higher than the median value (+9.0 per mil) from the row crop and/or livestock production dominated basins. The median $\delta^{18}O$ of NO_3 isotope ratio value (+21.5 per mil) from urban basins is 6.5 per mil higher than the median value (+14.0 per mil) from the undeveloped basins. The majority of NO_3 concentrations are greater than 3 milligrams per liter (mg/L) in basins dominated by row crops and row crops and/or livestock production, whereas all NO_3 concentrations are less than 2 mg/L in basins dominated by urban and undeveloped land.

INTRODUCTION

Problem

Nitrate (NO_3) and other nutrients discharged from the Mississippi River basin along with seasonal stratification of the water column are known to cause a zone of depleted dissolved oxygen (hypoxic zone) in the Gulf of Mexico (Turner and Rabalais, 1991; Rabalais and others, 1996; 1999). The magnitude of nitrogen (N) inputs contributed from various sources in the Mississippi basin can be estimated (Battaglin and others, 1997; Burkart and James, 1999; Goolsby and others, 1999), but N from each source is affected differently by physical, chemical, and biological processes that control N transport and cycling in terrestrial and aquatic systems (Kendall, 1998). Hence, the relative contributions from the various N sources may not be in proportion to their inputs in the Mississippi River basin. It may be possible to determine the major sources of NO_3 in river water and gauge the importance of in-stream transformations of NO_3 using the stable isotopic ratios $\delta^{15}N$ and $\delta^{18}O$ of NO_3 in water and $\delta^{15}N$ and $\delta^{13}C$ of suspended particulate organic material.

Objectives and Hypotheses

The objective of this project is to determine if the $\delta^{15}N$ and $\delta^{18}O$ isotope ratio values of dissolved NO_3 in water ($\delta^{15}N$ and $\delta^{18}O$ of NO_3 values) and $\delta^{15}N$ and $\delta^{13}C$ isotope ratio values of suspended particulate organic material ($\delta^{15}N$ and $\delta^{13}C$ values of POM) can be used to help identify the sources of inorganic and organic N to the main-stem Mississippi River. Specific objectives include: determination of geographic sources of N; the proportion of contributions from various land uses within large and small tributary basins; and the effects and types of N transformation and cycling processes that affect the eventual transport of NO_3 to the Gulf of Mexico. The following hypotheses are tested (Battaglin and others, 1997):

1. There are significant temporal and spatial variations in $\delta^{15}N$ and $\delta^{18}O$ of NO_3 values in water from the Mississippi River and its major tributaries.
2. The NO_3 in small streams draining areas of distinctly different land use (corn and soybean production, livestock production, urban land, or undeveloped land) will have distinctly different $\delta^{15}N$ and $\delta^{18}O$ of NO_3 values.
3. The $\delta^{15}N$ and $\delta^{18}O$ of NO_3 values in Mississippi River water can be used to determine the principal sources of the NO_3 that enters the Gulf of Mexico.
4. The $\delta^{15}N$ and $\delta^{18}O$ of NO_3 values in Mississippi River water provide information about NO_3 transformations in the river.
5. There are significant temporal and spatial variations in $\delta^{15}N$ and $\delta^{13}C$ of POM values in suspended organic material from the Mississippi River and its major tributaries.
6. The suspended organic material in small streams draining areas of distinctly different land use will have distinctly different $\delta^{15}N$ and $\delta^{13}C$ of POM values.
7. Results from selected samples collected as Lagrangian sets can be used in simple mixing models to determine how conservatively NO_3 behaves in the Lower Mississippi River.

Background

Gulf of Mexico Hypoxia and Mississippi River Discharge

When the concentration of dissolved oxygen in seawater drops below 2 mg/L for prolonged periods, benthic communities can be disrupted and mass mortalities of aquatic life can occur (Diaz and Rosenberg, 1995; Council for Agricultural Science and Technology, 1999). This condition, called hypoxia, currently occurs in many parts of the world and probably has occurred in some locations periodically throughout geologic time (Rabalais and others, 1999). The hypoxic zone in the bottom waters of the northern Gulf of Mexico along the Louisiana and Texas coast is the largest such area in the coastal waters of the United States. Hypoxia here occurs during late spring and summer following inputs of freshwater and nutrients. Evidence from analysis of benthic foraminifera species in sediment cores from the northern Gulf of Mexico suggest that (1) there was little or no hypoxia prior to 1900, (2) there was a change in the offshore ecosystem with regard to hypoxia at the turn of the last century, and (3) that hypoxia severity has worsened since the 1950s (Rabalais and others, 1999). From 1985 to 1992, the area of the hypoxic zone averaged about 10,000 square kilometers (km^2); following the 1993 flood, the zone nearly doubled in size to 17,000 km^2. Subsequently, the hypoxic zone area has been reported to be 15,500 km^2 or more in 1994–97, and 1999 (Council for Agricultural Science and Technology, 1999; N. Rabalais,, Louisiana Universities Marine Consortium, written commun., 1999).

The Mississippi and Atchafalaya Rivers (fig. 1) are the primary riverine sources of freshwater and nutrients discharged to the Gulf of Mexico. The combined annual mean discharge, 21,800 cubic meters per second (m^3/s), for the Mississippi and Atchafalaya Rivers represents about 80 percent of the freshwater discharge to the Gulf of Mexico (Dunn, 1996). This river system drains approximately 3.2 million km^2 of the midwestern USA, making it the third-largest drainage basin in the world after the Amazon and Congo River basins (Van der Leeden and others, 1990).

The Atchafalaya River currently functions as a distributary of the Mississippi River. About 225 km downstream from Vicksburg, Miss, approximately 25 percent of the Mississippi River discharge is diverted into the Old River outflow channel (Goolsby and others, 1999). The diverted flow joins the Red River to form the Atchafalaya River, which flows almost directly south about 200 km to the Gulf of Mexico. Historically, the lower Mississippi River meandered in a 300-kilometer wide arc and the location of the outlet to the Gulf of Mexico shifted dramatically about every millennium (McPhee, 1989; Meade, 1995). It is likely that the Mississippi River would no longer flow past New Orleans, were it not for the control structures built by the U.S. Army Corps of Engineers (McPhee, 1989). These structures keep the lower Mississippi River in its current channel and prevented the Atchafalaya River from capturing the entire flow of the Mississippi River.

Currently, the Mississippi and Atchafalaya Rivers account for an estimated 90% of the total N load and 87 percent of the total phosphorus (P) load discharged annually by rivers and streams to the Gulf of Mexico (Dunn, 1996). Analysis of historical data (Palmer, ca. 1903; Leighton, 1907; Dole, 1909) suggests that at the beginning of the twentieth century (1905–06) the average concentration of NO_3 (as N) in the lower Mississippi River was about 0.55 milligram per liter (mg/L) (Goolsby and Battaglin, 2001). The concentration of NO_3 in the lower Mississippi River has increased since that time to an average of 1.45 mg/L during 1980–98. The resulting flux of NO_3 to the Gulf of Mexico from the Mississippi and Atchafalaya Rivers has also increased substantially. During the 1950s and 1960s, the NO_3 flux to the Gulf of Mexico never exceeded 0.5 million metric tons per year (Mton/y), but during the 1980s and 1990s the NO_3 flux to the Gulf of Mexico averaged 1.0 Mton/y, and exceeded 1.5 Mton/y during the 1993 flood (Goolsby and others, 1999; Goolsby and Battaglin, 2001). The NO_3 flux generally peaks during the spring and early summer months and can exceed 6,000 metric tons per day (Battaglin and others, 1997; Goolsby and others, 1999).

Nitrogen Sources

Major sources of N in the Mississippi River basin are mineralization of organic N in soils, application of nitrogen based fertilizer, fixation of atmospheric N by legumes, application of N in animal manure, deposition of atmospheric N in precipitation, and discharge of N in municipal and industrial waste. The magnitudes of these sources in large subbasins of the Mississippi basin have been estimated in previous investigations (Battaglin and others, 1997; Burkart and James, 1999; Goolsby and others, 1999). Estimates of annual N inputs from various sources during 1951–99 were compiled for 20 states that account for most of the agricultural land in the Mississippi River Basin (fig. 1). The 20 States are: Arkansas, Colorado, Illinois, Indiana, Iowa, Kansas, Kentucky, Louisiana, Minnesota, Mississippi, Missouri, Montana, Nebraska, Ohio, Oklahoma, South Dakota, Tennessee, West Virginia, Wisconsin, and Wyoming.

The relative magnitudes and the temporal trends of estimated N inputs from the 20 States in the Mississippi River basin are shown in figure 2. The state-level fertilizer N inputs shown (fig. 2) include both agricultural and nonagricultural (home and garden) fertilizer use (Alexander and Smith; 1990; Battaglin and Goolsby, 1995; National Agricultural Statistics Service, 1999). Estimates of non-agricultural fertilizer use range between 5 and 20 percent of the total usage (H. Taylor, U.S. Department of Agriculture, written commun., 1998). Other N inputs were estimated using the best available data or the most current estimation technique (Goolsby and others, 1999). Fertilizer N inputs have increased substantially, from less than 1 to about 7 million Mton/y between the 1950s and 1990s (fig. 2); other N inputs have not changed very much during that time.

During the 1800s, increases in food production in the USA resulted from an expanding cropland base, the addition of nutrients in animal manure, and the

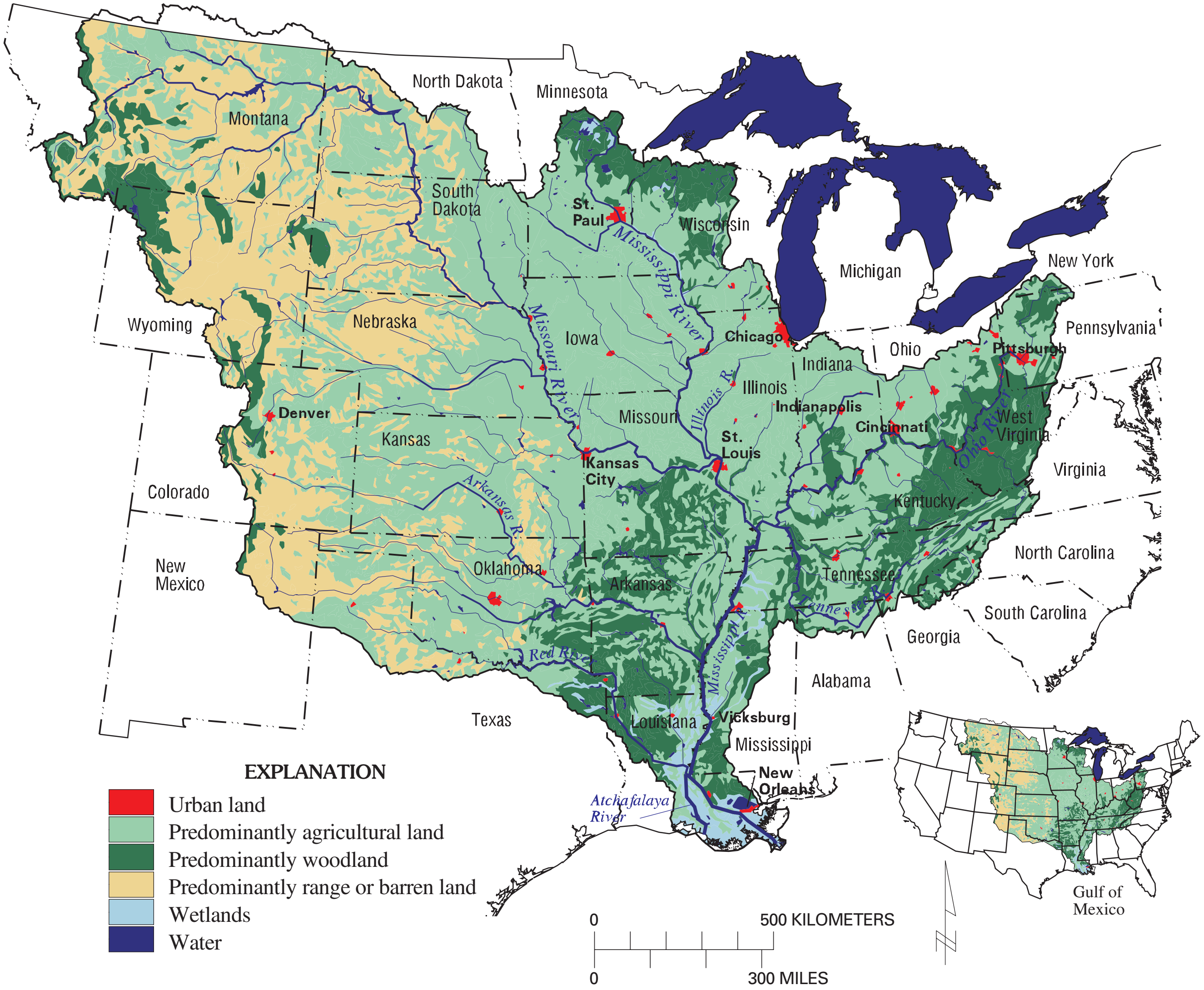

Figure 1. Land cover in the Mississippi River Basin.

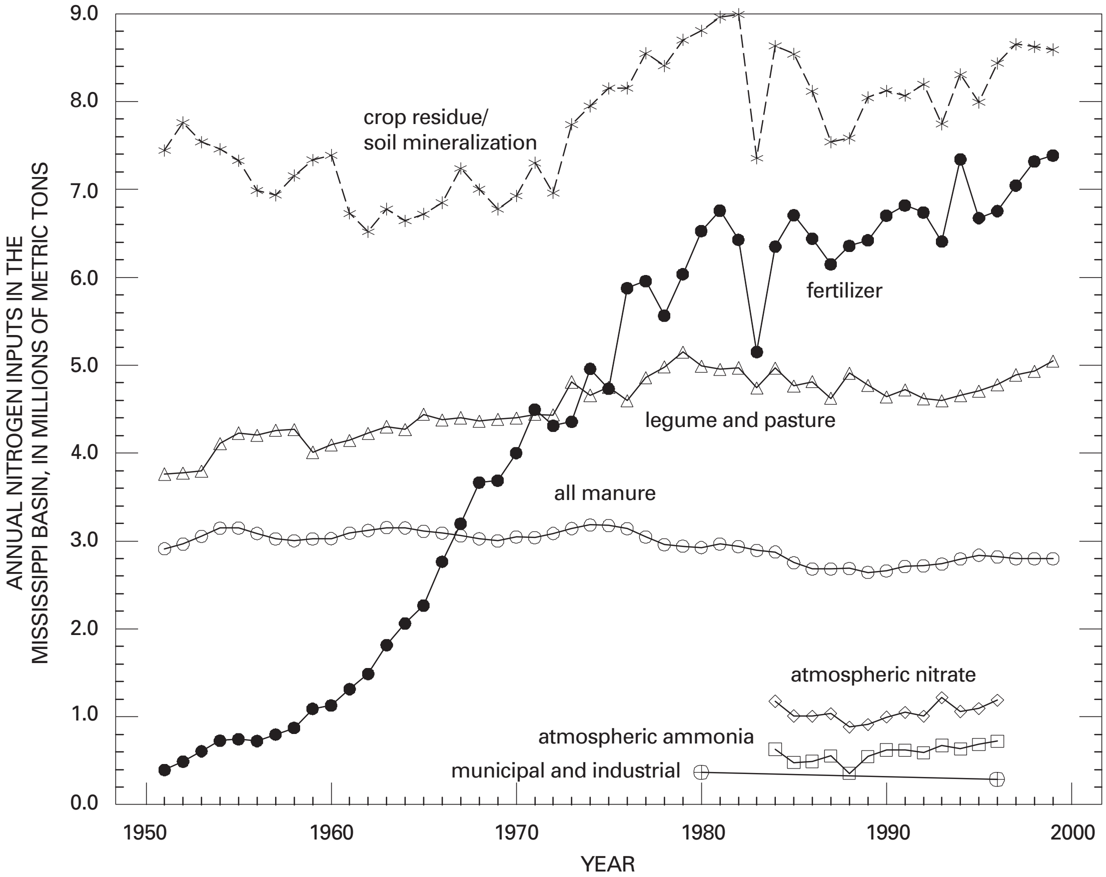

Figure 2. Estimated annual nitrogen inputs in the 20 States that account for most of the agricultural land in the Mississippi River basin, 1951 to 1999 (modified from Goolsby and others, 1999).

utilization of soil nutrients. In the early 1900s, soil fertility and crop yields were maintained by the addition of N- and P-containing natural waste materials like animal manure, seaweed, bone meal, and guano. Beginning in the 1940s, manufactured fertilizers like super-phosphates, urea, and anhydrous ammonia replaced most natural fertilizers (U.S. Department of Agriculture, 1997). Since the 1930s, yields per acre for major crops like corn and wheat have doubled or tripled (Mannion, 1995). Some of this increase can be attributed to better plant hybrids and some can be attributed to increased application of crop nutrients.

As indicated in the problem statement, the N from each source is affected differently by physical, chemical, and biological processes that control N cycling in terrestrial and aquatic systems. Hence, the relative contributions from the various N sources to NO_3 loads in the Mississippi River may not be proportional to their inputs in the basin.

Previous Isotope Investigations

Stable isotopes of NO_3 have been used in N source and cycling investigations for over 30 years (Kreitler, 1975; Hubner, 1986; Heaton, 1986; Clark and Fritz, 1997; Kendall, 1998). One of the first studies (Kohl and others, 1971) used $\delta^{15}N$ of NO_3 to investigate the sources NO_3 in an agricultural watershed. They estimated that 55% of N found as NO_3 in the Sangamon River originated as fertilizer N. Several recent studies have utilized isotopic techniques to identify the sources and transformations of NO_3 in rivers with varying degrees of success. Showers and others (1990) used NO_3 $\delta^{15}N$ values in the Neuse River, NC, to determine that the relative contributions from point and nonpoint sources varied seasonally and by water discharge rate. They also determined that nitrate's isotopic composition was exponentially related to river discharge, and they concluded that the mixing of point and nonpoint source N reservoirs was not entirely controlled by surface water runoff of agricultural fertilizer and excess soil NO_3, but that nonpoint source NO_3 passing through a reservoir (either groundwater or wetlands) modulated the mixing. Cravotta (1995) attempted to use the stable isotopes of carbon, N, and sulfur to identify sources of N in the Susquehanna River, and found that variations in source isotopic compositions, transformation, and fractionation during natural cycling of N prevented accurate estimation of relative contributions of multiple N sources to N loads in streams.

Böhlke and Denver (1995) used isotope, water chemistry, chlorofluorocarbons (for determining water recharge date), and nitrogen gas measurements in two adjacent but geologically and hydrologically different basins to show that water age and aquifer composition can influence the amount of N delivered from a groundwater system to a stream. Kendall and others (1995) used $\delta^{18}O$ and $\delta^{15}N$ of NO_3 values to determine NO_3 sources in snowmelt runoff from three small mountainous watersheds in the United States. They determined that most of the NO_3 in early runoff was derived from the soil, and not from atmospheric NO_3 released from the current year's snowpack. Campbell and others (U.S. Geological Survey, written commun., 2001) used $\delta^{18}O$ and $\delta^{15}N$ of NO_3 values to show that most NO_3 in streams and ground water of N-saturated alpine watersheds was affected by microbial processes, even in landscapes with little vegetation or soil. Burns and Kendall (U.S. Geological Survey, written commun., 2001) used $\delta^{18}O$ and $\delta^{15}N$ on NO_3 values to show that NO_3 in stream water was similar to soil water, and that microbial cycling of NO_3 from atmospheric deposition was rapid. Kellman and Hillaire-Marcel (1998) used $\delta^{15}N$ values to determine the importance of in-stream denitrification on the N-budget of a small watershed. The isotopes showed that denitrification was significant during dry conditions in late summer.

Nitrogen Transformations

The isotopic composition of NO_3 sources can be altered by reactions that fractionate the stable isotopes. Nitrogen can be transformed in vegetation, the soil, the unsaturated zone, the saturated zone, or in-stream. Assimilation and denitrification are the most likely transformation processes that may have an in-stream effect on NO_3 and total N concentrations and loads in rivers. Use of both $\delta^{15}N$ and $\delta^{18}O$ enhances identification of N transformations and identification of NO_3 sources (Böttcher and others, 1990; Kendall, 1998).

Nitrogen assimilation, the use of N-bearing compounds by plants or organisms, slightly favors the ^{14}N isotope over ^{15}N isotope. A large range of isotope fractionations [–27 to 0 per mil (‰)] have been measured in field and laboratory experiments for assimilation of NO_3 and ammonium by algae (Fogel and Cifuentes, 1993). However, the average apparent fractionations caused by assimilation by microorganisms in soils is about –0.5‰ (Hubner, 1986). The larger fractionation of NO_3 in aquatic versus soil environments reflects the interplay of several kinetic and equilibrium isotope effects. In general, smaller fractionations are observed for higher growth rates and for lower NO_3 and ammonium concentrations. Assimilation would likely favor the ^{16}O isotope relative to the ^{18}O isotope in the same way the ^{14}N isotope is utilized in preference to ^{15}N isotope (Kendall, 1998); hence it would increase the $\delta^{18}O$ and $\delta^{15}N$ isotope ratio of the residual NO_3 pool.

Denitrification, the biologically mediated reduction of NO_3 to N_2, causes the $\delta^{15}N$ and $\delta^{18}O$ of the residual NO_3 pool to increase exponentially as NO_3 concentration decreases (Böttcher and others, 1990; Kendall, 1998). The ratio of enrichment of O to N tends to be close to 1:2 (Böttcher and others, 1990; Voerkelius and Schmidt, 1990). In-stream loss of N coupled with significant positive shifts in isotope ratios can indicate that denitrification is consuming NO_3 (Kellman and Hillaire-Marcel, 1998).

Volatilization, the loss of N usually as ammonia (NH_3), involves several steps that can cause fractionation. The remaining dissolved NH_3 tends to be enriched in the ^{15}N isotope relative to the NH_3 that is volatilized. The enriched NH_3 in solution is rapidly nitrified to produce ^{15}N-enriched NO_3 in most natural conditions (Feigin and others, 1974; Kendall, 1998).

The loss of N in streams, whether by assimilation, denitrification, or volatilization, tends to cause a decrease in N concentration, a loss of N mass (to the atmosphere or plants), and a shift towards higher $\delta^{15}N$ and $\delta^{18}O$ of NO_3 isotope ratio values between upstream and downstream measuring points. In larger rivers, the magnitude and mechanism of N loss can be difficult to identify because small errors in discharge measurements and small differences in concentrations or isotope ratios can significantly affect data interpretation.

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METHODS

Plan of Study

The study plan (Battaglin and others, 1997) provides details about sample station selection and sampling procedures. In 1997, about 150 water and particulate organic material (POM) samples were collected from 24 stations on rivers in the Mississippi River basin, and in 1998, about 100 water and POM samples were collected from 23 stations on rivers in the Mississippi River basin. Some of the 1997 samples and most 1998 samples have complete (both $\delta^{15}N$ and $\delta^{18}O$ of NO_3 values in water, and $\delta^{15}N$ and $\delta^{13}C$ of POM values) isotope analyses. Several water samples did not contain sufficient NO_3 to analyze, and a few were ruined during sample processing.

Sampling Stations

All sampling stations are in the Mississippi and Atchafalaya River basin. Some stations were sampled in association with ongoing U.S. Geological Survey (USGS) National Stream Quality Accounting Network (NASQAN) and National Water-Quality Assessment (NAWQA) programs.

Large River Stations

Samples were collected from eight stations on the Mississippi River or its major tributaries (table 1; fig. 3a). mostly in conjunction with NASQAN (NASQAN, 2001) sample collection activities. These stations are on large rivers that drain more than 200,000 km^2 (except the Yazoo River, that drains only 34,590 km^2). Land use in these basins is mixed (table 2); hence, water samples from these stations contain NO_3 from several sources. Drainage basins for the Mississippi River at Clinton, Iowa (MSR1) and Thebes, Ill. (MSR2), and the Yazoo River at Long Lake, Miss. (YZR1) are more than 50 percent cropland. The Ohio River at Grand Chain, Ill. (OHR1) basin is more than 50 percent forested land. Estimated N input from manure production (Goolsby and others, 1999) exceeded 1,000 kg/km^2/yr only in the drainage basin of the MSR1 station.

Small Stream Stations

Samples were collected from 16 stations on smaller streams in the Mississippi River basin. Many of these stations are within NAWQA (NAWQA, 2001) study units. The small stream stations all drain areas less than 2,500 km^2. These stations were selected to represent four distinct land-use categories: land in row crop agriculture (corn, soybean and sorghum); land in hog, cattle, or poultry (livestock) production; urban land; or undeveloped land (fig. 3b; tables 2 and 3).

Land use was not always solely composed of one of the four categories, but making more categories would leave too few samples in each category to perform data analysis. For this report, four categories were used, but the original livestock category was redefined to include basins with both high-density livestock production and row-crop agriculture. The four stations in this category all had estimated manure production of greater than 3,200 kg N/km^2 per year (table 2). Two of these stations also had land use dominated by row crop agriculture (table 3). The basin type for each station on table 1 and shown in figure 3.

Sampling Schedule and Procedure

Six samples were collected at each station during the winter, spring, and summer of 1996–97 (Battaglin and others, 1997). Most of these samples were not analyzed for $\delta^{15}N$ and $\delta^{18}O$ of NO_3 in water due to a problem with sample preparation. The $\delta^{15}N$ and $\delta^{13}C$ of POM isotope ratio values are available for some of these samples.

Table 1. Selected characteristics of sampling stations in the Mississippi River basin

(square kilometers, km^2)

Map no. (fig. 3)	Sampling station name	Station number	Latitude (ddmmss)	Longitude (ddmmss)	Drainage area (km^2)	Basin type
	Large rivers					
1	Mississippi River at Clinton, IA	05420500	414650	901507	221,700	mixed agricultural land/forest
2	Missouri River at Hermann, MO	06934500	384236	912621	1,357,700	mixed rangeland/agricultural land
3	Mississippi River at Thebes, IL	07022000	371300	892750	1,847,200	mixed agricultural land/rangeland
4	Ohio River at Grand Chain, IL	03612500	371211	890230	526,000	mixed forest/agricultural land
5	Yazoo River below Steele Bayou near Long Lake, MS	07288955	322637	905400	34,590	mixed agricultural land/forest
6a	Mississippi River at St. Francisville, LA	07373420	304530	912345	2,914,500	mixed agricultural land/forest/ rangeland
6b	Mississippi River at Vicksburg, MS	07289000	321845	905425	~2,900,000	mixed agricultural land/forest/ rangeland
6c	Mississippi River at Belle Chasse, LA	07374525	295125	895840	2,916,200	mixed agricultural land/forest/ rangeland/wetland
	Small streams					
7	S. Fork Iowa River northeast of New Providence, IA	05451210	421855	930907	596	row crop agriculture and/or livestock production
8	Fourmile Creek near Traer, IA	05464137	421207	923344	50.5	row crop agriculture
9	Walnut Creek near Vandalia, IA	05487550	413213	931532	52.6	row crop agriculture
10	Panther Creek near El Paso, IL	05567000	404605	890430	243	row crop agriculture
11	Indian Creek near Wyoming, IL	05568800	410106	895007	162	row crop agriculture
12	Sugar Creek at Co Rd 400 S at New Palstine, IN	03361650	394251	855308	243	row crop agriculture
13	Little Buck Creek near Indianapolis, IN	03353637	394000	861148	44	urban land
14	North Dry Creek near Kearney, NE	06770195	403828	990656	201	row crop agriculture and/or livestock production
15	Dismal River near Thedford, NE	06775900	414645	1003130	2,500	undeveloped land
16	South Fabius River near Taylor, MO	05500000	395340	913449	1,606	row crop agriculture
17	Elk River near Tiff City, MO	07189000	363753	943512	2,260	row crop agriculture and/or livestock production
18	Shingle Creek at Queen Ave. N., MN	05288705	450300	931836	73	urban land
19	Little Cobb River near Beauford, MN	05320270	435948	935430	336.7	row crop agriculture
20	Namekagon River at Leonards, WI	05331833	461017	911945	326	undeveloped land
21	Rattlesnake Creek near North Andover, WI	05413449	424649	905632	110	row crop agriculture and/or livestock production
22	Bogue Phalia near Leland, MS	07288650	332347	905047	1,254	row crop agriculture

Most stations sampled in 1997 were sampled again four times during 1998. The first sample set was collected in April or May, 1998, prior to crop emergence. The second and third sample sets were collected in June and July 1998 after fertilizer application to fields when stream flows were elevated due to storm runoff. The fourth sample set was collected in August and September 1998 after harvest, when streams were generally dominated by baseflow.

Samples were collected with a depth integrating sampler (where conditions were appropriate for this collection method) from three or more vertical profiles using USGS protocols (Shelton, 1994). Before samples were collected, all sampling equipment was precleaned with non-phosphate detergent, rinsed thoroughly with tap water, and then rinsed with distilled or deionized water. Samples from vertical profiles were composited into a glass, polyethylene, or Teflon

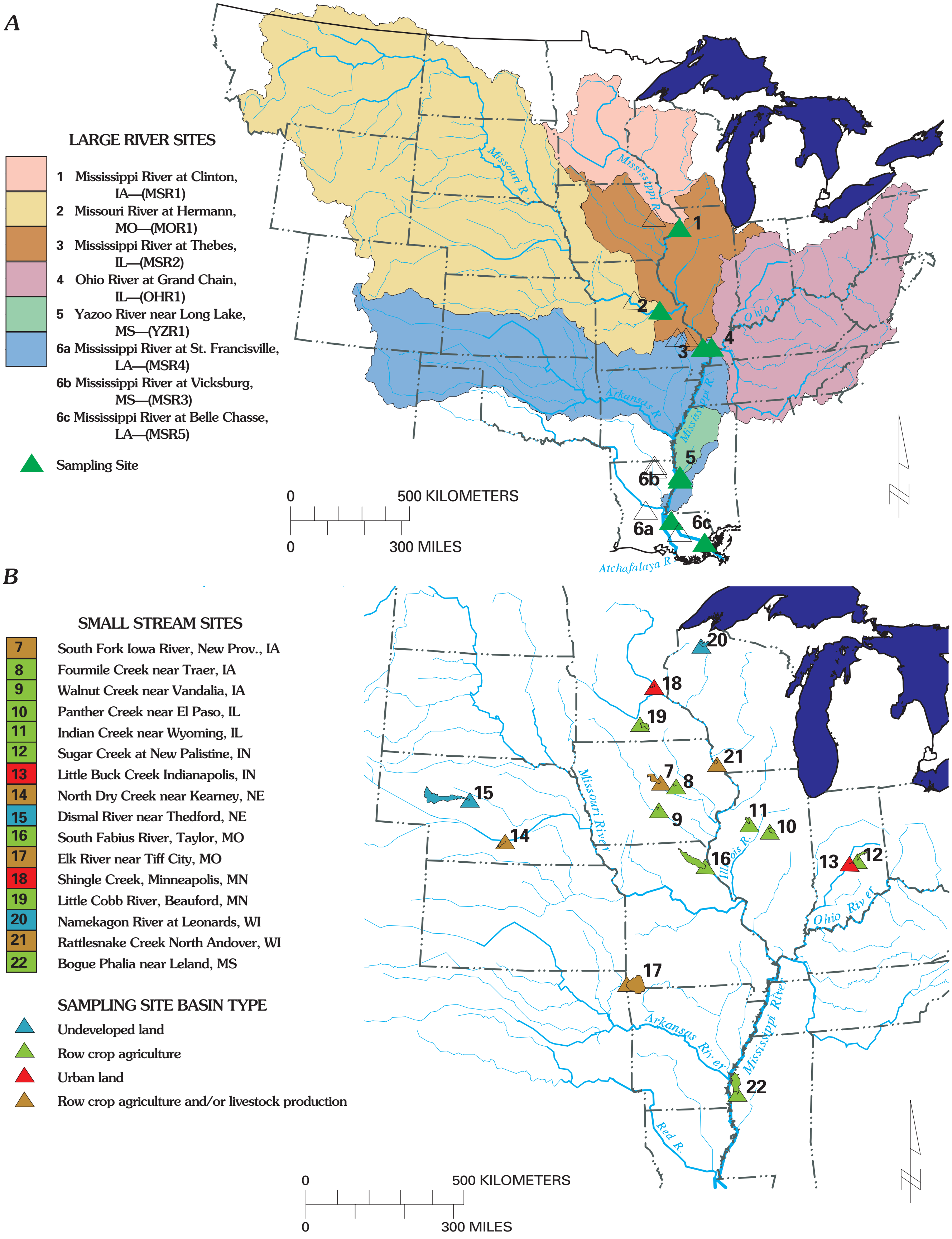

Figure 3. Locations of sampling stations and associated drainage basins for (*A*) large rivers and (*B*) small streams.

Table 2. Generalized land cover and estimated annual manure nitrogen production in the large river and small stream drainage basins (land cover derived from reclassified Advanced Very High Resolution Radiometer data with a 1,000 meter-cell size)

Station number	Percentage of basin							Estimated manure nitrogen production in kg/km^2			
	Urban	Agricultural	Rangeland	Forest	Water	Wetland	Barren or Tundra	Cattle	Hogs	Poultry	Total[1]
Large rivers											
05420500	1.1	61.4	0.3	35.7	1.5	0	0	1,004	292	48.4	1,368
06934500	0.4	42.6	45.3	10.6	0.4	0	0.7	742	92.9	6.7	866
07022000	0.8	51.3	33.0	13.8	0.6	0	0	767	179	13.1	984
03612500	2.2	30.1	0.1	67.0	0.6	0	0	704	110	83.7	933
07288955	0.5	55.1	1.4	41.8	1.1	0.1	0	213	5.3	< 0.05	228
07373420[2]	1.1	45.5	26.2	26.3	0.6	0.01	0.3	780	139	49.4	993
Small streams											
05451210	0	100	0	0	0	0	0	422	2,710	74.7	3,232
05464137	0	98.4	0	1.6	0	0	0	814	544	0.6	1,388
05487550	0	100	0	0	0	0	0	1,055	944	0.1	2,031
05567000	0.8	99.2	0	0	0	0	0	247	561	2.0	827
05568800	0	98.8	0	1.2	0	0	0	413	662	0.1	1,099
03361650	0.7	99.3	0	0	0	0	0	229	575	0.2	842
03353637	42.5	57.5	0	0	0	0	0	40.8	7.0	< 0.05	71.6
06770195	0	100	0	0	0	0	0	4,157	169	0.1	4,351
06775900	0	54.6	45.3	0.1	0	0	0	590	0.2	< 0.05	599
05500000	0	86.8	0.3	12.9	0	0	0	1,030	152	0.2	1,203
07189000	1.0	2.8	0	96.1	0.1	0	0	1,949	76.6	2,822	4,887
05288705	89.7	10.3	0	0	0	0	0	298	15.7	0.2	372
05320270	0	97.9	0	2.1	0	0	0	505	1,395	17.5	1,945
05331833	0	5.2	0	93.0	1.8	0	0	132	2.1	0.1	141
05413449	0	98.9	0	1.1	0	0	0	2,874	377	8.9	3,287
07288650	0.2	84.9	8.9	4.8	0.8	0.4	0	61.0	0.6	< 0.05	63.3

[1] Total includes cattle, hogs, poultry, horses, and sheep.

[2] Estimates of land cover in the drainage basins associated with stations 6b and 6c (table 1) are the same as for station 07373420.

container. Isotope samples for NO_3 analysis were filtered through a 0.45-micron cartridge filter into 1-liter or 1-gallon pre-cleaned polyethylene bottles, chilled without preservative, and shipped to USGS district water-quality laboratories in Missouri (prior to January 1, 1998) or Colorado (after January 1, 1998) for extraction onto anion exchange columns. Samples for other analytes including nutrients, major ions, and dissolved organic carbon were collected concurrently, processed according to standard protocols, and analyzed by the USGS National Water Quality Laboratory (NWQL) in Denver, Colo..

Lagrangian Samples

Lagrangian sampling (Meade and Stevens, 1990; Moody, 1993) is a sampling method in which a mass of water is sampled repeatedly as it moves down a river. The timing of sample collection is determined by the velocity (converted to travel time) of the water in the river. Major tributaries also are sampled when the water mass is near their mouth. Because Lagrangian sample sets provide data on the changes in water-quality characteristics as a water mass moves downstream, these sample sets can be more useful than traditional Eulerian sample sets for constructing transport models of dissolved chemicals and suspended sediment, and for identifying the chemical, physical, and hydrologic processes that affect stream chemistry (Meade and Stevens, 1990).

In this study, the collection of a Lagrangian sample set for the lower Mississippi River involved sampling the Mississippi River at Thebes (MSR2) and the Ohio River at Grand Chain (OHR1) (fig. 3a) at about the same time. During average spring flow

Table 3. Land cover in the small stream drainage basins (derived from National Land Cover data with a 30-meter cell size)

	Percentage of basin									
Station number	Low or high intensity residential and urban grasses	Commercial/ industrial/ transportation	Deciduous, evergreen or mixed forest	Open water/ perennial snow	Barren land	Shrubland or grassland	Wetlands	Row crops	Small grains	Pasture or fallow
05451210	0.1	1.4	2.6	0.1	<0.1	3.3	0.7	87.5	0.1	4.2
05464137	0.1	1.3	1.6	<0.1	<0.1	4.5	0.1	85.7	<0.1	6.6
05487550	0.1	1.2	3.0	1.1	<0.1	5.4	0.1	75.3	0.4	13.4
05567000	0.7	0.1	0.4	0.1	<0.1	0.1	0.2	94.6	<0.1	3.8
05568800	1.7	0.3	3.0	<0.1	<0.1	<0.1	0.3	82.6	<0.1	12.0
03361650	1.8	0.3	4.9	0.3	<0.1	<0.1	0.7	75.9	<0.1	16.1
03353637	43.4	5.7	3.9	0.1	<0.1	<0.1	0.3	26.1	<0.1	20.4
06770195	<0.1	<0.1	0.4	0.4	<0.1	16.3	0.8	74.0	0.8	7.3
06775900	<0.1	<0.1	0.4	0.8	0.5	93.2	4.6	0.1	<0.1	0.4
05500000	0.4	1.1	19.9	0.6	<0.1	4.1	5.9	24.0	5.6	38.4
07189000	1.5	0.3	49.7	0.4	0.3	2.2	0.4	2.6	2.1	40.5
05288705	62.0	8.7	6.2	5.2	4.6	<0.1	11.0	0.6	<0.1	1.7
05320270	0.2	0.4	2.4	0.8	<0.1	<0.1	3.8	87.2	<0.1	5.2
05331833	0.1	0.1	71.6	7.1	0.2	0.4	16.2	2.2	<0.1	2.1
05413449	<0.1	0.6	3.7	<0.1	<0.1	<0.1	0.1	46.0	<0.1	49.6
07288650	0.7	0.2	1.3	1.3	<0.1	<0.1	10.5	71.2	9.3	5.5

conditions, it takes water about 8 days to travel from the MSR2 or OHR1 stations to the St. Francisville (MSR4) station and 2 or 3 more days to travel to the Belle Chasse (MSR5) station (Broshears and others, 2001). Water (and solutes) diverted from the Mississippi River into the Atchafalaya River via the Old River outflow (about 25% of Mississippi discharge on average) are included in discharge and flux values reported for the MSR4 and MSR5 stations.

Samples from the MSR2 on June 11, 1997, the OHR1 on June 12, 1997, YZR1 on June 19, 1997, the MSR4 on June 19, 1997, and the MSR5 on June 20, 1997 (table 4) are referred to as the first Lagrangian set. While not specifically collected as such, samples from the MSR2 on April 16, 1998, the OHR1 on April 23, 1998, and the MSR4 on April 30, 1998 constitute a nearly Lagrangian sample set, and are referred to as the second Lagrangian set.

Analytical Methods

Analysis of $\delta^{15}N$ and $\delta^{18}O$ of NO_3 in Water

Details of the water sample collection protocol used are given in Battaglin and others (1997) and Chang and others (1999). In early 1997, water samples for isotope analysis were passed through 2 ml of anion exchange resin to isolate the NO_3 from the samples (Silva and others, 2000). In most of the previous studies, and in many samples collected in this study, large volumes of water (up to 20 liters) were passed through exchange columns in order to obtain sufficient NO_3 for isotope analysis. However, when the anion capacity of the columns is exceeded because of the high concentrations of other anions, the competition for exchange sites may result in isotopic fractionation (Silva and others, 2000). The highly variable chemistry of samples collected within the Mississippi River basin posed a significant challenge to the single column method used, especially when concentrations of SO_4, Cl, and HCO_3 were high relative to NO_3. After analyzing the water-quality data collected concurrently with each isotope sample, it was determined that many samples collected and processed in 1997 exceeded the anion exchange capacity of the columns. These samples were not analyze for the isotope ratios of NO_3.

Later in 1997 and in 1998, this problem was alleviated by using larger anion columns with 5 ml of resin and a cation column in front of the anion column to reduce concentrations of adsorbed organic constituents and neutralize HCO_3 (Chang and others, 1999). The cation column protonates and/or adsorbs

Table 4. Nitrite plus nitrate concentration, daily mean discharge and δ^{15}N and δ^{18}O of NO_3 values in water samples collected in 1997–98 (*, results not available)

Sampling station name and station number	Sample ID	Sample collection date	Daily mean discharge in cubic feet per second	Nitrite plus nitrate as N in mg/L[1]	Average δ^{15}N in per mil	Average δ^{18}O in per mil
		Large river stations				
Mississippi River at Clinton, IA - 05420500	IS-119	6/2/97	60,900	0.449	12.1	15.5
	IS-112	9/2/97	53,300	0.914	9.4	10.0
	IS-33	5/13/98	58,500	1.82	10.4	11.0
	IS-34	5/13/98	58,500	1.85	10.4	9.5
	IS-42	5/27/98	56,600	1.22	10.3	10.5
	IS-56	6/10/98	48,600	2.00	9.9	15.0
	IS-60	7/1/98	101,000	3.00	11.0	9.0
	IS-76	7/28/98	41,400	1.51	10.5	11.0
	IS-83	8/25/98	38,000	0.620	9.2	17.5
	IS-84	8/25/98	38,000	0.624	lost during preparation	
	IS-97	9/23/98	23,000	0.850	8.5	15.0
Missouri River at Hermann, MO - 06934500	IS-26	4/20/98	159,000	1.90	8.1	9.5
	IS-45	6/1/98	87,400	2.12	8.4	14.0
	IS-64	7/7/98	159,000	1.20	8.3	14.0
	IS-86	8/31/98	86,700	1.27	8.8	13.0
Mississippi River at Thebes, IL - 07022000	IS-101	6/11/97	247,000	2.55	6.9	7.5
	IS-25	4/16/98	574,000	3.60	7.0	6.5
	IS-50	6/10/98	284,000	3.20	7.8	7.0
	IS-51	6/10/98	284,000	3.63	7.7	3.0
	IS-74	7/22/98	272,000	3.43	8.5	12.0
	IS-91	9/9/98	130,000	1.27	12.4	21.0
Ohio River at Grand Chain, IL - 03612500	IS-102	6/12/97	653,000	2.47	3.1	7.0
	IS-27	4/23/98	734,000	1.10	5.7	10.5
	IS-44	6/5/98	366,000	1.73	6.3	9.5
	IS-77	7/22/98	260,000	1.38	6.0	11.0
	IS-78	7/22/98	260,000	1.38	lost during preparation	
	IS-85	8/12/98	185,000	0.73	4.8	too little N
Yazoo River below Steele Bayou near Long Lake, MS - 07288955	IS-103	6/19/97	24,800	0.743	3.8	9.0
	IS-19	4/13/98	11,900	0.380	2.8	11.0
	IS-57	6/17/98	6,840	0.890	4.8	6.5
	IS-66	7/16/98	25,600	0.480	9.1	24.0
	IS-96	9/17/98	9,310	0.206	3.6	18.0
Mississippi River, St. Francisville, LA - 07373420	IS-117	5/6/97	1,006,000	1.43	6.3	7.5
	IS-106	6/19/97	1,079,000	2.01	4.0	7.5
	IS-10	4/2/98	1,213,000	1.50		ruined in the field
	IS-11	4/2/98	1,213,000	1.50		ruined in the field
	IS-31	4/30/98	1,266,000	1.97	6.5	8.5
	IS-32	4/30/98	1,266,000	1.98	6.3	7.5
	IS-49	6/9/98	739,000	2.06	7.1	7.5
	IS-63	7/9/98	1,053,000	2.70	7.8	7.0
	IS-99	9/28/98	309,000	0.81	9.4	14.0
Mississippi River at Vicksburg, MS - 07289000	IS-2A	1/13/98	933,000	0.87	ruined lab	11.0
	IS-2B	1/13/98	933,000	0.87	8.0	12.5
	IS-2C	1/13/98	933,000	0.87	7.7	17.5

Table 4. Nitrite plus nitrate concentration, daily mean discharge and δ^{15}N and δ^{18}O of NO_3 values in water samples collected in 1997–98 (*, results not available)—Continued

Sampling station name and station number	Sample ID	Sample collection date	Daily mean discharge in cubic feet per second	Nitrite plus nitrate as N in mg/L[1]	Average δ^{15}N in per mil	Average δ^{18}O in per mil
Large river stations—Continued						
Mississippi River at Belle Chasse, LA - 07374525	IS-118	5/7/97	823,000[1]	1.23	6.4	8.5
	IS-105	6/20/97	937,000[1]	1.81	3.4	7.5
Small stream stations						
S. Fork Iowa River northeast of New Providence, IA - 05451210	IS-3A	1/30/98	23	4.30	12.9	10.5
	IS-3B	1/30/98	23	4.30	12.9	9.5
	IS-3C	1/30/98	23	4.30	12.9	10.5
	IS-5	3/30/98	329	13.0	8.2	5.5
	IS-8	3/30/98	329	12.0	7.6	5.0
	IS-41	5/29/98	833	15.4	5.3	6.0
	IS-79	8/3/98	33	7.79	10.9	10.5
Fourmile Creek near Traer, IA - 05464137	IS-107	6/30/97	*	14.9	3.1	5.5
	IS-20	4/15/98	54.1	18.0	4.1	3.5
	IS-67	7/16/98	23.4	16.0	5.5	9.5
	IS-80	8/12/98	9.06	12.0	4.8	9.0
Walnut Creek near Vandalia, IA - 05487550	IS-104	6/21/97	21	9.69	4.9	8.0
	IS-9	4/3/98	52	11.0	4.7	5.0
	IS-28	5/7/98	167	9.72	3.7	4.5
	IS-29	5/7/98	167	9.20	3.8	4.0
	IS-54	6/11/98	100	5.57	5.4	5.0
Panther Creek near El Paso, IL - 05567000	IS-115	11/13/97	14	11.5	12.3	ruined in the lab
	IS-16	4/9/98	151	18.0	5.6	5.5
	IS-48	6/9/98	100	16.2	7.2	6.0
	IS-61	7/7/98	145	12.0	8.5	8.0
Indian Creek near Wyoming, IL - 05568800	IS-111	8/27/97	36	9.65	7.8	8.0
	IS-15	4/9/98	261	12.0	5.1	4.5
	IS-39	5/25/98	80	11.7	5.6	6.0
	IS-72	7/22/98	97	7.72	6.3	9.5
	IS-73	7/22/98	97	7.68	9.7	9.5
Sugar Creek at Co Rd 400 S at New Palistine, IN - 03361650	IS-13	4/9/98	439	2.30	6.3	7.5
	IS-38	5/24/98	414	8.48	5.5	8.0
Little Buck Creek near Indianapolis, IN - 03353637	IS-113	9/9/97	4.0	0.862	3.3	31.0
	IS-14	4/9/98	305	0.79	2.4	too little N
	IS-37	5/24/98	131	1.28	3.5	4.0
	IS-71	7/20/98	44	0.57	1.9	25.0
North Dry Creek near Kearney, NE - 06770195	IS-6	4/1/98	31	8.00	8.3	9.0
	IS-40	5/22/98	83	5.30	7.7	10.5
	IS-43	6/8/98	37	7.70	8.3	8.5
	IS-92	9/9/98	10	7.01	9.4	13.5
Dismal River near Thedford, NE - 06775900	IS-17	4/13/98	225	0.460	5.1	11.0
	IS-36	5/19/98	225	0.500	3.2	14.5
	IS-55	6/16/98	219	0.421	5.0	6.0
	IS-95	9/15/98	219	0.498	4.2	8.0

Table 4. Nitrite plus nitrate concentration, daily mean discharge and δ^{15}N and δ^{18}O of NO_3 values in water samples collected in 1997–98 (*, results not available)—Continued

Sampling station name and station number	Sample ID	Sample collection date	Daily mean discharge in cubic feet per second	Nitrite plus nitrate as N in mg/L[1]	Average δ^{15}N in per mil	Average δ^{18}O in per mil
Small stream stations—Continued						
South Fabius River near Taylor, MO - 05500000	IS-23	4/7/98	685	0.780	7.4	11.5
	IS-46	6/2/98	213	0.600	8.1	6.5
	IS-75	7/27/98	55	0.284	11.9	18.0
	IS-89	9/1/98	15	0.006		too little N
Elk River near Tiff City, MO - 07189000	IS-24	4/14/98	767	1.10	10.3	11.0
	IS-52	6/9/98	318	1.73	9.6	6.0
	IS-68	7/14/98	240	0.88	13.0	8.5
	IS-87	9/2/98	72	0.396	13.4	10.5
	IS-88	9/2/98	72	0.398	13.0	8.0
Shingle Creek at Queen Ave. N., MN - 05288705	IS-108	7/7/97	27	0.327	0.9	21.5
	IS-12	4/6/98	56	0.510	15.5	too little N
	IS-30	5/8/98	45	0.443	-1.2	23.5
	IS-53	6/11/98	5.2	0.183	1.6	19.5
	IS-62	7/8/98	5.5	0.217	5.9	19.0
Little Cobb River near Beauford, MN - 05320270	IS-109	7/16/97	162	9.71	5.6	7.0
	IS-114	10/28/97	19	8.16	9.2	6.5
	IS-1A	1/14/98	2.1	8.0	11.7	8.5
	IS-1B	1/14/98	2.1	8.0	12.0	9.0
	IS-1C	1/14/98	2.1	8.0	12.1	9.0
	IS-4	3/30/98	381	14.0	6.3	7.0
	IS-7	3/30/98	381	14.0	6.3	4.5
	IS-35	5/18/98	166	16.0	6.5	5.0
	IS-70	7/15/98	64	7.4	9.3	5.0
	IS-90	8/17/98	2.8	<0.002		too little N
Namekagon River at Leonards, WI - 05331833	IS-116	11/11/97	105	0.12	2.8	14.0
	IS-21	3/30/98	458	0.140	-1.4	20.0
	IS-47	6/2/98	195	0.041	8.1	too little N
	IS-69	7/15/98	102	0.015		too little N
	IS-94	9/9/98	51	0.053	6.9	20.0
Rattlesnake Creek near North Andover, WI - 05413449	IS-110	8/1/97	*	5.98	6.3	5.5
	IS-22	4/15/98	32	7.4	9.5	5.0
	IS-59	6/19/98	70	6.7	10.3	11.5
	IS-81	8/21/98	29	7.0	6.4	9.0
	IS-82	8/21/98	29	7.0	6.5	8.5
	IS-98	9/22/98	26	7.98	9.0	10.0
Bogue Phalia near Leland, MS - 07288650	IS-18	4/14/98	41	0.006		too little N
	IS-58	6/18/98	126	0.860	7.5	9.0
	IS-65	7/15/98	2,080	1.10	10.3	43.5
	IS-93	9/16/98	218	0.187	9.6	21.0

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[1] Low-level analyses (reporting limit of 0.002 mg/L) were conducted by the USGS Quality of Water Unit in Ocala, Florida.

[2] Calculated as the sum of the instantaneous discharge at the time of sample collection, plus the discharge out the Old River Diversion 2 days earlier.

dissolved organic carbon (DOC), thereby making it less likely for the DOC to compete with NO_3 for exchange stations on the anion column (Chang and others, 1999). About 200 µmol of NO_3 (equivalent to about 2.8 mg of N) was required for the dual isotope analysis. A special low-level analyses (0.002 mg/L reporting limit) for NO_2 plus NO_3 (table 4) conducted at the USGS Quality of Water Unit in Ocala, Florida, was used along with estimated concentrations of other anions from historic data to determine how much water to pass through the exchange column pair and to test for NO_3 passing through the column pair. Both the minimum volume needed to obtain sufficient NO_3 and the maximum volume that would avoid exceeding the anion column exchange capacity were considered to determine the sample volume to be processed.

To verify that all of the sample NO_3 was adsorbed by the anion column, eluent that passed through the cation and anion exchange columns was saved and a sub-sample analyzed for NO_2 plus NO_3. If 95% or more of the NO_3 was retained by the anion column, the sample was analyzed for $\delta^{15}N$ and $\delta^{18}O$ of NO_3 isotope ratios values using methods described by Silva and others (2000). If more than 5% of the NO_3 was not retained by the anion column the sample was not analyzed for $\delta^{15}N$ and $\delta^{18}O$ of NO_3 values. Dissolved organic carbon (DOC) and other non-nitrate oxygen bearing species are eliminated during this laboratory preparation procedure. Oxygen-isotope analyses were performed on a Finnigan Mat 251 (the use of trade names here or elsewhere in this report does not constitute an endorsement by the USGS) stable isotope mass spectrometer and nitrogen isotope analyses were performed on an Optima mass spectrometer. N isotope values ($\delta^{15}N$) are reported in per mil (‰) relative to atmospheric N_2, which by definition has a $\delta^{15}N$ of 0‰. Oxygen isotope values ($\delta^{18}O$) are reported in ‰ relative to the standard VSMOW (Vienna Standard Mean Ocean Water), also defined as 0‰.

Analysis of $\delta^{15}N$, $\delta^{13}C$, and $\delta^{34}S$ of Suspended POM in Water

Suspended sediment was collected with each sample for isotopic analysis of $\delta^{15}N$, $\delta^{13}C$, and $\delta^{34}S$ of the POM. Details of suspended sediment sample collection and analysis are given in Battaglin and others (1997) and Kendall and others (2001). Approximately 1 liter of water was filtered through a 0.7-micrometer heat-cleaned glass-fiber filter (142-mm diameter) with a peristaltic pump and an aluminum plate filter. After filtration the glass fiber filter was sealed in aluminum foil and a plastic bag and then frozen.

In the laboratory, filters were thawed and scraped and the resulting material was freeze-dried and ground to a fine powder. After acidification (Kendall and others, 2001), the POM samples were analyzed for carbon and nitrogen isotopic and elemental composition on a Carlo Erba 1500 elemental analyzer attached to a Micromass Optima mass spectrometer. Isotopic compositions are reported in per mil (‰) relative to atmospheric air for nitrogen and VPDB (Vienna Pee Dee Belemnite) for carbon. Due to problems with equipment, and in many cases an insufficient amount of material, POM samples were not analyzed for $\delta^{34}S$.

Nutrients and Major Ions

All samples were analyzed for nutrient concentrations including NO_2 plus NO_3, NO_2, ammonia, ammonia plus organic nitrogen, orthophosphate, and total phosphorus. The samples were analyzed by automated colorimetric procedures (Fishman and Friedman, 1989) at the USGS NWQL. The method reporting limit for NO_2 plus NO_3 as N is 0.05 mg/L. Samples also were analyzed for calcium, chloride, magnesium, potassium, sodium, and sulfate by standard analytical methods (Fishman and Friedman, 1989).

Discharge and Physical Properties

Specific conductance, pH, and water temperature were measured at the time samples were collected. Water-discharge normally was measured with current meters. These measurements were used to confirm or adjust a rating for converting river stage to water discharge. At most stations, estimates of daily mean discharge for the dates of sample collection were calculated, and are available in the USGS Water-Data Reports for the states in the study area.

GIS Data and Analysis

A geographic information system (GIS) was used to manage spatial information on station locations and associated drainage basins and to quantify land cover within the drainage basins. Land cover data are derived from two sources: (1) Gridded and reclassified Advanced Very High Resolution Radiometer (AVHRR) data (D. Wolock, U.S. Geological Survey, written commun., 2000), and (2) the National Land Cover Data (NLCD) (U.S. Geological Survey, 2000). The AVHRR data were used to quantify land cover in the large river and small stream basins; the pixels in the AVHRR data set are 1000 meters on a side. Estimates of percent land cover in each basin using AVHRR are given in tables 2, and the spatial distribution of land cover within the Mississippi River basin is shown in figure 1.

The NLCD data also were used to quantify land cover in the small stream basins. Landsat Thematic Mapper (TM) data and supporting information, including topography, census data, agricultural statistics, soil characteristics, other land-cover maps, and wetlands data were used to determine and label the land-cover type for each 30 meter pixel in the NLCD. Estimates of percent land cover for each small stream basin are given in table 3. An example of spatial distribution of land cover within one of the small-river basins is shown in figure 4 (plots for all 16 smaller river basins can be viewed in the web version of this report at http://wwwrcolka.cr.usgs.gov/midconherb/on.line.rep.html).

Quality Assurance

Sample Collection

Quality assurance (QA) samples were collected at selected stations to assess the variability and bias of the measured isotope ratios. Eighteen pairs of field-collected QA samples were analyzed for $\delta^{15}N$ and $\delta^{18}O$ of NO_3 in water and eight pairs were analyzed for $\delta^{15}N$ and $\delta^{13}C$ of the suspended POM. All QA samples were concurrent duplicates, which are two samples collected concurrently in the same location but processed, handled, and analyzed separately.

NO_3 in Water Isotope Analysis

Details of laboratory QA procedures used for isotope analysis are reported in Kendall and Grim (1990), Chang and others, (1999), and Silva and others, (2000). The standard error (Iman and Conover, 1983) of analysis of laboratory standards for $\delta^{15}N$ of NO_3 was ±0.05‰ (n=10), and for $\delta^{18}O$ of NO_3 was ±0.21‰ (n=19). For simulated field samples (a solution containing KNO_3 reagent and DOC in deionized water), the standard error (n=12) was ±0.07‰ for $\delta^{15}N$ and ±0.36‰ for $\delta^{18}O$ (Chang and others, 1999). Eighteen pairs of concurrent duplicate water samples collected during this study are used to identify both sampling and laboratory precision (variability) NO_3 concentration, and for $\delta^{15}N$ and $\delta^{18}O$ of NO_3 values reported in this study. These include duplicate samples collected in 1997–98 from stations on both large rivers and smaller streams (Battaglin and others, 1997). The standard error of the differences between the pairs of samples is ±0.11 mg/L for NO_3 (n=11), ±0.22‰ for $\delta^{15}N$ of NO_3 (n=16), and ±0.58‰ for $\delta^{18}O$ of NO_3 (n=18). The distributions of the difference values are shown in figure 5(a). The mean of the differences between NO_3 concentrations is 0.18 mg/L, between $\delta^{15}N$ values is 0.38‰, and between $\delta^{18}O$ values is 1.6‰. The standard errors for $\delta^{15}N$ and $\delta^{18}O$ quantified from QA samples are significantly larger than those from laboratory standards or simulated field samples. This difference suggests either that sample handling introduces significant variability, or that matrix effects in natural waters from the Mississippi basin are more difficult to account for than those of snowmelt samples, for which the analytical method was originally developed.

Particulate Organic Material Isotope Analysis

Details of laboratory QA procedures used for isotope analysis of POM samples are reported in Kendall and others (2001). Analytical precision for laboratory standards is ±0.15 ‰ for both $\delta^{15}N$ and $\delta^{13}C$ of POM (Kendall and others, 2001). Eight pairs of concurrent duplicate QA samples are used to identify sampling and laboratory precision (variability) for $\delta^{15}N$ and $\delta^{13}C$ of POM values. The standard error of the differences between the pairs of samples is ±0.30‰ for $\delta^{15}N$ (n=7) and ±0.31‰ for $\delta^{13}C$ (n=8). Distributions of the difference values are shown in figure 5(b). The mean of the absolute value of differences between $\delta^{15}N$ values is 0.60‰ and between $\delta^{13}C$ values is 0.71‰. The standard errors for $\delta^{15}N$ and $\delta^{13}C$ of POM from QA samples are significantly larger than those from laboratory standards. This is probably caused by insufficient homogenization of the POM samples.

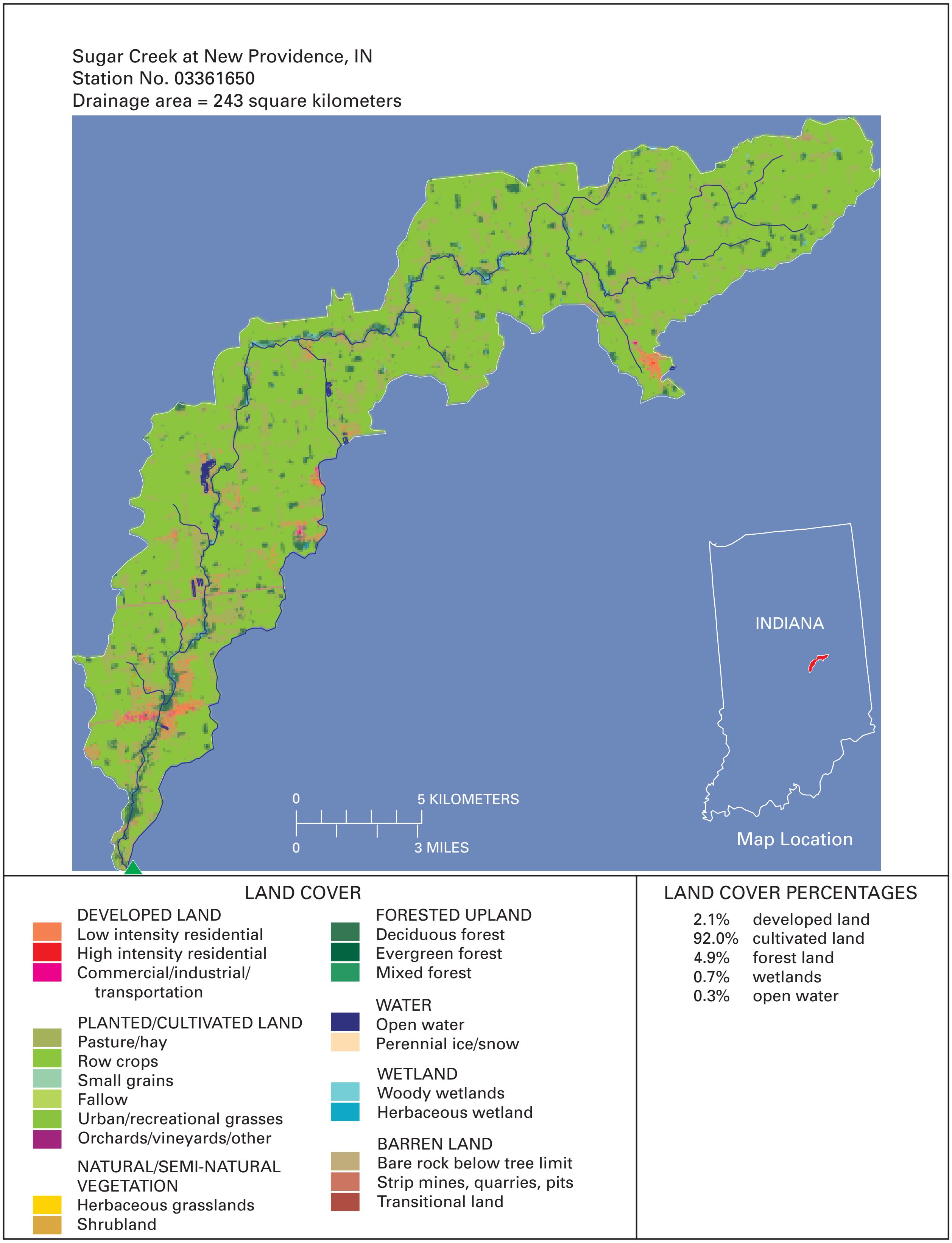

Figure 4. Land cover in the Sugar Creek at New Providence, Indiana, basin.

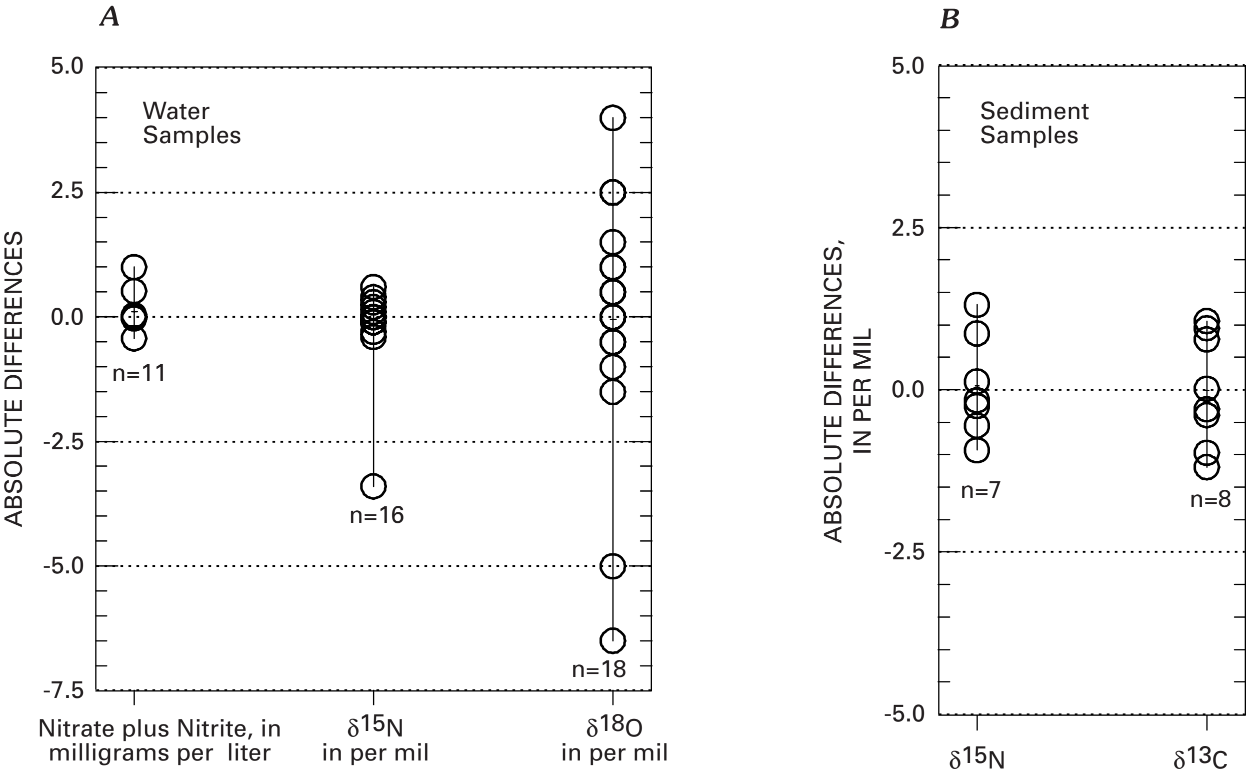

Figure 5. Differences between: (*A*) NO_2 plus NO_3 concentrations (in mg/L), and $\delta^{15}N$ and $\delta^{18}O$ of NO_3 values (in per mil) in 18 pairs of concurrent duplicate water samples; and (*B*) $\delta^{15}N$ and $\delta^{13}C$ of POM values (in per mil) in 8 pairs of field collected concurrent duplicate sediment samples.

RESULTS

$\delta^{15}N$ and $\delta^{18}O$ of NO_3 Isotope Ratio Values

The $\delta^{15}N$ and $\delta^{18}O$ of NO_3 isotope ratio values, the concentration of NO_2 plus NO_3 from the low-level (Ocala) analysis, and the daily mean discharge for samples from 1997 and 1998 are listed in table 4, and statistically summarized in table 5. Discharge measurements ranged from 2.1 to 1,266,000 cubic feet per second (cfs). The concentration of NO_2 plus NO_3 ranged from less than the reporting limit of 0.002 mg/L to 18.0 mg/L. The $\delta^{15}N$ values ranged from –1.4‰ to +15.5‰, while the $\delta^{18}O$ values ranged from +3.0‰ to +43.5‰ (table 5). In the following sections, the results are analyzed by drainage basin size (large basins verses small basins) and for the small basins, by dominant land cover type within the drainage basin.

Large Rivers

The largest discharge values (6,840 to 1,266,000 ft^3/s) are from the large river stations. The ranges of NO_2 plus NO_3 concentrations and isotope ratio values from the large river stations are generally narrow and near the middle of their ranges in measurements from all stations. The concentration of NO_2 plus NO_3 ranges from 0.2 to 3.6 mg/L, the $\delta^{15}N$ of NO_3 values range from +2.8‰ to +12.4‰, and the $\delta^{18}O$ of NO_3 values range from +3.0‰ to +24.0‰ (table 5). The fact that the isotope ratio values from the large river stations are within the range of values in smaller streams supports the theory that N exported from tributaries is not significantly altered by denitrification in the Mississippi and its major tributaries (Goolsby and others, 1999; Alexander and others, 2000).

Time-series plots of the data should show whether there are significant temporal and spatial variations in NO_3 $\delta^{15}N$ and $\delta^{18}O$ of NO_3 values in Mississippi River water and its major tributaries. There are insufficient data from 1997 to identify a temporal trend in the results (fig. 6). However, the $\delta^{15}N$ and $\delta^{18}O$ of NO_3 values (fig. 6b and 6c) from the most up-stream station, the Mississippi River at Clinton (fig. 3, map no. 1), are distinct from the values at down stream stations such as the Mississippi River at St. Francisville (fig. 3, map no. 6a). Looking at the samples from the first Lagrangian set (collected in June, 1997), one can also see that the $\delta^{15}N$ of NO_3

Table 5. Statistical summary of δ^{15}N and δ^{18}O of nitrate values, nitrite plus nitrate concentrations, and daily mean discharges in water sampled collected in 1997–98

Parameter	Number of analyses	Minimum value	Maximum value	Mean value	Median value	Standard deviation
All stations						
Nitrite plus nitrate, in mg/L	124	<0.002	18.0	4.3	1.8	4.83
δ^{15}N, in per mil	115	-1.4	15.5	7.3	7.4	3.21
δ^{18}O, in per mil	111	3.0	43.5	10.6	9.0	6.08
Daily mean discharge, in cfs	122	2.1	1,266,000	156,660	232	331,040
Large river stations						
Nitrite plus nitrate, in mg/L	46	0.2	3.6	1.6	1.4	0.87
δ^{15}N, in per mil	41	2.8	12.4	7.5	7.8	2.46
δ^{18}O, in per mil	41	3.0	24.0	11.1	10.5	4.31
Daily mean discharge, in cfs	46	6,840	1,266,000	415,220	253,500	430,079
Small stream stations with basins dominated by row crop agriculture and/or livestock production						
Nitrite plus nitrate, in mg/L	22	0.4	15.4	6.2	6.9	3.98
δ^{15}N, in per mil	22	5.3	13.4	9.6	9.5	2.54
δ^{18}O, in per mil	22	5.0	13.5	8.8	9.0	2.37
Daily mean discharge, in cfs	21	10	833	162	37	238
Small stream stations with basins dominated by row crop agriculture						
Nitrite plus nitrate, in mg/L	38	0.01	18.0	8.4	8.8	5.60
δ^{15}N, in per mil	35	3.1	12.3	7.2	6.3	2.66
δ^{18}O, in per mil	34	3.5	43.5	8.8	7.3	7.11
Daily mean discharge, in cfs	37	2.1	2,080	190	97	354
Small stream stations with basins dominated by urban land						
Nitrite plus nitrate, in mg/L	9	0.2	1.3	0.58	0.51	0.35
δ^{15}N, in per mil	9	-1.2	15.5	3.8	2.4	4.81
δ^{18}O, in per mil	7	4.0	31.0	20.5	21.5	8.33
Daily mean discharge, in cfs	9	4.0	305	69	44	97
Small stream stations with basins dominated by undeveloped land						
Nitrite plus nitrate, in mg/L	9	0.02	0.50	0.25	0.14	0.21
δ^{15}N, in per mil	8	-1.4	8.1	4.2	4.6	2.88
δ^{18}O, in per mil	7	6.0	20.0	13.4	14.0	5.45
Daily mean discharge, in cfs	9	51	458	200	219	117

values from the Mississippi River at Thebes (+6.9‰), and the Ohio River at Grand Chain (+3.1‰) are substantially different and bracket the values from St. Francisville (+4.0‰) and Belle Chasse (+3.4‰) (fig. 6b). The δ^{18}O of NO_3 values from the Mississippi River at Thebes (+7.5‰) and the Ohio River at Grand Chain (+7.0‰) are similar, and are approximately equal to the values from the St. Francisville (+7.5‰) and Belle Chasse (+7.5‰) stations (fig. 6c).

These results support the theory that denitrification does not remove much of the NO_3 transported by the Mississippi River. However, the NO_3 concentration and resulting flux data conflict. NO_3 concentrations in samples from the Mississippi River at Thebes and the Ohio River at Grand Chain (2.55 mg/L and 2.47 mg/L, respectively in samples IS–101 and IS–102; table 4) are greater than those in samples from the Mississippi River at St. Francisville and Belle Chasse (2.01 mg/L and 1.81 mg/L, respectively in samples IS–106 and IS–105; figure 6d and table 4). The sum of the NO_3 fluxes from samples IS–101, IS–102, and IS–103 (Yazoo River) is ~4% larger than the flux calculated from sample IS–106 from the Mississippi River at St. Francisville, even though the sum of the discharges from the three samples is smaller (Battaglin and others, 2001). This difference suggests a mechanism other than denitrification decreases NO_3 flux in the lower Mississippi River. Battaglin and others (2001) provide a more complete analysis of the two sets of Lagrangian samples and suggest that assimilation by aquatic and riparian plants is a likely mechanism for that loss.

Temporal variability can be observed in the 1998 data (fig. 7) from the large river stations. In some

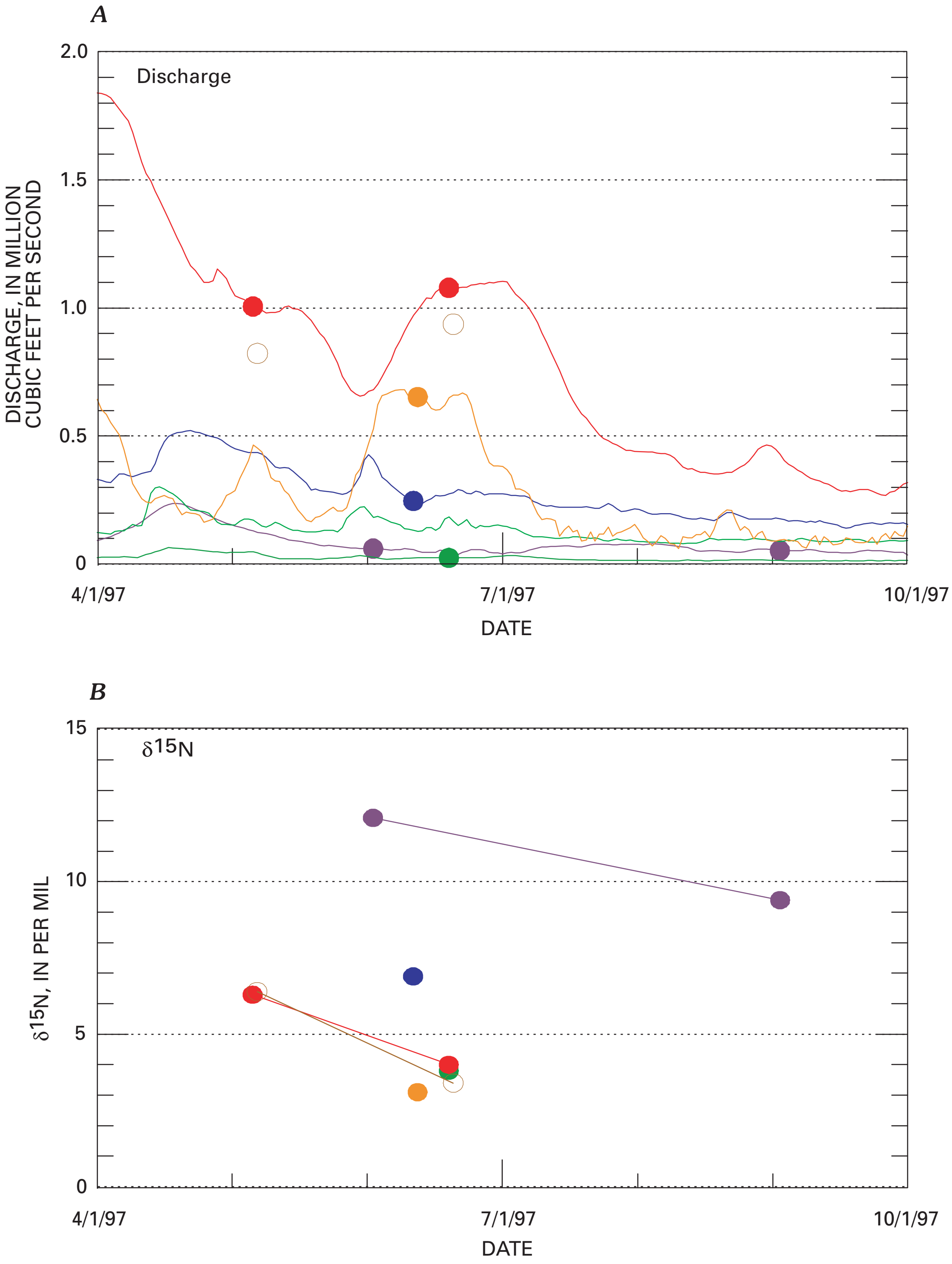

Figure 6. Time series of 1997 data for large river stations; (*A*) discharge, (*B*) $\delta^{15}N$, (*C*) $\delta^{18}O$, and (*D*) NO_2 plus NO_3.

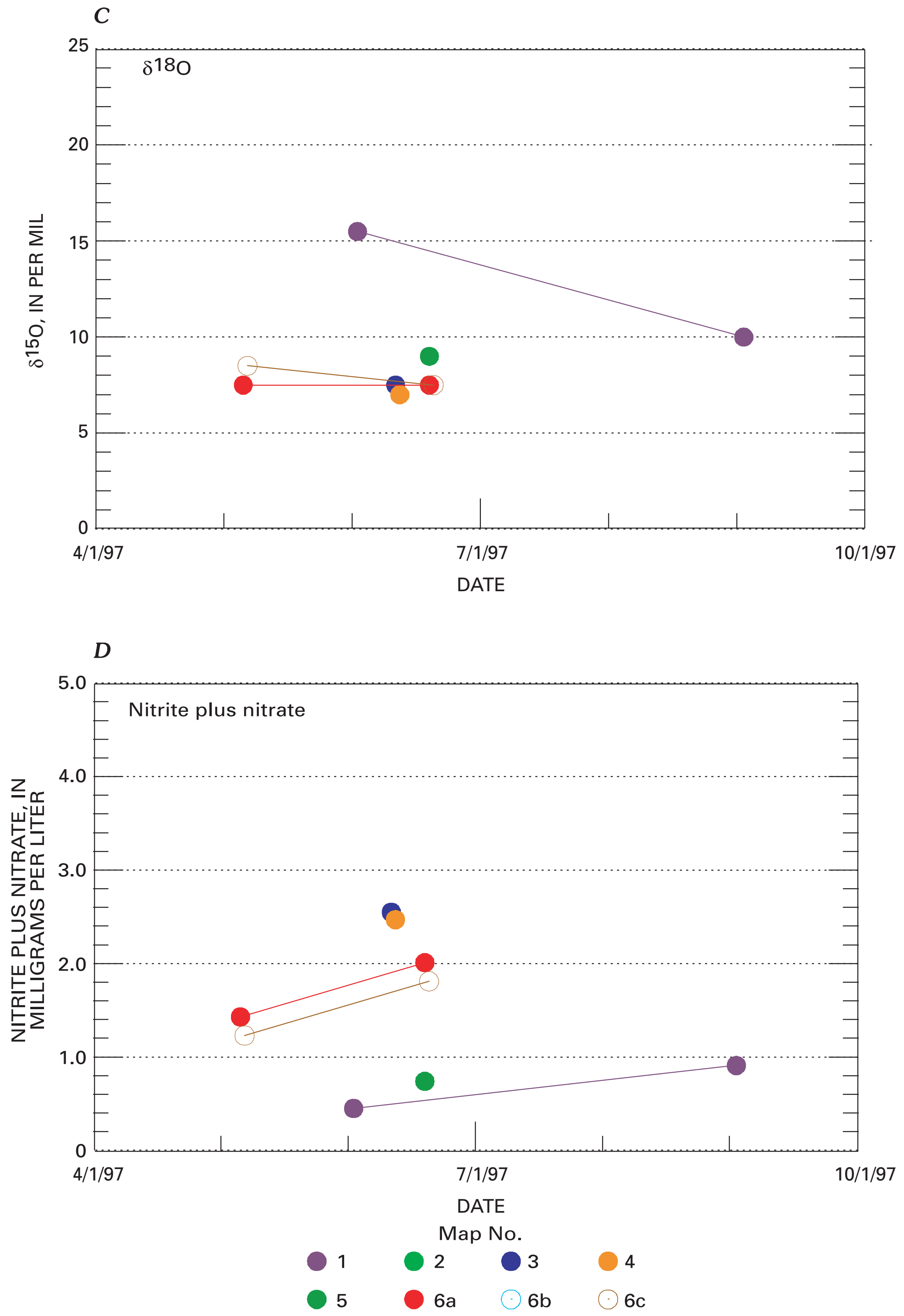

Figure 6. Time series of 1997 data for large river stations; (*A*) discharge, (*B*) δ^{15}N, (*C*) δ^{18}O, and (*D*) NO_2 plus NO_3—Continued.

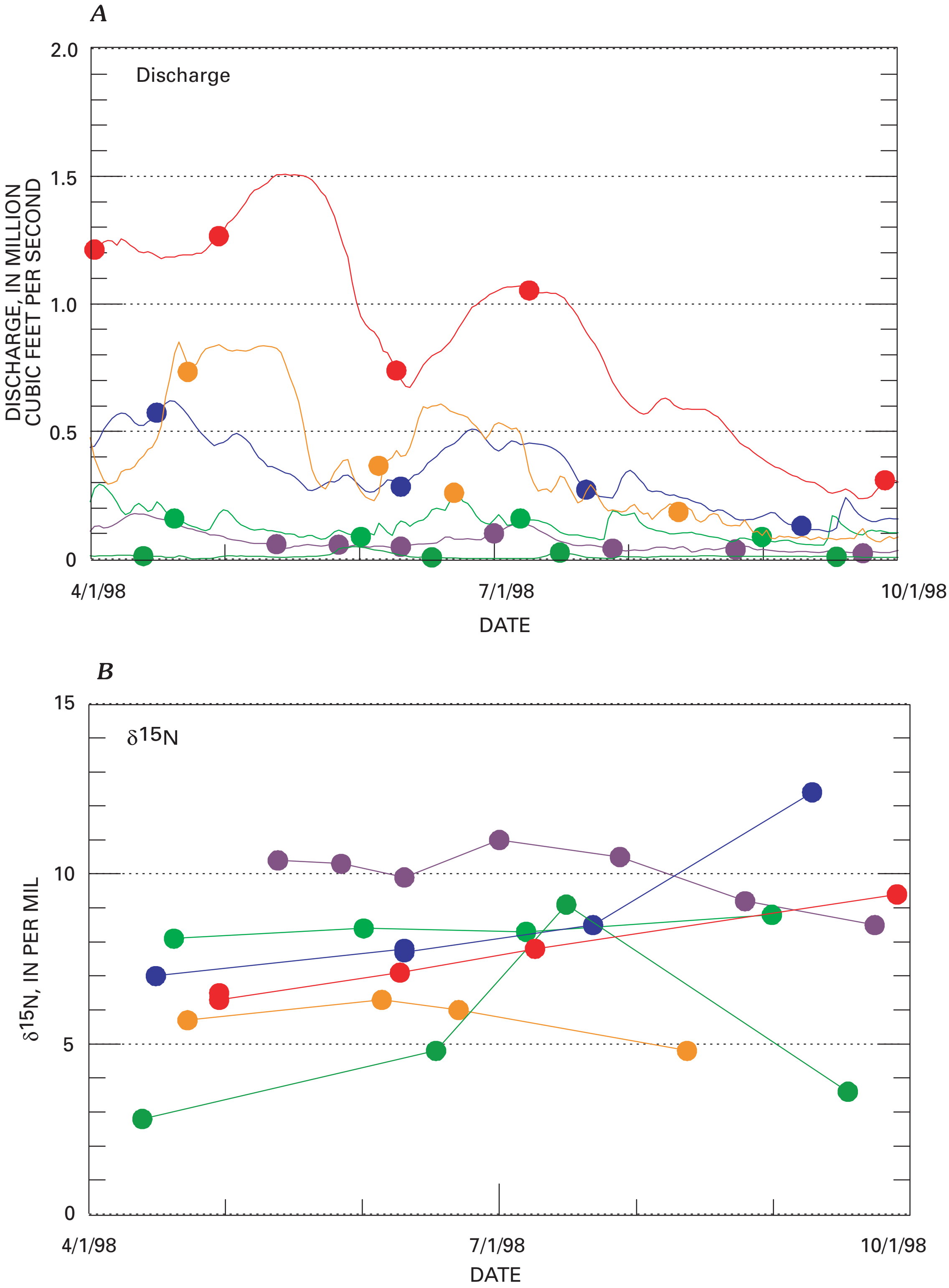

Figure 7. Time series of 1998 data for large river stations; (*A*) discharge, (*B*) $\delta^{15}N$, (*C*) $\delta^{18}O$, and (*D*) NO_2 plus NO_3.

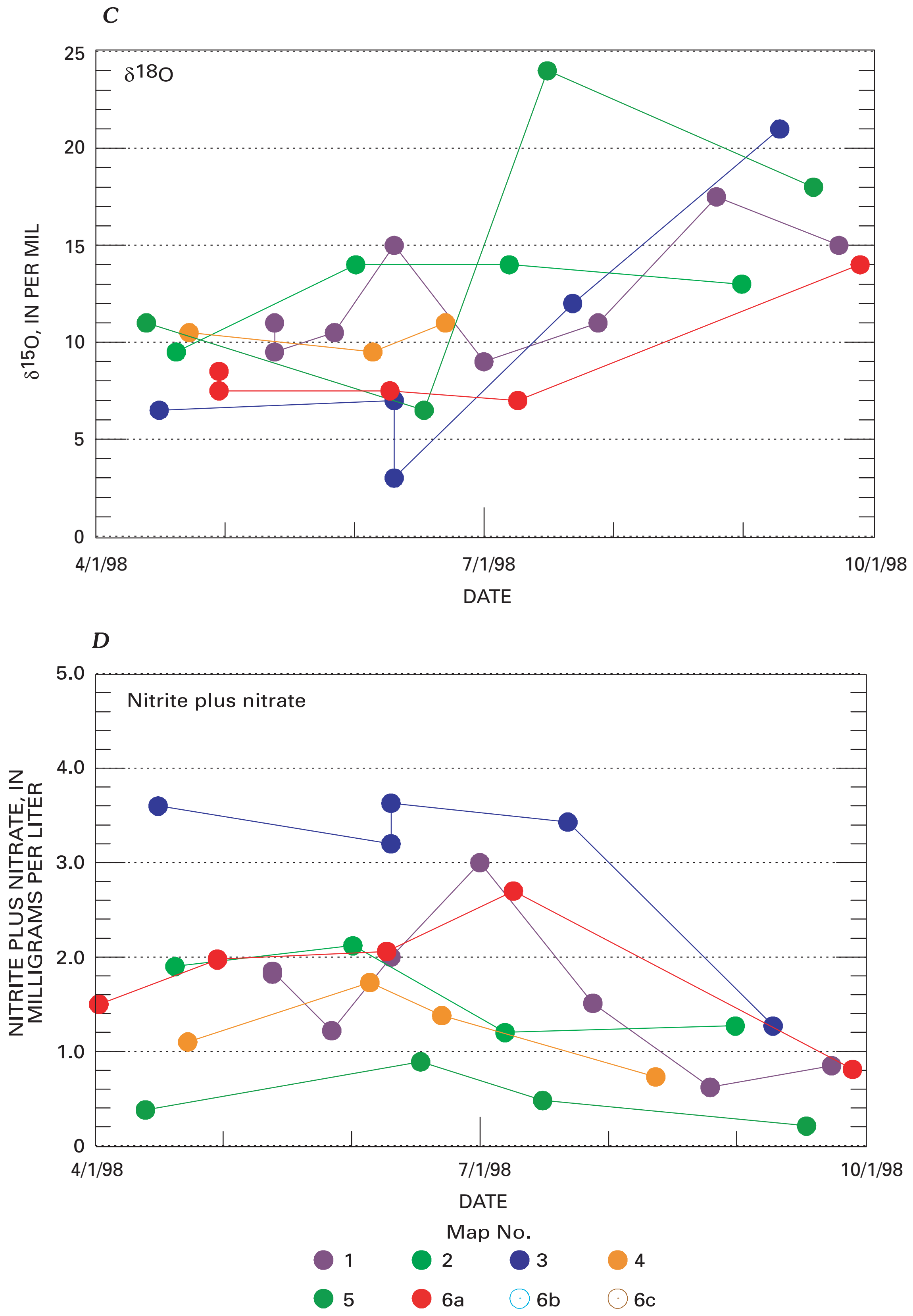

Figure 7. Time series of 1998 data for large river stations; (*A*) discharge, (*B*) $\delta^{15}N$, (*C*) $\delta^{18}O$, and (*D*) NO_2 plus NO_3.—Continued.

cases, both $\delta^{15}N$ and $\delta^{18}O$ of NO_3 values show a slight upward trend from April to September 1998, while NO_3 concentrations show a slight decreasing trend. The minor temporal differences in isotope values could be the result of mixing between or changing of NO_3 sources, or increased transformation of NO_3. The discharge decreased between April and September 1998 at most of the large river stations (fig. 7a). The surface-runoff component of stream flow is likely more dominant during spring and early summer, whereas the ground-water component of stream flow is more dominant under low-flow conditions in late summer and fall (Winter and others, 1998). Surface-runoff would be more likely to contribute recently applied fertilizer NO_3 or recently mineralized NO_3, while ground water would be more likely to contribute NO_3 that was applied to fields or mineralized months, years, or decades ago (BÖhlke and Denver, 1995).

Spatial variations in $\delta^{15}N$ and $\delta^{18}O$ of NO_3 values and NO_3 concentration in water from the Mississippi River and its major tributaries are also apparent (fig. 7). Nitrate concentrations are nearly always largest in the Mississippi River at Thebes (map no. 3) and smallest in the Yazoo River near Long Lake (map no. 5). The $\delta^{15}N$ and $\delta^{18}O$ of NO_3 values from the Mississippi River at Thebes (map no. 3), and the Ohio River at Grand Chain (map no. 4) stations are substantially different and again bracket the values from the Mississippi River at St. Francisville (map no. 6a).

Small Streams

The $\delta^{15}N$ and $\delta^{18}O$ of NO_3 isotope ratio values, the concentration of NO_2 plus NO_3, and the daily mean discharge for samples collected from small streams in 1997 and 1998 are given in table 4. A statistical summary of the small stream results, analyzed by the predominant land cover type in the drainage basins, is given in table 5. Discharge at stations in basins dominated by row crop agriculture and undeveloped land tended to be slightly higher than discharge at stations in basins dominated by urban land or row crops and/or livestock production (table 5; fig. 9a and 10a). This variability is likely a result of differences in basin size and local climatic variability, not directly a function of the land cover in the drainage basins.

We hypothesized that NO_3 in small streams draining areas dominated by distinctly different land use (corn and soybean production, livestock production, urban land, or undeveloped land) would have distinctly different $\delta^{15}N$ and $\delta^{18}O$ of NO_3 isotope ratio values (Battaglin and others, 1997). In figure 8, the ranges of NO_2 plus NO_3 concentrations and $\delta^{15}N$ and $\delta^{18}O$ of NO_3 values for samples from basins dominated by the four land cover types are shown in boxplots (Helsel and Hirsch, 1992). NO_2 plus NO_3 concentrations are significantly smaller in basins dominated by urban and undeveloped land compared to those dominated by row crops or row crops and/or livestock production. The maximum NO_3 concentration in basins dominated by urban or undeveloped land (1.12 mg/L) is exceeded by more than 75% of samples from basins dominated by row crops or row crops and/or livestock production (table 5, fig. 8). There is a difference in $\delta^{15}N$ of NO_3 values between basins dominated by urban or undeveloped land, and basins dominated by row crops or row crops and/or livestock production. The majority of $\delta^{15}N$ of NO_3 values from basins dominated by urban or undeveloped land are less than +5‰, while the majority of values from basins dominated by row crops or row crops and/or livestock production are greater than +5‰ (fig. 8). However, the range of $\delta^{15}N$ of NO_3 values from just the basins dominated by urban land nearly span the entire range of the data (table 5). There is also a difference in $\delta^{18}O$ of NO_3 values between basins dominated by urban or undeveloped land, and those dominated by row crops or row crops and/or livestock production. The majority of the $\delta^{18}O$ of NO_3 values from basins dominated by urban or undeveloped land are greater than +10‰, while the majority of values from basins dominated by row crops or row crops and/or livestock production are less than +10‰ (fig. 8). The range of $\delta^{18}O$ of NO_3 values from basins dominated by row-crops nearly span the entire range of the data (table 5).

Time-series plots should show if there are significant temporal and spatial variations in $\delta^{15}N$ and $\delta^{18}O$ of NO_3 values in small streams sampled in 1997 and 1998. There are insufficient data from 1997 to identify a temporal trend in the results (fig. 9), but some spatial variability is evident. $\delta^{15}N$ of NO_3 values from basins dominated by row crops (open circles) and row crop and/or livestock production (filled circles) tend to be greater than values from basins dominated by urban land (squares) or undeveloped land (triangles) (fig. 9b). The opposite pattern is evident for $\delta^{18}O$ of NO_3; values from basins dominated by urban or undeveloped land are greater than values from basins

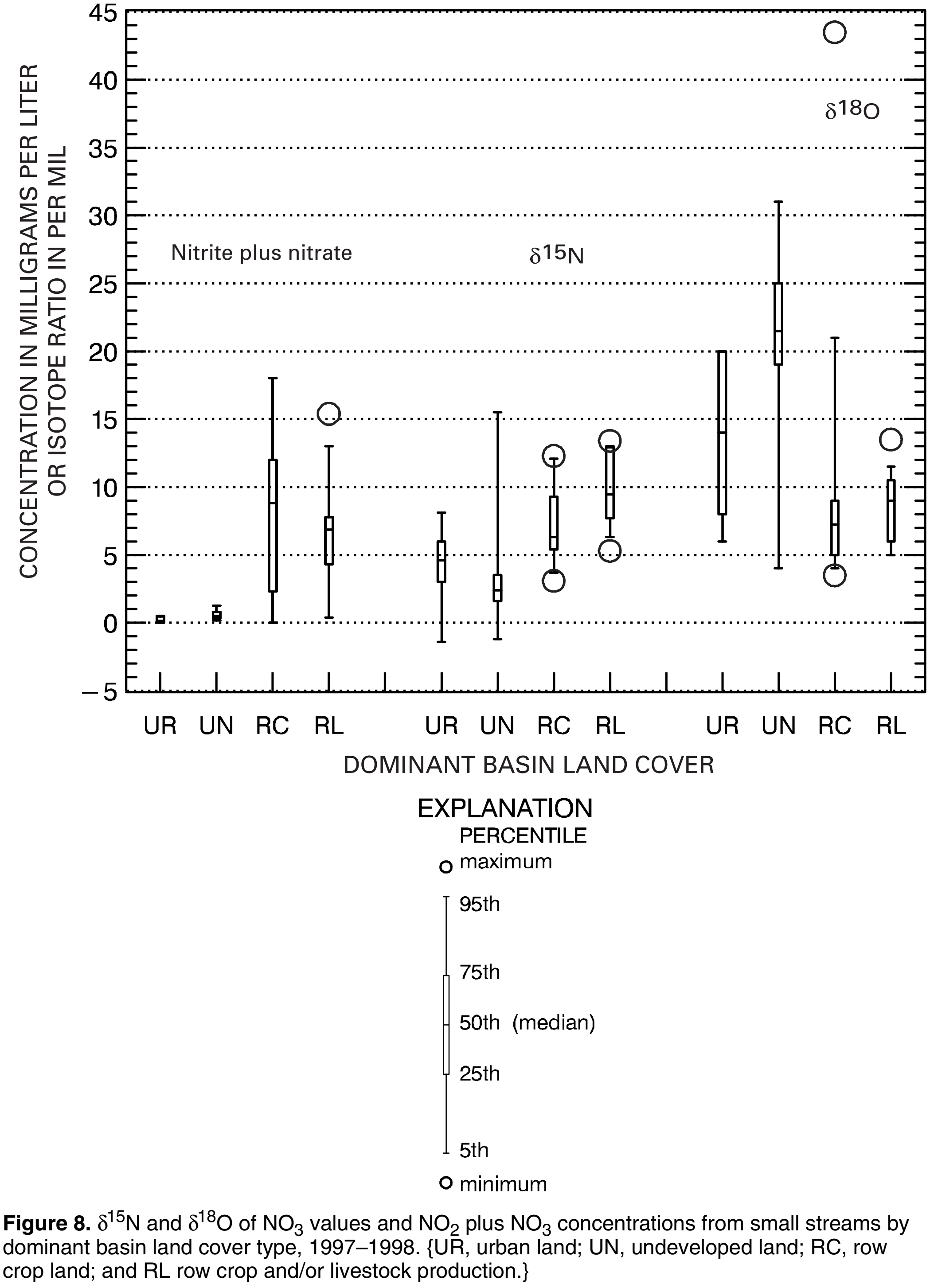

Figure 8. $\delta^{15}N$ and $\delta^{18}O$ of NO_3 values and NO_2 plus NO_3 concentrations from small streams by dominant basin land cover type, 1997–1998. {UR, urban land; UN, undeveloped land; RC, row crop land; and RL row crop and/or livestock production.}

dominated by row crops or row crops and/or livestock production (fig. 9c). NO_2 plus NO_3 concentrations in samples from basins dominated by row crops and row crops and/or livestock production are all greater than 5 mg/L while values from basins dominated by urban or undeveloped land are less than 1.5 mg/L (fig. 9d; table 5).

Some temporal variability is apparent in the 1998 data from the small stream stations. At some stations, $\delta^{15}N$ and $\delta^{18}O$ of NO_3 values decrease from January to May, then increase from May through September, 1998 (fig. 10b and 10c). NO_2 plus NO_3 concentrations show the opposite pattern, increasing from January to May, then decreasing from May

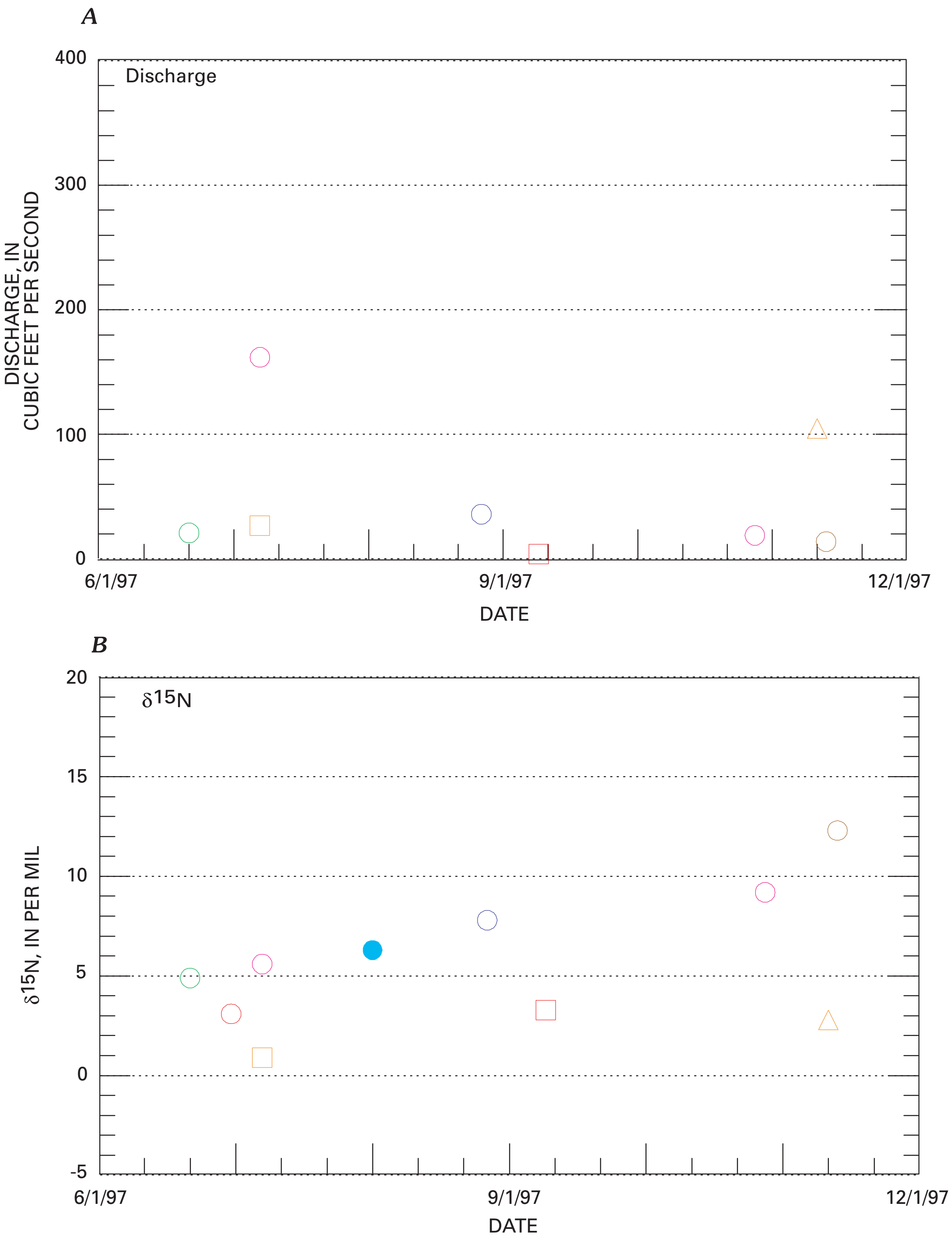

Figure 9. Time series of 1997 data for small stream stations; (*A*) discharge, (*B*) $\delta^{15}N$, (*C*) $\delta^{18}O$, and (*D*) NO_2 plus NO_3.

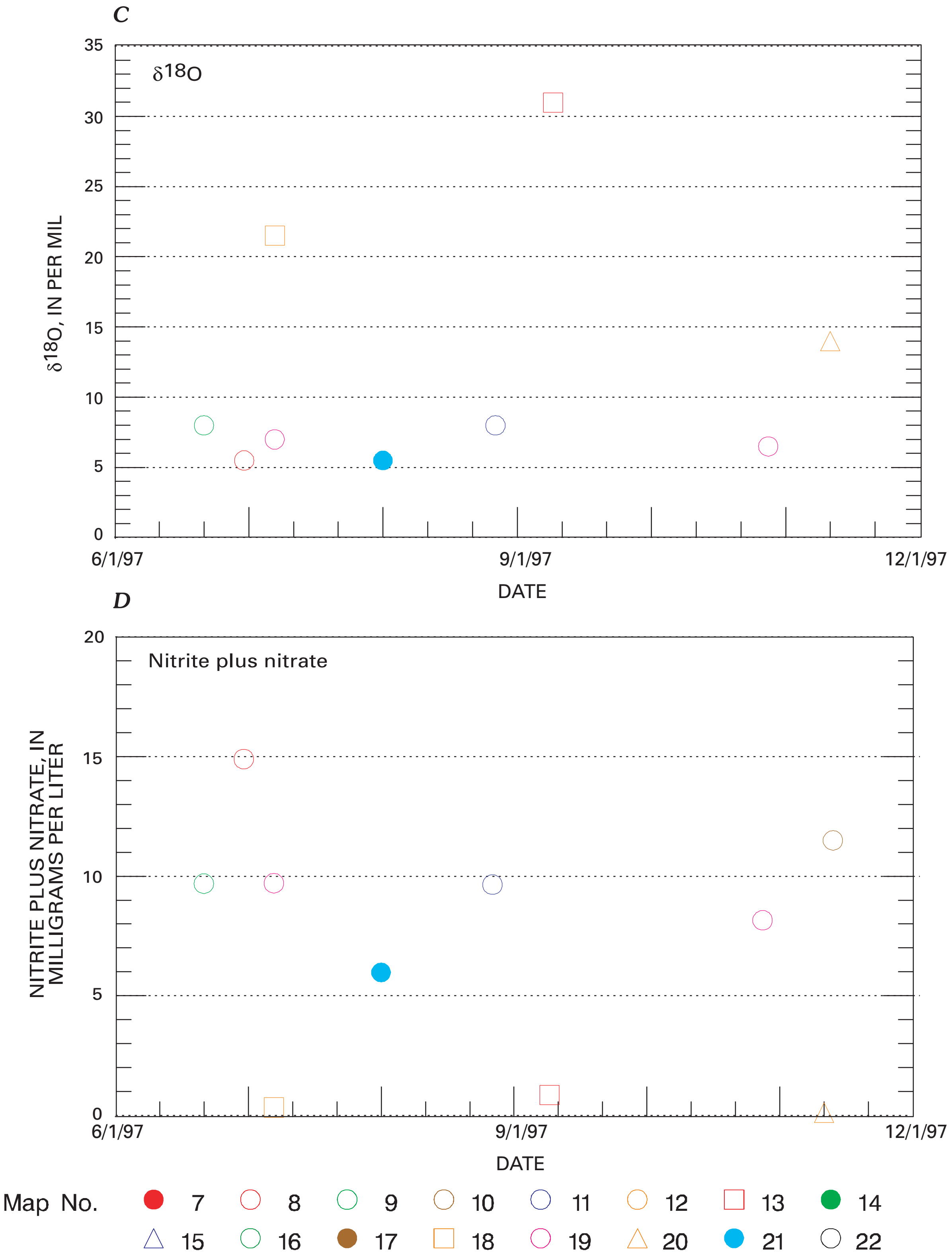

Figure 9. Time series of 1997 data for small stream stations; (*A*) discharge, (*B*) $\delta^{15}N$, (*C*) $\delta^{18}O$, and (*D*) NO_2 plus NO_3—Continued.

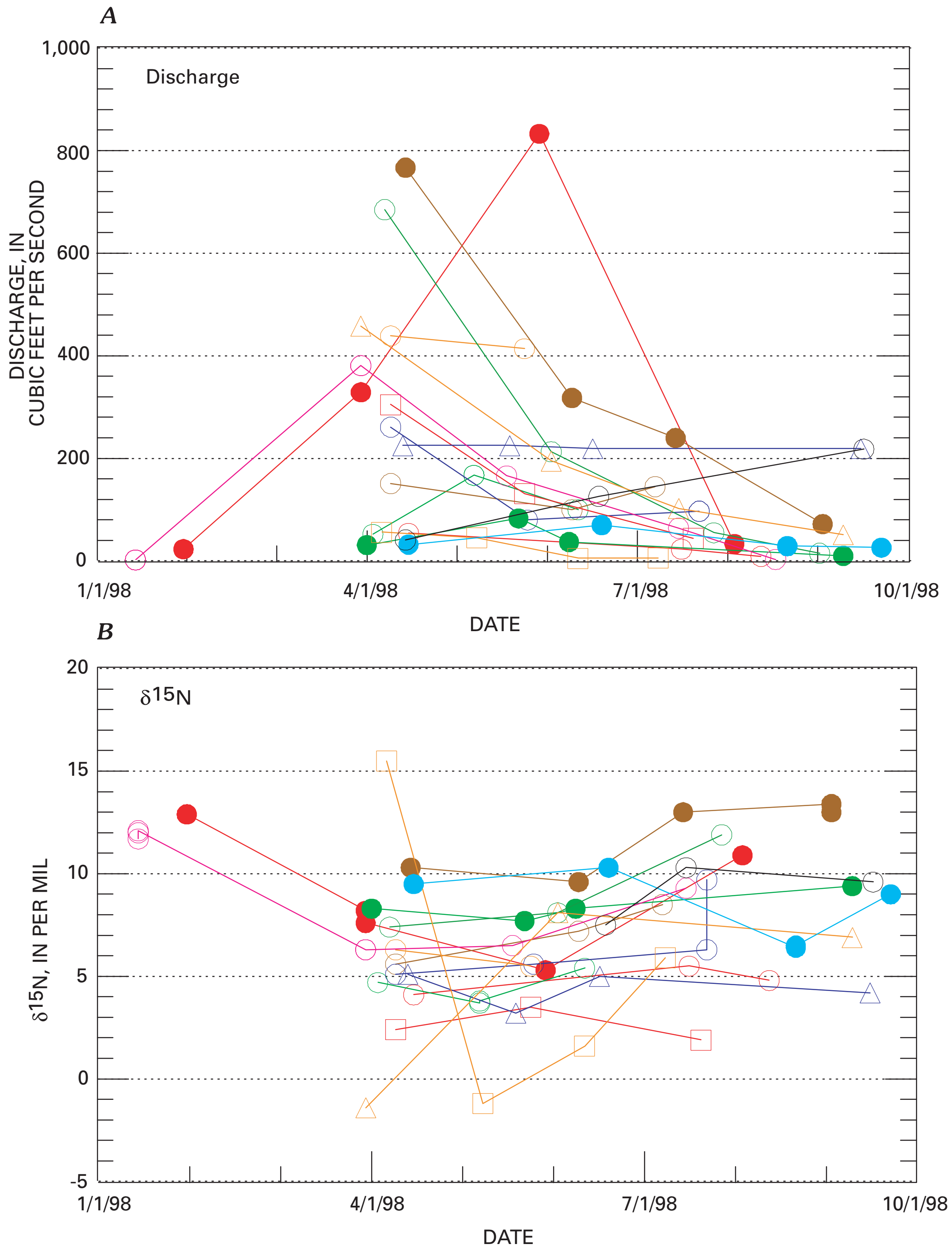

Figure 10. Time series of 1998 data for small stream stations; (*A*) discharge, (*B*) δ^{15}N, (*C*) δ^{18}O, and (*D*) NO_2 plus NO_3.

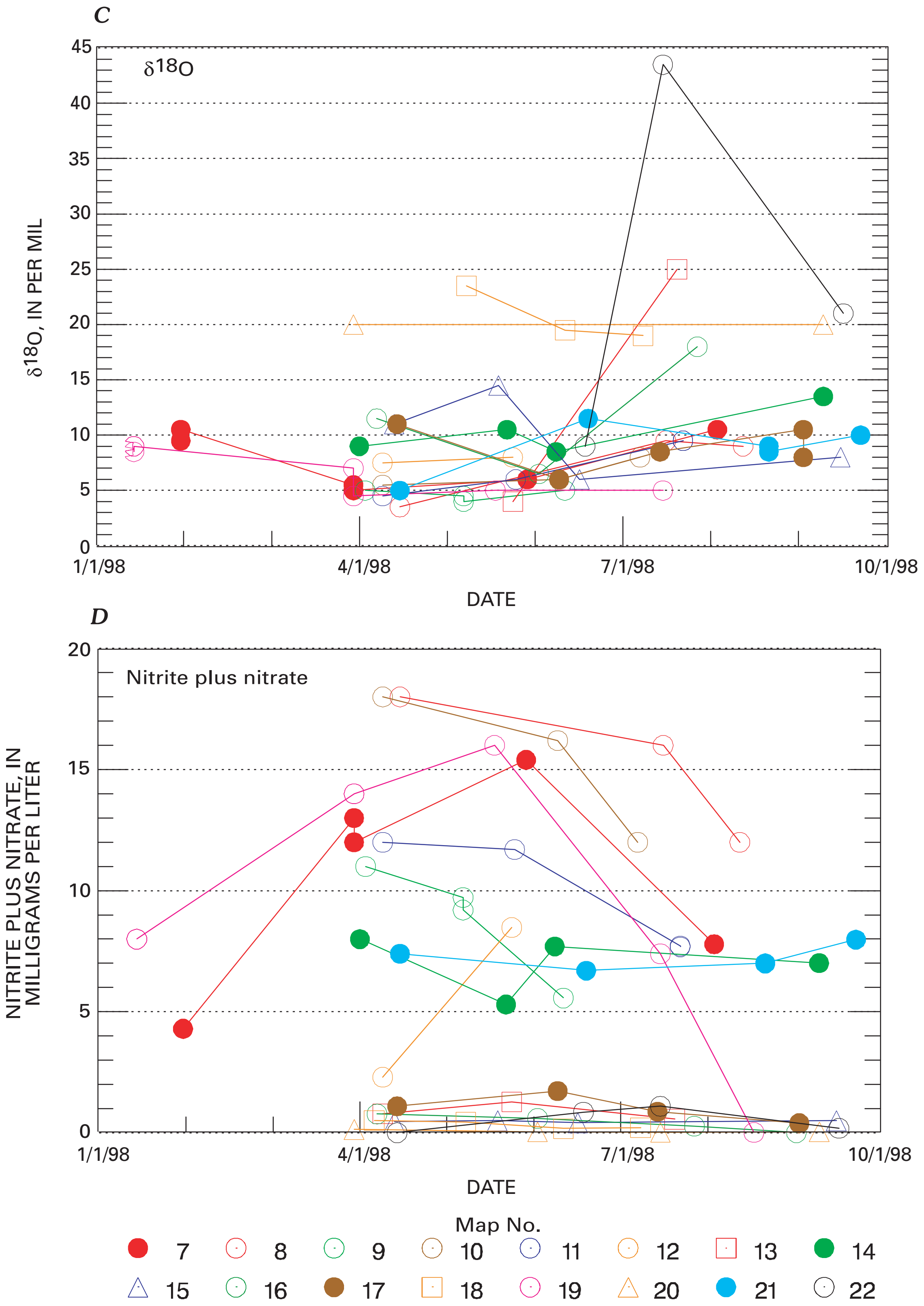

Figure 10. Time series of 1998 data for small stream stations; (*A*) discharge, (*B*) δ^{15}N, (*C*) δ^{18}O, and (*D*) NO_2 plus NO_3—Continued.

through September (fig. 10d). The variability in $\delta^{15}N$ and $\delta^{18}O$ of NO_3 values with respect to dominant basin type in 1998 is similar to that in 1997. The $\delta^{15}N$ of NO_3 values from drainage basins dominated by row crops and row crop and/or livestock production tend to be greater than values from drainage basins dominated by urban or undeveloped land (fig. 10b). The $\delta^{18}O$ of NO_3 values from basins dominated by urban or undeveloped land tend to be greater than values from basins dominated by row crops or row crops and/or livestock production (figure 10c). Most of the NO_2 plus NO_3 concentrations from stations with drainage basins dominated by row crops and row crop and/or livestock production are higher than 5 mg/L, while values from stations with drainage basins dominated by urban or undeveloped land are all less than 1.5 mg/L (fig. 10d; table 5).

$\delta^{15}N$ and $\delta^{13}C$ of POM Isotope Ratio Values

The $\delta^{15}N$ and $\delta^{13}C$ of POM isotope ratio values in suspended sediment for samples from 1997 and 1998 are listed in table 6, and statistically summarized in table 7. In this study, $\delta^{15}N$ of POM values ranged from –1.2‰ to +12.1‰, while $\delta^{13}C$ of POM values ranged from –33.2‰ to –17.3‰ (table 7). There was considerable and unexpected temporal and spatial variation in the $\delta^{15}N$ and $\delta^{13}C$ of POM values from the Mississippi basin. Below the POM isotope data are analyzed by drainage basin size (large basins compared to small basins), and for the small basins, by dominant land cover type within the drainage basin.

Large Rivers

The $\delta^{15}N$ of POM values range from +2.5‰ to +12.1‰, and $\delta^{13}C$ of POM values range from –31.3‰ to –19.3‰ (table 7; fig. 11). Isotope values measured in the large rivers are near the high end of all measurements for $\delta^{15}N$ of POM and near the middle range of all measurements for $\delta^{13}C$ of POM. The distribution of $\delta^{15}N$ POM values from large river stations appears to match the values from basins dominated by row crops or row crops and/or livestock production (fig. 11), suggesting that the bulk of particulate organic nitrogen in large rivers originates in agricultural watersheds. $\delta^{13}C$ of POM values from large river stations are more intermediate being generally between values from basins dominated by urban or undeveloped land and those from basins dominated by row crops or row crops and/or livestock production. The $\delta^{13}C$ of POM values for the stations on the Lower Mississippi River (map numbers 6a and 6c in fig. 3) ranged from –31.3‰ to –22.7‰, with an average of –25.9‰ in 10 samples (table 6). Previous studies (Goni and others, 1998; Onstad and others, 2000) had insufficiently sampled POM and sediment in the Mississippi Basin, and had estimated that the $\delta^{13}C$ of POM value for Mississippi River was about –20‰. They had concluded that terrestrial soil and C4 plant debris were the dominant sources of carbon to the gulf. The data reported here indicate that the dominant source of carbon is more biologically labile aquatic plants (algae, macrophyte debris, and heterotrophic bacteria). The difference between these results could effect models of sedimentation in the gulf and global carbon models.

Small Streams

We hypothesized that POM in small streams draining areas of distinctly different land use would have distinctly different $\delta^{15}N$ and $\delta^{13}C$ of POM values (Battaglin and others, 1997). Boxplots of $\delta^{15}N$ and $\delta^{13}C$ of POM values (fig. 11) from stations with basins dominated by the four land cover types (and the large river stations), show a clear difference in POM isotope ratio values between basins dominated by urban or undeveloped land and basins dominated row crops or row crops and/or livestock production. As with $\delta^{15}N$ of NO_3, the majority of $\delta^{15}N$ of POM values from basins dominated by urban or undeveloped land are less than +5‰, while the majority of values from basins dominated by row crops or row crops and/or livestock production are greater than +5‰ (fig. 11). The difference in $\delta^{13}C$ of POM values between basins dominated by urban or undeveloped land and basins dominated by row crops or row crops and/or livestock production is less distinct. The majority of $\delta^{13}C$ of POM values from basins dominated by urban or undeveloped land are less than –25‰, while the majority of values from basins dominated by row crops or row crops and/or livestock production are greater than –25‰ (fig. 11). The $\delta^{13}C$ of POM values from basins dominated by row-crops nearly span the entire data set (table 7).

Table 6. The $\delta^{15}N$ and $\delta^{13}C$ of particulate organic material in suspended-sediment samples (*, sample not collected; #, analysis not completed; $, insufficient sample material; sample ID's that begin with XX-, matching NO_3 isotope analysis is not available) collected in 1997–98

Sampling station name and station number	Sample ID	Sample collection date	Average $\delta^{15}N$	Average $\delta^{13}C$
Large river stations				
Mississippi River at Clinton, IA - 05420500	XX-29	2/19/97	4.6	-23.3
	XX-44	3/19/97	4.4	-26.4
	IS-119	6/2/97	7.6	-25.6
	XX-99	6/27/97	6.2	-23.6
	IS-112	9/2/97	*	*
	IS-33	5/13/98	6.2	-26.8
	IS-34	5/13/98	6.1	-26.5
	IS-42	5/27/98	5.8	-27.9
	IS-56	6/10/98	*	*
	IS-60	7/1/98	6.0	-23.8
	IS-76	7/28/98	12.1	-27.9
	IS-83	8/25/98	7.0	-26.2
	IS-84	8/25/98	7.5	-27.0
	IS-97	9/23/98	*	*
Missouri River at Hermann, MO - 06934500	XX-138	10/15/97	6.7	-24.3
	IS-26	4/20/98	*	*
	IS-45	6/1/98	5.5	-19.3
	IS-64	7/7/98	*	*
	IS-86	8/31/98	5.4	-21.6
Mississippi River at Thebes, IL - 07022000	IS-101	6/11/97	7.3	-25.1
	XX-116	8/13/97	7.3	-26.5
	XX-151	11/24/97	3.6	-24.9
	IS-25	4/16/98	*	*
	IS-50	6/10/98	5.5	-21.6
	IS-51	6/10/98	#	#
	IS-74	7/22/98	*	*
	IS-91	9/9/98	8.8	-25.0
Ohio River at Grand Chain, IL - 03612500	XX-22	1/22/97	4.8	-26.6
	XX-24	2/11/97	3.7	-24.8
	XX-64	5/14/97	4.9	-25.1
	IS-102	6/12/97	5.9	-26.7
	XX-124	9/4/97	7.9	-28.0
	XX-142	11/6/97	7.8	-27.5
	IS-27	4/23/98	4.7	-26.4
	IS-44	6/5/98	5.9	-27.4
	IS-77	7/22/98	8.3	-28.4
	IS-78	7/22/98	$, combined with IS-77	
	IS-85	8/12/98	7.7	-29.5

Table 6. The $\delta^{15}N$ and $\delta^{13}C$ of particulate organic material in suspended-sediment samples (*, sample not collected; #, analysis not completed; $, insufficient sample material; sample ID's that begin with XX-, matching NO_3 isotope analysis is not available) collected in 1997–98—Continued

Sampling station name and station number	Sample ID	Sample collection date	Average $\delta^{15}N$	Average $\delta^{13}C$
Large river stations—Continued				
Yazoo River below Steele Bayou near Long Lake, MS - 07288955	XX-14	12/17/96	4.1	-26.0
	XX-33	3/11/97	3.0	-25.8
	IS-103	6/19/97	6.6	-27.1
	XX-107	7/21/97	#	#
	XX-108	7/21/97	6.9	-28.5
	IS-19	4/13/98	#	#
	IS-57	6/17/98	#	#
	IS-66	7/16/98	9.6	-29.3
	IS-96	9/17/98	3.9	-27.4
Mississippi River, St. Francisville, LA - 07373420	XX-23	1/15/97	2.5	-26.5
	XX-45	3/14/97	6.4	-26.5
	IS-117	5/6/97	6.7	-31.3
	IS-106	6/19/97	7.1	-24.8
	IS-10	4/2/98	6.1	-23.8
	IS-11	4/2/98	4.8	-24.7
	IS-31	4/30/98	*	*
	IS-32	4/30/98	*	*
	IS-49	6/9/98	7.1	-24.9
	IS-63	7/9/98	6.3	-22.7
	IS-99	9/28/98	8.0	-25.7
Mississippi River at Vicksburg, MS - 07289000	IS-2A	1/13/98	*	*
	IS-2B	1/13/98	*	*
	IS-2C	1/13/98	*	*
Mississippi River at Belle Chasse, LA - 07374525	IS-118	5/7/97	5.9	-27.6
	IS-105	6/20/97	*	*
Small stream stations				
S. Fork Iowa River northeast of New Providence, IA - 05451210	IS-3a	1/30/98	*	*
	IS-5	3/30/98	7.6	-22.2
	IS-8	3/30/98	$, combined with IS-5	
	IS-41	5/29/98	*	*
	IS-79	8/3/98	4.7	-26.0
Fourmile Creek near Traer, IA - 05464137	IS-107	6/30/97	*	*
	IS-20	4/15/98	4.8	-22.2
	IS-67	7/16/98	4.3	-22.0
	IS-80	8/12/98	4.5	-21.9
Walnut Creek near Vandalia, IA - 05487550	IS-104	6/21/97	*	*
	IS-9	4/3/98	4.5	-21.0
	IS-28	5/7/98	4.6	-21.8
	IS-29	5/7/98	3.8	-20.7
	IS-54	6/11/98	5.1	-19.8

Table 6. The $\delta^{15}N$ and $\delta^{13}C$ of particulate organic material in suspended-sediment samples (*, sample not collected; #, analysis not completed; $, insufficient sample material; sample ID's that begin with XX-, matching NO_3 isotope analysis is not available) collected in 1997–98—Continued

Sampling station name and station number	Sample ID	Sample collection date	Average $\delta^{15}N$	Average $\delta^{13}C$
Small stream stations—Continued				
Panther Creek near El Paso, IL - 05567000	IS-115	11/13/97	*	*
	IS-16	4/9/98	6.5	-23.8
	IS-48	6/9/98	7.0	-24.0
	IS-61	7/7/98	7.8	-23.5
Indian Creek near Wyoming, IL - 05568800	IS-111	8/27/97	*	*
	IS-15	4/9/98	5.3	-21.6
	IS-39	5/25/98	5.8	-20.3
	IS-72	7/22/98	4.9	-24.8
	IS-73	7/22/98	$, combined with IS-72	
Sugar Creek at Co Rd 400 S at New Palistine, IN - 03361650	IS-13	4/9/98	5.5	-26.1
	IS-38	5/24/98	5.9	-25.4
Little Buck Creek near Indianapolis, IN - 03353637	IS-113	9/9/97	2.2	-26.8
	IS-14	4/9/98	4.6	-26.7
	IS-37	5/24/98	4.6	-26.8
	IS-71	7/20/98	4.1	-28.8
North Dry Creek near Kearney, NE - 06770195	XX-70	5/27/97	6.5	-20.3
	XX-71	5/27/97	6.7	-20.3
	XX-106	7/17/97	8.2	-20.5
	XX-114	8/11/97	9.2	-19.1
	XX-147	11/19/97	6.4	-21.9
	IS-6	4/1/98	5.6	-17.3
	IS-40	5/22/98	5.0	-20.2
	IS-43	6/8/98	6.3	-21.7
	IS-92	9/9/98	6.4	-22.8
Dismal River near Thedford, NE - 06775900	IS-17	4/13/98	#	#
	IS-36	5/19/98	#	#
	IS-55	6/16/98	2.3	-25.5
	IS-95	9/15/98	1.5	-26.0
South Fabius River near Taylor, MO - 05500000	IS-23	4/7/98	*	*
	IS-46	6/2/98	5.6	-31.1
	IS-75	7/27/98	*	*
	IS-89	9/1/98	6.7	-31.2
Elk River near Tiff City, MO - 07189000	IS-24	4/14/98	*	*
	IS-52	6/9/98	$	-26.2
	IS-68	7/14/98	*	*
	IS-87	9/2/98	$	-26.1
	IS-88	9/2/98	$	-25.1

Table 6. The δ^{15}N and δ^{13}C of particulate organic material in suspended-sediment samples (*, sample not collected; #, analysis not completed; $, insufficient sample material; sample ID's that begin with XX-, matching NO$_3$ isotope analysis is not available) collected in 1997–98—Continued

Sampling station name and station number	Sample ID	Sample collection date	Average δ^{15}N	Average δ^{13}C
Small stream stations—Continued				
Shingle Creek at Queen Ave. N., MN - 05288705	IS-108	7/7/97	*	*
	IS-12	4/6/98	2.2	-30.1
	IS-30	5/8/98	1.2	-28.9
	IS-53	6/11/98	1.6	-31.0
	IS-62	7/8/98	0.3	-30.5
Little Cobb River near Beauford, MN - 05320270	IS-109	7/16/97	*	*
	IS-114	10/28/97	*	*
	IS-1A	1/14/98	*	*
	IS-4	3/30/98	5.1	-23.6
	IS-7	3/30/98	6.0	-24.6
	IS-35	5/18/98	6.3	-25.4
	IS-70	7/15/98	6.8	-25.4
	IS-90	8/17/98	*	*
Namekagon River at Leonards, WI - 05331833	IS-116	11/11/97	*	*
	IS-21	3/30/98	-1.2	-27.5
	IS-47	6/2/98	#	#
	IS-69	7/15/98	8.6	-27.0
	IS-94	9/9/98	$	-26.7
Rattlesnake Creek near North Andover, WI - 05413449	IS-110	8/1/97	*	*
	IS-22	4/15/98	1.1	-26.4
	IS-59	6/19/98	6.5	-23.5
	IS-81	8/21/98	# - ruined in analysis	
	IS-82	8/21/98	$, combined with IS-81	
	IS-98	9/22/98	#	#
Bogue Phalia near Leland, MS - 07288650	XX-25	2/6/97	4.9	-25.0
	XX-53	4/28/97	5.7	-25.5
	XX-68	5/21/97	5.9	-25.1
	XX-89	6/18/97	5.4	-24.0
	XX-103	7/9/97	9.2	-29.7
	XX-131	7/9/97	9.4	-29.3
	IS-18	4/14/98	7.26	-33.2
	IS-58	6/18/98	7.0	-28.2
	IS-65	7/15/98	4.2	-26.9
	IS-93	9/16/98	7.1	-30.4

Table 7. Statistical summary of δ^{15}N and δ^{13}C of particulate organic material values in suspended sediment samples collected in 1997–98 (all values in per mil)

Parameter	Number of analyses	Minimum value	Maximum value	Mean value	Median value	Standard deviation
All stations						
δ^{15}N in per mil	101	-1.2	12.1	5.7	5.9	2.1
δ^{13}C in per mil	105	-33.2	-17.3	-25.4	-25.6	3.1
Large river stations						
d^{15}N in per mil	45	2.5	12.1	5.9	6.2	1.8
δ^{13}C in per mil	45	-31.3	-19.3	-25.9	-26.4	2.2
Small stream stations with basins dominated by row crop agriculture and/or livestock production						
δ^{15}N in per mil	13	1.1	9.2	6.2	6.4	2.0
δ^{13}C in per mil	16	-26.4	-17.3	-22.5	-22.0	2.8
Small stream stations with basins dominated by row crop agriculture						
δ^{15}N in per mil	31	3.8	9.4	5.9	5.7	1.4
δ^{13}C in per mil	31	-33.2	-19.8	-25.1	-24.8	3.5
Small stream stations with basins dominated by urban land						
δ^{15}N in per mil	8	0.3	4.6	2.6	2.2	1.6
δ^{13}C in per mil	8	-31.0	-26.7	-28.7	-28.9	1.8
Small stream stations with basins dominated by undeveloped land						
δ^{15}N in per mil	4	-1.2	8.6	2.8	1.9	4.2
δ^{13}C in per mil	5	-27.5	-25.5	-26.5	-26.7	0.8

Concentrations of Nutrients and Major Ions

Nutrient concentrations for samples from 1997 and 1998 are listed in table 8, and statistically summarized in table 9. NO_2 plus NO_3 concentrations ranged from less than 0.05 to 18.3 mg/L. Ammonia plus organic N concentrations ranged from less than 0.1 to 3.42 mg/L. Dissolved organic carbon concentrations ranged from 0.7 to 14.0 mg/L. Orthophosphate concentrations ranged from less than 0.01 to 0.71 mg/L.

Major ion concentrations for samples from 1997 and 1998 are listed in table 10, and statistically summarized in table 11. Major ions, in particular sulfate and chloride, can compete with NO_3 for sites on the anion exchange column. Overloading the anion columns with these ions can result in NO_3 being preferentially displaced from the column thus biasing the isotope analyses (Silva and others, 2000). In samples from 1997 and 1998, chloride concentrations ranged from 0.7 to 148.3 mg/L, sulfate concentrations ranged from 2.6 to 339 mg/L, and sodium concentrations ranged from 1.4 to 69.4 mg/L.

Large Rivers

The NO_2 plus NO_3 concentrations in samples collected in 1997 and 1998 from the large river stations are in the middle range (0.21 to 3.78 mg/L) of all measurements (<0.05 to 18.3 mg/L). Ammonia plus organic N concentration are in the low range (<0.10 to 0.59 mg/L) of all measurements (<0.10 to 3.42 mg/L). Dissolved organic carbon concentrations are in the middle range (2.5 to 6.6 mg/L) of all measurements (0.7 to 14.0 mg/L). Orthophosphate concentration are in the low range (<0.10 to 0.24 mg/L) of all measurements (<0.10 to 0.71 mg/L).

Major ions concentrations in samples collected from the large river stations are in general towards the middle range of all measurements. Chloride concentrations range from 2.9 to 22.7.3 mg/L, sulfate concentrations range from 5.0 to 129.5 mg/L, and sodium concentrations range from 3.9 to 42.4 mg/L.

Small Streams

The median NO_2 plus NO_3 concentrations from basins dominated by row crops or row crops and/or livestock production (9.62 and 7.39 mg/L, respectively) are greater than median concentrations from

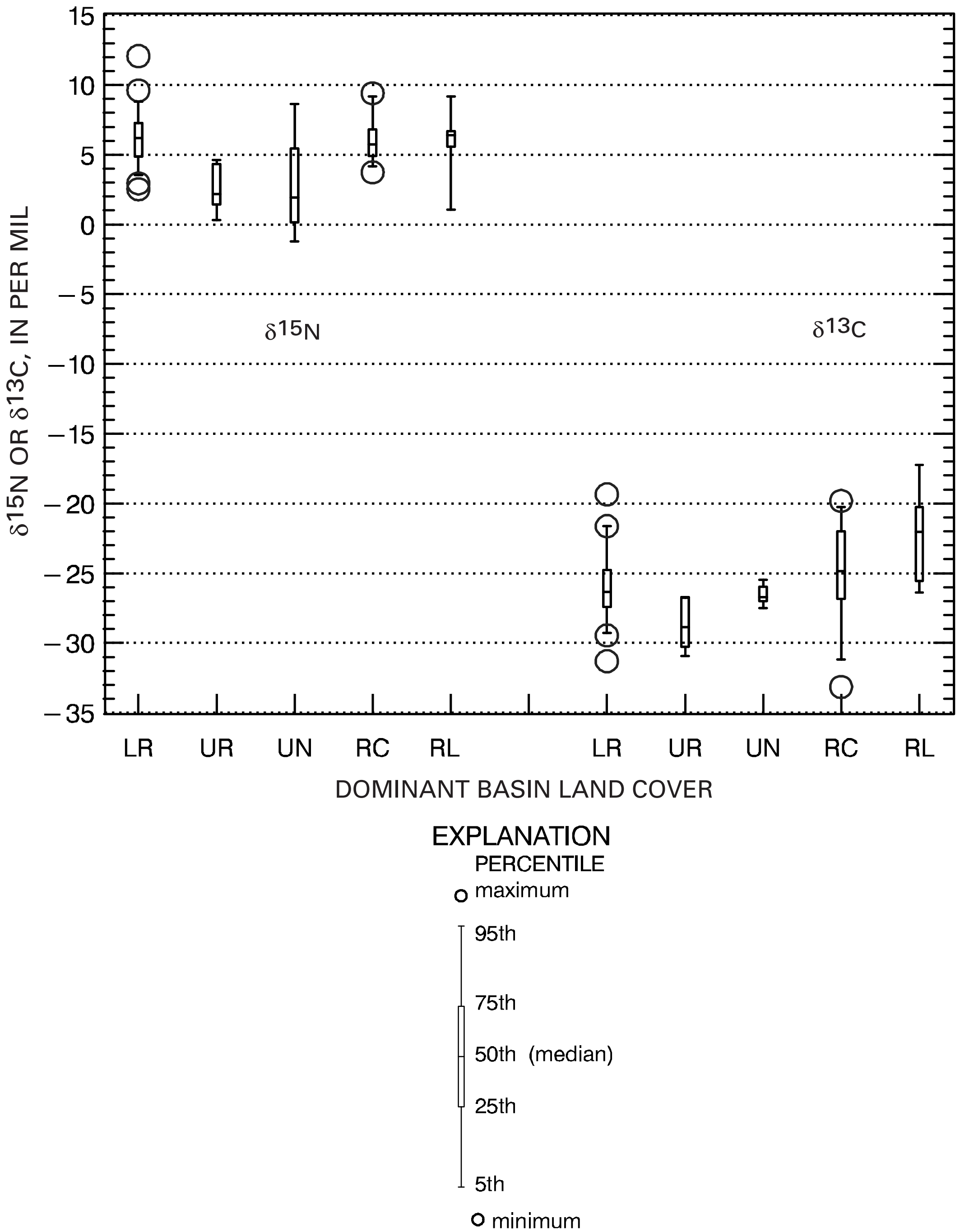

Figure 11. $\delta^{15}N$ and $\delta^{13}C$ of POM values by basin type, 1997–1998. {LR, large river; UR, urban land; UN, undeveloped land; RC, row crop land; and RL row crop and/or livestock production.}

Table 8. Nutrient concentrations in water samples collected in 1997–1998 (*, results not available; mg/L, milligrams per liter)

Sampling station name and station number	Sample ID	Sample collection date	Ammonia as N (mg/L)	Ammonia plus organic N (mg/L)	Nitrite as N (mg/L)	Nitrite plus nitrate as N (mg/L)	Phosphorus (dissolved) as P (mg/L)	Orthophosphate as P (mg/L)	Dissolved organic carbon (mg/L)
Large river stations									
Mississippi River at Clinton, IA - 05420500	IS-119	6/2/97	<0.015	0.38	0.012	0.45	<0.010	<0.001	6.3
	IS-112	9/2/97	0.049	0.47	0.024	0.91	0.142	0.100	6.1
	IS-33	5/13/98	0.066	0.54	0.024	1.89	0.019	0.012	5.9
	IS-34	5/13/98	0.061	0.52	0.024	1.84	0.013	0.013	6.0
	IS-42	5/27/98	0.033	0.59	0.063	1.17	0.026	0.065	6.5
	IS-56	6/10/98	0.138	0.52	0.051	2.00	0.048	0.007	5.2
	IS-60	7/1/98	<0.020	0.47	0.146	2.80	0.132	0.141	5.0
	IS-76	7/28/98	<0.020	0.46	0.023	1.53	0.090	0.126	6.4
	IS-83	8/25/98	0.126	0.49	0.019	0.70	0.118	0.128	5.5
	IS-84	8/25/98	.	.	.	.	.	.	.
	IS-97	9/23/98	0.125	.	0.027	0.87	0.121	0.115	5.2
Missouri River at Hermann, MO - 06934500	IS-26	4/20/98	0.026	0.38	0.036	2.02	0.091	0.092	5.8
	IS-45	6/1/98	0.060	0.37	0.018	2.39	0.096	0.115	4.1
	IS-64	7/7/98	<0.020	0.37	<0.010	1.84	0.091	0.094	4.9
	IS-86	8/31/98	<0.020	0.33	<0.010	1.29	0.135	0.135	4.6
Mississippi River at Thebes, IL - 07022000	IS-101	6/11/97	0.032	0.36	0.030	2.55	0.071	0.083	6.1
	IS-25	4/16/98	0.071	0.49	0.044	3.64	0.089	0.080	4.6
	IS-50	6/10/98	<0.020	0.47	0.045	3.78	0.135	0.119	4.3
	IS-51	6/10/98	.	.	.	.	.	.	.
	IS-74	7/22/98	<0.020	0.43	0.016	3.23	0.143	0.163	6.6
	IS-91	9/9/98	<0.020	0.37	0.014	1.16	0.139	0.144	4.1
Ohio River at Grand Chain, IL - 03612500	IS-102	6/12/97	<0.015	0.24	0.020	2.46	0.025	0.042	3.2
	IS-27	4/23/98	<0.020	0.22	0.024	1.20	0.042	0.049	3.4
	IS-44	6/5/98	0.026	0.23	0.043	1.74	<0.010	0.242	2.5
	IS-77	7/22/98	0.020	0.22	0.016	1.27	0.024	0.054	3.2
	IS-78	7/22/98	.	.	.	.	.	.	.
	IS-85	8/12/98	0.039	0.14	0.025	0.75	0.040	0.050	2.9
Yazoo River below Steele Bayou near Long Lake, MS - 07288955	IS-103	6/19/97	<0.015	0.33	<0.010	0.74	0.042	0.049	5.4
	IS-19	4/13/98	0.059	0.29	0.014	0.37	0.033	0.036	4.4
	IS-57	6/17/98	0.054	0.28	<0.010	0.81	0.063	0.060	4.4
	IS-66	7/16/98	0.129	0.49	0.107	0.55	0.064	0.070	4.9
	IS-96	9/17/98	0.039	0.25	0.013	0.21	0.041	0.045	3.7

Table 8. Nutrient concentrations in water samples collected in 1997–1998 (*, results not available; mg/L, milligrams per liter)—Continued

Sampling station name and station number	Sample ID	Sample collection date	Ammonia as N (mg/L)	Ammonia plus organic N (mg/L)	Nitrite as N (mg/L)	Nitrite plus nitrate as N (mg/L)	Phosphorus (dissolved) as P (mg/L)	Orthophosphate as P (mg/L)	Dissolved organic carbon (mg/L)
Large river stations—Continued									
Mississippi River, St. Francisville, LA - 07373420	IS-117	5/6/97	<0.015	0.24	0.028	1.43	0.045	0.048	4.0
	IS-106	6/19/97	0.015	<0.20	<0.010	2.01	0.052	0.061	3.3
	IS-10	4/2/98	*	*	*	*	*	*	*
	IS-11	4/2/98	*	*	*	*	*	*	*
	IS-31	4/30/98	0.035	0.26	0.019	1.96	0.043	0.056	5.5
	IS-32	4/30/98	*	*	*	*	*	*	*
	IS-49	6/9/98	0.052	0.26	0.011	2.01	0.076	0.080	3.7
	IS-63	7/9/98	0.039	0.23	<0.010	2.63	0.091	0.108	3.9
	IS-99	9/28/98	<0.020	*	<0.010	0.92	0.088	0.079	*
Mississippi River at Vicksburg, MS - 07289000	IS-2A	1/13/98	*	*	*	*	*	*	*
	IS-2B	1/13/98	*	*	*	*	*	*	*
	IS-2C	1/13/98	*	*	*	*	*	*	*
Mississippi River at Belle Chasse, LA - 07374525	IS-118	5/7/97	<0.015	0.21	0.017	1.23	0.046	0.043	3.8
	IS-105	6/20/97	<0.015	<0.20	<0.010	1.81	0.086	0.066	3.6
Small stream stations									
S. Fork Iowa River northeast of New Providence, IA - 05451210	IS-3A	1/30/98	*	*	*	*	*	*	*
	IS-3B	1/30/98	*	*	*	*	*	*	*
	IS-3C	1/30/98	*	*	*	*	*	*	*
	IS-5	3/30/98	0.089	0.52	0.021	12.97	0.135	0.140	3.4
	IS-8	3/30/98	0.106	0.51	0.024	13.74	0.137	0.140	3.4
	IS-41	5/29/98	0.259	1.06	0.089	16.92	0.198	0.174	7.0
	IS-79	8/3/98	0.047	0.41	0.051	7.58	0.016	0.031	4.0
Fourmile Creek near Traer, IA - 05464137	IS-107	6/30/97	0.177	0.50	0.071	14.88	0.200	0.159	2.2
	IS-20	4/15/98	0.057	0.20	0.014	17.51	0.020	0.024	2.0
	IS-67	7/16/98	0.052	0.17	0.032	16.39	0.013	0.016	1.7
	IS-80	8/12/98	0.042	0.22	0.045	11.05	0.032	0.048	2.1
Walnut Creek near Vandalia, IA - 05487550	IS-104	6/21/97	0.097	0.66	0.102	9.69	0.148	0.073	5.2
	IS-9	4/3/98	0.058	0.30	0.042	13.08	0.057	0.062	3.9
	IS-28	5/7/98	0.125	<0.10	0.037	9.62	0.179	0.101	4.4
	IS-29	5/7/98	0.127	<0.10	0.039	9.46	0.146	0.106	4.4
	IS-54	6/11/98	0.157	0.84	0.041	5.26	0.241	0.229	9.5
Panther Creek near El Paso, IL - 05567000	IS-115	11/13/97	0.175	0.52	0.144	11.52	0.025	0.049	2.6
	IS-16	4/9/98	0.083	0.42	0.050	18.29	0.077	0.077	2.2
	IS-48	6/9/98	0.033	0.42	0.086	15.45	0.080	0.078	2.0
	IS-61	7/7/98	0.058	0.67	0.059	12.35	0.232	0.226	4.0

Table 8. Nutrient concentrations in water samples collected in 1997–1998 (*, results not available; mg/L, milligrams per liter)—Continued

Sampling station name and station number	Sample ID	Sample collection date	Ammonia as N (mg/L)	Ammonia plus organic N (mg/L)	Nitrite as N (mg/L)	Nitrite plus nitrate as N (mg/L)	Phos-phorus (dissolved) as P (mg/L)	Ortho-phos-phate as P (mg/L)	Dissolved organic carbon (mg/L)
			Small stream stations—Continued						
Indian Creek near Wyoming, IL - 05568800	IS-111	8/27/97	0.025	0.27	0.042	9.65	0.117	0.085	1.7
	IS-15	4/9/98	0.146	0.56	0.035	11.79	0.124	0.125	3.0
	IS-39	5/25/98	0.097	0.49	0.078	12.49	0.079	0.084	4.0
	IS-72	7/22/98	<0.020	0.51	0.081	7.99	0.154	0.089	3.8
	IS-73	7/22/98	*	*	*	*	*	*	*
Sugar Creek at Co Rd 400 S at New Palistine, IN - 03361650	IS-13	4/9/98	0.058	0.62	0.019	2.25	0.075	0.072	5.6
	IS-38	5/24/98	0.174	0.74	0.084	8.61	0.079	0.063	6.2
Little Buck Creek near Indianapolis, IN - 03353637	IS-113	9/9/97	0.041	0.32	0.031	0.86	0.010	0.014	4.6
	IS-14	4/9/98	0.071	0.48	0.015	0.68	0.058	0.055	6.0
	IS-37	5/24/98	0.129	0.60	0.042	1.12	0.050	0.051	8.8
	IS-71	7/20/98	<0.020	0.40	0.044	0.63	<0.01	0.012	5.7
North Dry Creek near Kearney, NE - 06770195	IS-6	4/1/98	1.897	3.42	0.244	8.33	0.806	0.714	12.0
	IS-40	5/22/98	0.763	2.04	0.220	5.37	0.627	0.567	9.1
	IS-43	6/8/98	0.231	0.91	0.223	7.57	0.539	0.503	6.1
	IS-92	9/9/98	<0.020	0.54	0.048	7.32	0.312	0.293	4.8
Dismal River near Thedford, NE - 06775900	IS-17	4/13/98	0.037	<0.10	0.011	0.46	0.137	0.144	1.4
	IS-36	5/19/98	0.038	0.11	<0.010	0.48	0.132	0.150	1.3
	IS-55	6/16/98	0.034	0.11	<0.010	0.39	0.124	0.011	2.2
	IS-95	9/15/98	0.031	<0.10	0.015	0.51	0.127	0.135	1.7
South Fabius River near Taylor, MO - 05500000	IS-23	4/7/98	0.044	0.77	0.017	0.75	0.071	0.053	6.6
	IS-46	6/2/98	<0.020	*	0.023	0.62	0.021	<0.010	6.2
	IS-75	7/27/98	<0.020	0.44	<0.010	0.28	<0.010	<0.010	5.1
	IS-89	9/1/98	0.043	1.26	0.013	<0.05	0.156	0.013	4.7
Elk River near Tiff City, MO - 07189000	IS-24	4/14/98	0.029	0.13	<0.010	1.16	0.019	0.014	1.7
	IS-52	6/9/98	<0.020	0.13	0.014	1.63	0.098	0.086	0.7
	IS-68	7/14/98	0.059	0.13	0.017	0.86	0.111	0.113	1.1
	IS-87	9/2/98	0.032	1.24	0.016	0.43	0.208	0.063	1.4
	IS-88	9/2/98	*	*	*	*	*	*	*
Shingle Creek at Queen Ave. N., MN - 05288705	IS-108	7/7/97	0.206	0.74	0.030	0.24	0.042	0.032	14.0
	IS-12	4/6/98	0.061	0.66	0.018	0.40	0.012	0.012	7.0
	IS-30	5/8/98	0.063	0.43	0.052	0.41	<0.010	<0.010	6.1
	IS-53	6/11/98	0.214	0.64	0.028	0.21	0.029	0.022	6.9
	IS-62	7/8/98	0.225	0.82	0.069	0.22	0.021	0.045	7.7

Table 8. Nutrient concentrations in water samples collected in 1997–1998 (*, results not available; mg/L, milligrams per liter)—Continued

Sampling station name and station number	Sample ID	Sample collection date	Ammonia as N (mg/L)	Ammonia plus organic N (mg/L)	Nitrite as N (mg/L)	Nitrite plus nitrate as N (mg/L)	Phosphorus (dissolved) as P (mg/L)	Orthophosphate as P (mg/L)	Dissolved organic carbon (mg/L)
Small stream stations—Continued									
Little Cobb River near Beauford, MN - 05320270	IS-109	7/16/97	<0.015	0.62	0.071	9.71	0.103	0.104	6.4
	IS-114	10/28/97	<0.020	0.60	0.041	8.16	<0.010	<0.010	5.9
	IS-1A	1/14/98	*	*	*	*	*	*	*
	IS-1B	1/14/98	*	*	*	*	*	*	*
	IS-1C	1/14/98	*	*	*	*	*	*	*
	IS-4	3/30/98	0.074	1.03	0.067	15.03	0.239	0.216	7.7
	IS-7	3/30/98	*	*	*	*	*	*	*
	IS-35	5/18/98	0.068	0.89	0.127	16.19	0.103	0.103	6.6
	IS-70	7/15/98	0.056	0.94	0.059	7.09	0.093	0.086	6.6
	IS-90	8/17/98	0.037	0.89	<0.010	<0.05	0.092	0.084	8.5
Namekagon River at Leonards, WI - 05331833	IS-116	11/11/97	<0.020	0.19	0.010	0.12	0.014	0.033	4.0
	IS-21	3/30/98	0.057	0.43	<0.010	0.09	0.021	0.011	11.0
	IS-47	6/2/98	0.023	0.39	0.017	0.07	0.021	<0.010	8.9
	IS-69	7/15/98	<0.020	0.26	<0.010	<0.05	<0.010	<0.010	4.5
	IS-94	9/9/98	0.045	0.12	<0.010	0.84	<0.050	<0.010	2.2
Rattlesnake Creek near North Andover, WI - 05413449	IS-110	8/1/97	0.035	0.29	0.050	5.98	0.183	0.193	3.2
	IS-22	4/15/98	<0.020	0.32	0.035	7.39	0.086	0.076	2.9
	IS-59	6/19/98	0.334	1.58	0.134	5.37	0.534	0.462	7.5
	IS-81	8/21/98	0.116	0.55	0.068	7.57	0.209	0.220	3.0
	IS-82	8/21/98	*	*	*	*	*	*	*
	IS-98	9/22/98	0.028	0.31	0.030	8.70	0.111	0.119	2.2
Bogue Phalia near Leland, MS - 07288650	IS-18	4/14/98	0.039	0.50	0.012	<0.05	0.023	0.020	5.7
	IS-58	6/18/98	0.060	0.92	0.157	0.82	0.019	0.018	6.5
	IS-65	7/15/98	0.377	0.91	0.276	1.09	0.093	0.087	5.0
	IS-93	9/16/98	0.041	0.63	0.025	0.19	0.140	0.130	7.4

Table 9. Statistical summary of nutrient concentrations in water samples collected in 1997–198 (all value are in milligrams per liter)

Parameter	Analytical reporting limit	Number of analyses	Minimum value	Maximum value	Mean value	Median value	Standard deviation
All stations							
Ammonia as N	0.02	105	<0.02	1.90	0.09	0.04	0.20
Ammonia plus organic N	0.10	102	<0.10	3.42	0.50	0.43	0.44
Nitrite as N	0.01	105	<0.01	0.28	0.04	0.03	0.05
Nitrite plus nitrate as N	0.05	105	<0.05	18.3	4.42	1.84	5.13
Phosphorus (dissolved) as P	0.01	105	<0.01	0.81	0.10	0.08	0.12
Orthophosphate as P	0.01	105	<0.01	0.71	0.10	0.08	0.11
Dissolved organic carbon as C	0.33	105	0.7	14.0	4.8	4.6	2.4
Large river stations							
Ammonia as N	0.02	37	<0.02	0.14	0.03	0.03	0.04
Ammonia plus organic N	0.10	35	<0.10	0.59	0.34	0.36	0.14
Nitrite as N	0.01	37	<0.10	0.15	0.03	0.02	0.03
Nitrite plus nitrate as N	0.05	37	0.21	3.78	1.63	1.53	0.89
Phosphorus (dissolved) as P	0.01	37	<0.01	0.14	0.07	0.06	0.04
Orthophosphate as P	0.01	37	<0.01	0.24	0.08	0.07	0.05
Dissolved organic carbon as C	0.33	36	2.5	6.6	4.7	4.6	1.1
Small stream stations with basins dominated by row crop agriculture and/or livestock production							
Ammonia as N	0.02	17	<0.02	1.90	0.24	0.06	0.47
Ammonia plus organic N	0.10	17	0.13	3.42	0.83	0.52	0.86
Nitrite as N	0.01	17	<0.01	0.24	0.08	0.05	0.86
Nitrite plus nitrate as N	0.05	17	0.43	16.92	6.99	7.39	4.58
Phosphorus (dissolved) as P	0.01	17	0.02	0.81	0.25	0.18	0.23
Orthophosphate as P	0.01	17	0.01	0.71	0.23	0.14	0.21
Dissolved organic carbon as C	0.33	18	0.7	12.0	4.1	3.3	3.1
Small stream stations with basins dominated by row crop agriculture							
Ammonia as N	0.02	33	<0.02	0.38	0.08	0.06	0.08
Ammonia plus organic N	0.10	32	<0.10	1.26	0.58	0.58	0.30
Nitrite as N	0.01	33	<0.01	0.28	0.06	0.04	0.05
Nitrite plus nitrate as N	0.05	33	<0.05	18.29	8.40	9.62	6.01
Phosphorus (dissolved) as P	0.01	33	<0.01	0.24	0.10	0.09	0.07
Orthophosphate as P	0.01	33	<0.02	0.23	0.08	0.08	0.06
Dissolved organic carbon as C	0.33	33	1.7	9.5	4.8	5.0	2.1
Small stream stations with basins dominated by urban land							
Ammonia as N	0.02	9	<0.02	0.23	0.11	0.07	0.08
Ammonia plus organic N	0.10	9	0.32	0.82	0.56	0.60	0.17
Nitrite as N	0.01	9	0.02	0.07	0.04	0.03	0.02
Nitrite plus nitrate as N	0.05	9	0.21	1.12	0.53	0.41	0.32
Phosphorus (dissolved) as P	0.01	9	<0.01	0.06	0.02	0.02	0.02
Orthophosphate as P	0.01	9	<0.01	0.06	0.03	0.02	0.02
Dissolved organic carbon as C	0.33	9	4.6	14.0	7.4	6.9	2.7
Small stream stations with basins dominated by undeveloped land							
Ammonia as N	0.02	9	<0.02	0.06	0.03	0.03	0.02
Ammonia plus organic N	0.10	9	<0.10	0.43	0.18	0.12	0.15
Nitrite as N	0.01	9	<0.01	0.02	0.01	<0.01	0.01
Nitrite plus nitrate as N	0.05	9	<0.05	0.84	0.33	0.39	0.28
Phosphorus (dissolved) as P	0.01	9	<0.01	0.14	0.06	0.02	0.06
Orthophosphate as P	0.01	9	<0.01	0.15	0.05	0.01	0.07
Dissolved organic carbon as C	0.33	9	1.3	11.0	4.1	2.2	3.5

Table 10. Major ion concentrations in water samples collected in 1997–1998 (mg/L, milligrams per liter; *, results not available)

Sampling station name and station number	Sample ID	Sample collection date	Calcium (mg/L)	Chloride (mg/L)	Magnesium (mg/L)	Potassium (mg/L)	Sodium (mg/L)	Sulfate (mg/L)
Large River Stations								
Mississippi River at Clinton, IA - 05420500	IS-119	6/2/97	41.2	12.8	19.1	2.50	8.9	48.7
	IS-112	9/2/97	42.8	14.1	18.3	2.52	9.4	30.3
	IS-33	5/13/98	45.1	14.6	23.0	2.57	9.7	58.6
	IS-34	5/13/98	*	14.6	*	*	*	58.8
	IS-42	5/27/98	44.9	15.3	22.0	2.70	9.9	51.3
	IS-56	6/10/98	47.8	16.9	21.5	2.54	10.3	43.4
	IS-60	7/1/98	45.5	13.7	18.0	2.94	8.4	31.0
	IS-76	7/28/98	44.6	13.7	19.1	0.28	7.6	26.3
	IS-83	8/25/98	42.3	13.1	19.1	2.29	8.3	21.3
	IS-84	8/25/98	*	*	*	*	*	*
	IS-97	9/23/98	43.2	15.1	21.2	2.56	9.5	23.3
Missouri River at Hermann, MO - 06934500	IS-26	4/20/98	58.6	17.6	16.7	5.59	26.2	87.4
	IS-45	6/1/98	61.9	19.7	20.2	6.13	42.3	129.4
	IS-64	7/7/98	47.3	14.1	13.4	5.46	24.9	74.9
	IS-86	8/31/98	47.0	17.1	15.8	6.11	37.3	104.2
Mississippi River at Thebes, IL - 07022000	IS-101	6/11/97	58.4	19.5	22.5	4.70	30.2	97.3
	IS-25	4/16/98	47.1	17.0	15.7	3.73	14.7	44.0
	IS-50	6/10/98	49.0	20.8	18.4	4.11	19.1	58.5
	IS-51	6/10/98	*	*	*	*	*	*
	IS-74	7/22/98	54.9	18.5	18.8	4.32	18.7	51.6
	IS-91	9/9/98	52.0	21.9	19.6	5.57	30.7	84.1
Ohio River at Grand Chain, IL - 03612500	IS-102	6/12/97	33.5	10.6	7.7	2.65	7.2	31.5
	IS-27	4/23/98	32.8	9.7	7.2	2.30	7.1	29.5
	IS-44	6/5/98	36.4	11.2	9.7	2.53	8.5	34.2
	IS-77	7/22/98	32.9	11.0	9.0	2.93	7.8	30.0
	IS-78	7/22/98	*	*	*	*	*	*
	IS-85	8/12/98	29.3	10.4	7.1	2.65	7.5	23.7
Yazoo River below Steele Bayou near Long Lake, MS - 07288955	IS-103	6/19/97	7.9	2.8	2.6	2.94	3.8	4.9
	IS-19	4/13/98	7.8	3.9	2.7	2.07	4.9	7.2
	IS-57	6/17/98	11.9	4.5	4.0	2.94	6.2	7.6
	IS-66	7/16/98	27.8	10.1	9.7	3.82	15.2	16.0
	IS-96	9/17/98	16.6	5.7	6.0	2.81	9.0	9.4
Mississippi River, St. Francisville, LA - 07373420	IS-117	5/6/97	33.0	17.1	10.5	3.27	15.7	45.8
	IS-106	6/19/97	36.4	16.0	10.6	3.17	14.9	50.5
	IS-10	4/2/98	*	*	*	*	*	*
	IS-11	4/2/98	*	*	*	*	*	*
	IS-31	4/30/98	37.4	14.5	10.9	3.36	12.2	35.2
	IS-32	4/30/98	*	*	*	*	*	*
	IS-49	6/9/98	40.0	16.4	13.1	3.29	15.0	45.4
	IS-63	7/9/98	40.3	13.1	12.2	3.62	11.1	31.8
	IS-99	9/28/98	43.1	22.7	14.5	3.69	23.4	58.1
Mississippi River at Vicksburg, MS - 07289000	IS-2A	1/13/98	*	*	*	*	*	*
	IS-2B	1/13/98	*	*	*	*	*	*
	IS-2C	1/13/98	*	*	*	*	*	*

Table 10. Major ion concentrations in water samples collected in 1997–1998 (mg/L, milligrams per liter; *, results not available)—Continued

Sampling station name and station number	Sample ID	Sample collection date	Calcium (mg/L)	Chloride (mg/L)	Magnesium (mg/L)	Potassium (mg/L)	Sodium (mg/L)	Sulfate (mg/L)
Large river stations—Continued								
Mississippi River at Belle Chasse, LA - 07374525	IS-118	5/7/97	*	*	*	*	*	*
	IS-105	6/20/97	*	*	*	*	*	*
Small stream stations								
S. Fork Iowa River northeast of New Providence, IA - 05451210	IS-3A	1/30/98	83.3	18.9	29.4	2.14	9.2	28.1
	IS-3B	1/30/98	*	*	*	*	*	*
	IS-3C	1/30/98	*	*	*	*	*	*
	IS-5	3/30/98	89.7	24.4	27.1	1.90	7.9	26.4
	IS-8	3/30/98	87.8	25.3	26.5	1.88	7.7	26.2
	IS-41	5/29/98	69.4	14.8	19.6	3.04	3.7	13.6
	IS-79	8/3/98	74.4	16.3	29.6	2.06	7.0	24.2
Fourmile Creek near Traer, IA - 05464137	IS-107	6/30/97	68.3	17.7	23.1	1.84	7.0	20.4
	IS-20	4/15/98	60.6	17.1	20.4	0.81	6.4	18.6
	IS-67	7/16/98	63.8	13.7	21.6	0.55	6.7	16.8
	IS-80	8/12/98	68.3	13.2	22.9	0.78	6.9	18.2
Walnut Creek near Vandalia, IA - 05487550	IS-104	6/21/97	47.7	12.1	17.2	2.35	5.3	16.8
	IS-9	4/3/98	53.9	12.3	19.2	1.42	6.0	21.0
	IS-28	5/7/98	*	*	*	*	*	*
	IS-29	5/7/98	*	9.6	*	*	*	16.1
	IS-54	6/11/98	24.7	5.4	7.9	6.00	3.3	7.9
Panther Creek near El Paso, IL - 05567000	IS-115	11/13/97	94.8	58.5	41.6	2.78	23.0	49.1
	IS-16	4/9/98	80.9	36.2	35.2	1.32	11.4	40.7
	IS-48	6/9/98	79.4	35.2	35.4	1.38	14.5	41.6
	IS-61	7/7/98	61.3	23.7	26.8	3.22	9.5	30.9
Indian Creek near Wyoming, IL - 05568800	IS-111	8/27/97	99.4	23.7	36.3	1.15	13.2	38.8
	IS-15	4/9/98	67.2	17.4	27.4	1.86	8.3	27.7
	IS-39	5/25/98	73.9	18.7	31.2	1.52	9.8	31.5
	IS-72	7/22/98	65.3	20.6	27.5	3.29	14.2	29.3
	IS-73	7/22/98	*	*	*	*	*	*
Sugar Creek at Co Rd 400 S at New Palistine, IN - 03361650	IS-13	4/9/98	42.0	24.0	14.3	1.89	10.8	21.9
	IS-38	5/24/98	52.5	19.7	18.2	2.39	6.4	22.1
Little Buck Creek near Indianapolis, IN - 03353637	IS-113	9/9/97	39.7	41.5	11.0	2.03	24.2	20.4
	IS-14	4/9/98	37.9	25.1	10.2	2.39	16.2	19.8
	IS-37	5/24/98	52.5	34.1	14.5	2.92	21.3	24.4
	IS-71	7/20/98	34.6	24.2	9.6	2.60	14.7	18.3
North Dry Creek near Kearney, NE - 06770195	IS-6	4/1/98	149.6	33.0	25.5	27.60	49.8	283.2
	IS-40	5/22/98	115.4	21.2	21.0	23.80	47.0	255.2
	IS-43	6/8/98	117.1	21.5	20.9	19.05	41.5	233.3
	IS-92	9/9/98	152.7	32.5	27.4	21.50	69.4	339.1
Dismal River near Thedford, NE - 06775900	IS-17	4/13/98	22.2	0.8	3.4	4.95	6.8	5.8
	IS-36	5/19/98	22.3	0.7	3.4	5.08	7.0	5.9
	IS-55	6/16/98	23.0	0.8	3.7	5.20	8.1	5.4
	IS-95	9/15/98	21.1	1.0	3.2	5.27	10.1	5.8

Table 10. Major ion concentrations in water samples collected in 1997–1998 (mg/L, milligrams per liter; *, results not available)—Continued

Sampling station name and station number	Sample ID	Sample collection date	Calcium (mg/L)	Chloride (mg/L)	Magnesium (mg/L)	Potassium (mg/L)	Sodium (mg/L)	Sulfate (mg/L)
Small stream stations—Continued								
South Fabius River near Taylor, MO - 05500000	IS-23	4/7/98	*	*	*	*	*	*
	IS-46	6/2/98	50.1	8.0	9.3	3.95	10.1	39.7
	IS-75	7/27/98	62.3	9.8	11.2	5.11	12.4	42.9
	IS-89	9/1/98	57.8	10.5	11.6	5.04	13.0	40.6
Elk River near Tiff City, MO - 07189000	IS-24	4/14/98	45.0	5.3	2.3	1.56	7.1	7.8
	IS-52	6/9/98	51.1	6.7	2.6	2.09	4.6	5.7
	IS-68	7/14/98	49.4	7.8	2.6	2.42	6.0	5.1
	IS-87	9/2/98	48.7	9.6	3.0	3.18	7.2	6.9
	IS-88	9/2/98	48.5	10.0	3.0	3.20	7.2	6.9
Shingle Creek at Queen Ave. N., MN - 05288705	IS-108	7/7/97	56.1	79.3	14.2	3.26	43.2	34.1
	IS-12	4/6/98	55.0	115.3	15.0	3.98	63.1	34.3
	IS-30	5/8/98	61.8	99.8	18.2	2.58	49.0	59.5
	IS-53	6/11/98	69.1	148.2	20.6	2.39	52.1	60.8
	IS-62	7/8/98	70.3	104.1	19.8	<0.10	51.4	42.8
Little Cobb River near Beauford, MN - 05320270	IS-109	7/16/97	81.3	12.9	27.4	2.20	9.1	18.3
	IS-114	10/28/97	73.6	19.9	33.1	2.07	12.9	26.5
	IS-1A	1/14/98	*	*	*	*	*	*
	IS-1B	1/14/98	*	*	*	*	*	*
	IS-1C	1/14/98	*	*	*	*	*	*
	IS-4	3/30/98	73.5	14.9	23.3	3.59	6.7	22.8
	IS-7	3/30/98	*	*	*	*	*	*
	IS-35	5/18/98	81.3	15.9	28.3	2.22	8.9	21.3
	IS-70	7/15/98	53.1	13.8	21.4	1.76	7.2	17.3
	IS-90	8/17/98	62.3	21.2	28.3	2.51	14.5	21.7
Namekagon River at Leonards, WI - 05331833	IS-116	11/11/97	16.9	2.8	4.6	0.61	2.3	3.6
	IS-21	3/30/98	6.9	1.5	2.0	0.73	1.4	2.6
	IS-47	6/2/98	12.2	1.7	3.3	0.43	1.9	2.8
	IS-69	7/15/98	16.9	2.5	4.7	0.59	2.4	3.1
	IS-94	9/9/98	22.4	2.8	6.1	0.66	2.8	4.5
Rattlesnake Creek near North Andover, WI - 05413449	IS-110	8/1/97	81.4	27.9	43.3	3.32	8.5	25.9
	IS-22	4/15/98	80.6	27.2	44.3	2.23	9.1	24.7
	IS-59	6/19/98	71.0	22.6	37.6	9.66	7.8	19.1
	IS-81	8/21/98	86.9	25.3	47.7	3.20	8.9	22.8
	IS-82	8/21/98	*	*	*	*	*	*
	IS-98	9/22/98	84.9	26.4	46.0	2.07	8.4	25.0
Bogue Phalia near Leland, MS - 07288650	IS-18	4/14/98	52.1	6.2	15.4	3.31	11.6	27.5
	IS-58	6/18/98	52.5	13.0	21.1	4.32	28.2	89.2
	IS-65	7/15/98	37.7	5.0	13.0	3.82	13.4	30.6
	IS-93	9/16/98	53.4	*	20.0	8.91	19.0	*

Table 11. Statistical summary of major ion concentrations in water sampled collected in 1997–98 (all values are in milligrams per liter)

Parameter	Analytical reporting limit	Number of analyses	Minimum value	Maximum value	Mean value	Median value	Standard deviation
All stations							
Calcium	0.02	101	6.9	152.7	54.1	51.1	26.6
Chloride	0.29	102	0.7	148.3	20.5	15.3	22.9
Magnesium	0.014	101	2.0	47.7	17.8	18.3	10.9
Potassium	0.24	101	<0.24	27.6	3.8	2.7	4.3
Sodium	0.09	101	1.4	69.4	15.1	9.6	13.9
Sulfate	0.31	102	2.6	339	41.1	26.5	53.9
Large river stations							
Calcium	0.02	34	7.8	62.0	39.5	42.6	13.3
Chloride	0.29	35	2.9	22.7	14.0	14.5	4.8
Magnesium	0.014	34	2.7	23.0	14.2	15.2	6.1
Potassium	0.24	34	0.3	6.1	3.4	2.9	1.3
Sodium	0.09	34	3.9	42.4	14.6	10.1	9.5
Sulfate	0.31	35	5.0	129.5	45.3	43.5	28.8
Small stream stations with basins dominated by row crop agriculture and/or livestock production							
Calcium	0.02	19	45.0	152.7	83.6	81.4	31.6
Chloride	0.29	19	5.4	33.0	19.9	21.5	8.7
Magnesium	0.014	19	2.4	47.7	24.2	26.6	15.7
Potassium	0.24	19	1.6	27.6	7.2	3.0	8.7
Sodium	0.09	19	3.8	69.4	16.8	7.9	19.4
Sulfate	0.31	19	5.2	339.1	72.6	24.8	110.7
Small stream stations with basins dominated by row crop agriculture							
Calcium	0.02	30	24.7	99.4	63.2	62.4	16.2
Chloride	0.29	30	5.1	58.6	17.7	15.4	10.7
Magnesium	0.014	30	8.0	41.7	23.0	22.3	8.6
Potassium	0.24	30	0.6	8.9	2.8	2.3	1.8
Sodium	0.09	30	3.3	28.3	11.0	10.0	5.3
Sulfate	0.31	30	8.0	89.2	29.0	24.7	15.1
Small stream stations with basins dominated by urban land							
Calcium	0.02	9	34.6	70.3	53.0	55.1	13.2
Chloride	0.29	9	24.3	148.3	74.7	79.3	45.2
Magnesium	0.014	9	9.7	20.7	14.8	14.5	4.1
Potassium	0.24	9	<0.24	4.0	2.5	2.6	1.1
Sodium	0.09	9	14.7	63.1	37.3	43.2	18.2
Sulfate	0.31	9	18.4	60.8	35.0	34.2	16.5
Small stream stations with basins dominated by undeveloped land							
Calcium	0.02	9	6.9	23.0	18.2	21.2	5.6
Chloride	0.29	9	0.7	2.8	1.7	1.5	0.9
Magnesium	0.014	9	2.0	6.1	3.8	3.4	1.2
Potassium	0.24	9	0.4	5.3	2.6	0.7	2.4
Sodium	0.09	9	1.4	10.2	4.8	2.8	3.2
Sulfate	0.31	9	2.6	6.0	4.4	4.6	1.4

basins dominated by urban or undeveloped land (0.41 and 0.39 mg/L, respectively) (table 9). The median ammonia plus organic N concentrations from basins dominated by row crops, row crops and/or livestock production, or urban land (0.58, 0.52, and 0.60, respectively) are greater than the median concentration from basins dominated by undeveloped land (0.12 mg/L). The median dissolved organic carbon concentrations from basins dominated by row crops, row crops and/or livestock production, or urban land (5.0, 3.3, and 6.9 mg/L, respectively) are greater than the median concentration from undeveloped basins (2.2 mg/L). The median orthophosphate concentrations from basins dominated by row crops or row crops and/or livestock production (0.08 and 0.14 mg/L, respectively) are greater than median concentrations basins dominated by urban or undeveloped land (0.02 and 0.01 mg/L, respectively).

The median chloride concentration from basins dominated by urban land (79.3 mg/L) is greater than median concentrations from basins dominated by row crops, row crops and/or livestock production, or undeveloped land (15.4, 21.5, and 1.5 mg/L, respectively) (table 11). The median sodium concentration from basins dominated by urban land (43.2 mg/L) also is greater than median concentrations from basins dominated by row crops, row crops and/or livestock production, or undeveloped land (10.0, 7.9, and 2.8 mg/L, respectively). The median sulfate concentrations (4.6 mg/L) from basins dominated by undeveloped land is less than median concentrations from basins dominated by row crops, row crops and/or livestock production, or urban land (24.7, 24.8, and 34.2 mg/L, respectively) (table 11).

Physical Properties and Field Chemistry

Physical properties and field chemistry data for samples from 1997 and 1998 are listed in table 12, and statistically summarized by stream (basin) size and dominant drainage basin land cover in table 13.

Relations Between Isotopic Ratios and Basin Characteristics

A project objective was to determine if NO_3 and POM from streams draining areas of distinctly different land use and hence N sources have distinct isotope values. The intent was to select small stream stations that distinctly represented one of four land-use classes: land in corn and soybean production; land in hog, cattle, or poultry (livestock) production; urban land; or undeveloped land. This objective was difficult to accomplish because land use relating to N sources was mixed in most basins (tables 2 and 3).

Examples from three stations demonstrate the difficulty with assigning a basin type to each station. Little Buck Creek near Indianapolis in Indiana (station number 03353637) was selected as an urban station, but contains only slightly less agricultural (46.5%) than urban land (49.1%) in the associated drainage basin (table 3). Walnut Creek near Vandalia in Iowa (station number 05487550) was selected as an undeveloped station because some of the basin has been converted back to native prairie grasslands. However, on-site inspection and analysis of land cover data indicate that there is a mix of undeveloped and agricultural land in the basin associated with this station. Hence, the basin type designation for this station was changed to agricultural land (tables 1 and 3). Elk River near Tiff City in Missouri (station number 07189000) was selected as a row crops and/or livestock production station because several confined animal feeding operations (CAFO’s) were known to operate in the basin. Land-cover data show that more than 50% of this basin is forested or otherwise undeveloped land, which qualify it as an undeveloped type basin (table 3). However, the estimate rate of N input from manure (4,887 kg N/km^2) is greater than for any other basin in this study (table 2).

A more detailed analysis of the isotope results relative to land cover and N sources that utilizes multivariate statistics is merited but beyond the scope of this report. However, figures 8–11 clearly show some differences in isotope ratio values among the stations on small streams with basins dominated by different land cover types.

Evidence for Sources of Nitrogen in the Mississippi River

We proposed (Battaglin and others, 1997) that $\delta^{15}N$ and $\delta^{18}O$ of NO_3 values from Mississippi River water could be used to determine the principal sources of the NO_3 entering the Gulf of Mexico. Results from this study confirm the findings of other investigations (Goolsby and others, 1999; Council for Agricultural

Table 12. Physical properties and field chemistry in water samples collected in 1997–98 (mg/L, milligrams per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; ft^3/s, cubic feet per second; *, result not available)

Sampling station name and station number	Sample ID	Sample collection date	Alkalinity as $CaCO_3$ (mg/L)	Bicarbonate as HCO_3 (mg/L)	Dissolved oxygen (mg/L)	pH in standard units	Specific conductance in µs/cm	Water temperature (degrees Celsius)	Instantaneous discharge (ft^3/s)
Large river stations									
Mississippi River at Clinton, IA - 05420500	IS-119	6/2/97	161	197	10.7	8.59	378	16.9	61,000
	IS-112	9/2/97	163	199	6.9	7.66	424	21.8	53,400
	IS-33	5/13/98	142	167	9.0	8.24	450	19.0	57,700
	IS-34	5/13/98	146	166	9.0	8.24	450	19.0	57,700
	IS-42	5/27/98	161	197	5.0	7.60	461	20.5	56,500
	IS-56	6/10/98	170	207	6.5	7.42	478	18.5	47,500
	IS-60	7/1/98	152	185	4.7	7.40	440	25.7	97,000
	IS-76	7/28/98	176	193	7.6	8.02	425	25.5	43,500
	IS-83	8/25/98	164	188	6.3	8.05	409	25.7	34,700
	IS-84	8/25/98	*	*	*	*	324	25.7	34,700
	IS-97	9/23/98	206	251	7.3	7.80	442	20.1	22,500
Missouri River at Hermann, MO - 06934500	IS-26	4/20/98	152	185	9.3	7.70	501	12.8	160,000
	IS-45	6/1/98	168	205	7.8	7.91	658	23.0	86,400
	IS-64	7/7/98	115	141	6.3	7.77	456	26.5	159,000
	IS-86	8/31/98	139	169	6.6	7.91	570	27.6	86,800
Mississippi River at Thebes, IL - 07022000	IS-101	6/11/97	157	191	8.0	7.49	586	21.5	246,000
	IS-25	4/16/98	139	169	9.2	7.85	401	12.6	579,000
	IS-50	6/10/98	147	179	7.1	7.93	496	20.9	282,000
	IS-51	6/10/98	*	*	*	*	*	*	*
	IS-74	7/22/98	156	191	5.9	8.02	500	30.0	271,000
	IS-91	9/9/98	168	205	7.7	8.09	571	27.2	130,000
Ohio River at Grand Chain, IL - 03612500	IS-102	6/12/97	63	77	7.1	7.42	282	19.8	673000
	IS-27	4/23/98	78	95	8.2	7.70	256	15.0	734,000
	IS-44	6/5/98	90	109	7.3	7.50	307	25.0	366,000
	IS-77	7/22/98	84	102	6.4	7.70	296	29.0	260,000
	IS-78	7/22/98	*	*	*	*	*	*	*
	IS-85	8/12/98	78	96	6.4	7.70	250	28.0	185,000
Yazoo River below Steele Bayou near Long Lake, MS - 07288955	IS-103	6/19/97	27	33	4.4	6.07	91	26.7	24,900
	IS-19	4/13/98	30	37	8.0	6.50	92	20.0	11,800
	IS-57	6/17/98	144	*	7.5	7.10	*	28.5	6,870
	IS-66	7/16/98	119	145	2.5	7.00	247	30.5	27,100
	IS-96	9/17/98	62	75	6.6	6.80	202	27.0	9,290
Mississippi River, St. Francisville, LA - 07373420	IS-117	5/6/97	101	123	8.1	7.30	361	16.0	812,000
	IS-106	6/19/97	97	118	6.7	7.92	353	23.0	763,000
	IS-10	4/2/98	86	104	8.9	7.92	349	13.5	959,000
	IS-11	4/2/98	*	*	*	*	*	*	*
	IS-31	4/30/98	104	127	8.5	8.03	337	17.0	794,000
	IS-32	4/30/98	*	*	*	*	*	*	*
	IS-49	6/9/98	110	134	5.9	7.94	350	26.0	541,000
	IS-63	7/9/98	113	138	6.1	7.98	354	26.0	708,000
	IS-99	9/28/98	145	*	7.4	8.27	471	27.5	254,000
Mississippi River at Vicksburg, MS - 07289000	IS-2A	1/13/98	*	*	10.6	7.74	361	8.6	933,000
	IS-2B	1/13/98	*	*	*	*	*	*	933,000
	IS-2C	1/13/98	*	*	*	*	*	*	933,000

Table 12. Physical properties and field chemistry in water samples collected in 1997–98 (mg/L, milligrams per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; ft^3/s, cubic feet per second; *, result not available)—Continued

Sampling station name and station number	Sample ID	Sample collection date	Alkalinity as $CaCO_3$ (mg/L)	Bicarbonate as HCO_3 (mg/L)	Dissolved oxygen (mg/L)	pH in standard units	Specific conductance in µs/cm	Water temperature (degrees Celsius)	Instantaneous discharge (ft^3/s)
Large river stations—Continued									
Mississippi River at Belle Chasse, LA - 07374525	IS-118	5/7/97	*	*	8.6	7.28	364	16.0	682,000
	IS-105	6/20/97	*	*	6.4	7.90	357	23.5	676,000
Small stream stations									
S. Fork Iowa River northeast of New Providence, IA - 05451210	IS-3A	1/30/98	*	*	10.7	7.55	659	1.0	*
	IS-3B	1/30/98	*	*	*	*	*	*	*
	IS-3C	1/30/98	*	*	*	*	*	*	*
	IS-5	3/30/98	211	257	11.1	8.39	661	11.5	312
	IS-8	3/30/98	225	275	*	*	*	*	*
	IS-41	5/29/98	110	134	8.6	7.81	507	17.5	872
	IS-79	8/3/98	238	290	9.8	8.20	622	20.4	34.4
Fourmile Creek near Traer, IA - 05464137	IS-107	6/30/97	*	*	8.5	7.51	583	19.3	*
	IS-20	4/15/98	127	155	11.1	7.78	504	7.3	54.1
	IS-67	7/16/98	169	206	8.8	7.54	537	16.7	23.4
	IS-80	8/12/98	194	237	9.2	8.01	537	18.2	9.1
Walnut Creek near Vandalia, IA - 05487550	IS-104	6/21/97	*	*	8.0	7.90	421	20.5	21.0
	IS-9	4/3/98	146	178	11.4	8.00	467	6.0	54.6
	IS-28	5/7/98	117	143	8.0	7.80	382	12.5	135
	IS-29	5/7/98	123	150	8.0	7.80	384	12.5	135
	IS-54	6/11/98	70	85	6.8	7.40	240	19.0	210
Panther Creek near El Paso, IL - 05567000	IS-115	11/13/97	290	354	12.0	7.62	837	2.7	14.0
	IS-16	4/9/98	226	276	11.4	7.85	728	8.3	153
	IS-48	6/9/98	226	276	9.4	7.43	720	15.2	104
	IS-61	7/7/98	180	220	7.4	7.55	572	23.0	168
Indian Creek near Wyoming, IL - 05568800	IS-111	8/27/97	302	368	8.6	8.02	720	20.8	36.0
	IS-15	4/9/98	204	249	10.8	7.60	576	8.1	272
	IS-39	5/25/98	230	281	9.4	7.55	641	16.1	104
	IS-72	7/22/98	208	254	7.6	7.76	437	24.3	102
	IS-73	7/22/98	*	*	*	*	*	*	*
Sugar Creek at Co Rd 400 S at New Palistine, IN - 03361650	IS-13	4/9/98	130	159	8.9	7.82	391	11.8	405
	IS-38	5/24/98	*	*	8.1	7.75	455	16.1	423
Little Buck Creek near Indianapolis, IN - 03353637	IS-113	9/9/97	102	124	7.6	7.90	419	20.0	1.9
	IS-14	4/9/98	115	140	9.2	7.78	351	11.6	329
	IS-37	5/24/98	*	*	8.2	7.87	485	17.1	137
	IS-71	7/20/98	105	128	6.6	7.66	316	23.9	51.0
North Dry Creek near Kearney, NE - 06770195	IS-6	4/1/98	*	*	8.7	8.20	1,210	13.0	30.0
	IS-40	5/22/98	204	*	6.6	7.98	1,040	16.5	82.0
	IS-43	6/8/98	*	230	9.2	7.90	1,040	15.5	40.0
	IS-92	9/9/98	*	*	9.7	8.70	1,210	26.5	9.8

Table 12. Physical properties and field chemistry in water samples collected in 1997–98 (mg/L, milligrams per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; ft^3/s, cubic feet per second; *, result not available)—Continued

Sampling station name and station number	Sample ID	Sample collection date	Alkalinity as $CaCO_3$ (mg/L)	Bicarbonate as HCO_3 (mg/L)	Dissolved oxygen (mg/L)	pH in standard units	Specific conductance in µs/cm	Water temperature (degrees Celsius)	Instantaneous discharge (ft^3/s)
Small stream stations—Continued									
Dismal River near Thedford, NE - 06775900	IS-17	4/13/98	80	96	9.3	8.20	156	13.5	230
	IS-36	5/19/98	73	*	8.4	8.30	186	17.5	227
	IS-55	6/16/98	*	*	8.8	8.20	185	19.5	223
	IS-95	9/15/98	*	*	8.7	8.21	173	16.0	217
South Fabius River near Taylor, MO - 05500000	IS-23	4/7/98	82	101	10.2	7.77	243	12.0	640
	IS-46	6/2/98	135	161	11.3	8.41	377	24.6	213
	IS-75	7/27/98	*	*	10.3	8.21	455	24.7	56.0
	IS-89	9/1/98	168	205	8.4	8.29	439	26.0	15.0
Elk River near Tiff City, MO - 07189000	IS-24	4/14/98	119	145	11.7	8.09	259	14.3	858
	IS-52	6/9/98	126	154	7.5	7.68	280	20.1	243
	IS-68	7/14/98	133	162	9.1	8.07	305	28.0	329
	IS-87	9/2/98	133	162	9.1	8.00	336	27.9	12.2
	IS-88	9/2/98	*	*	*	*	*	*	*
Shingle Creek at Queen Ave. N., MN - 05288705	IS-108	7/7/97	146	175	5.8	7.29	417	18.0	55.1
	IS-12	4/6/98	136	163	8.8	7.34	706	8.7	60.0
	IS-30	5/8/98	140	171	7.7	7.59	607	14.4	40.0
	IS-53	6/11/98	201	245	5.2	7.75	934	16.7	4.5
	IS-62	7/8/98	180	219	3.2	7.44	790	22.4	5.9
Little Cobb River near Beauford, MN - 05320270	IS-109	7/16/97	233	281	6.6	7.98	622	24.0	162
	IS-114	10/28/97	274	329	12.8	8.50	629	2.3	19.0
	IS-1A	1/14/98	335	433	12.0	7.64	828	0.1	2.1
	IS-1B	1/14/98	*	*	*	*	*	*	*
	IS-1C	1/14/98	*	*	*	*	*	*	*
	IS-4	3/30/98	208	254	8.8	7.76	558	8.6	381
	IS-7	3/30/98	*	*	*	*	*	*	*
	IS-35	5/18/98	241	294	7.5	7.94	655	19.6	166
	IS-70	7/15/98	195	*	7.5	7.67	546	24.8	72.0
	IS-90	8/17/98	221	269	6.2	7.97	549	25.8	2.9
Namekagon River at Leonards, WI - 05331833	IS-116	11/11/97	58	70	13.8	7.60	134	2.2	106
	IS-21	3/30/98	20	24	12.3	6.80	62	3.5	473
	IS-47	6/2/98	37	46	10.0	7.15	108	13.6	195
	IS-69	7/15/98	51	62	9.2	8.47	135	23.4	104
	IS-94	9/9/98	81	99	10.9	8.30	164	14.9	51.0
Rattlesnake Creek near North Andover, WI - 05413449	IS-110	8/1/97	*	*	*	*	*	*	17.3
	IS-22	4/15/98	*	*	*	*	*	*	32.0
	IS-59	6/19/98	*	*	8.0	8.30	604	16.5	70.0
	IS-81	8/21/98	*	*	8.9	8.00	761	21.0	29.0
	IS-82	8/21/98	*	*	*	*	*	*	*
	IS-98	9/22/98	*	*	13.9	8.30	758	14.4	26.0
Bogue Phalia near Leland, MS - 07288650	IS-18	4/14/98	174	212	7.4	7.40	416	19.0	41.0
	IS-58	6/18/98	166	203	7.3	7.80	561	31.5	126
	IS-65	7/15/98	138	168	3.6	7.20	342	28.0	2,130
	IS-93	9/16/98	182	222	5.4	7.80	523	27.0	219

Table 13. Statistical summary of physical properties and field chemistry data in water sampled collected in 1997–98 (mg/L, milligrams per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; ft^3/s, cubic feet per second; C, Celsius)

Parameter	Analytical reporting limit	Number of analyses	Minimum value	Maximum value	Mean value	Median value	Standard deviation
All stations							
Alkalinity as $CaCO_3$ in mg/L	1.0	76	20	302	147	146	62
Bicarbonate as HCO_3 in mg/L	1.0	76	24	368	178	177	75
Dissolved oxygen in mg/L	0.1	104	2.5	13.9	8.2	8.1	2.1
pH in standard units	0.1	104	6.1	8.7	7.8	7.8	0.4
Specific conductance in µs/cm	1.0	102	62	1,210	467	446	223
Water temperature in degrees C	0.1	105	1.0	31.5	19.0	19.5	6.9
Instantaneous discharge in cfs	0.1	112	1.9	959,000	123,794	237	257,513
Large river stations							
Alkalinity as $CaCO_3$ in mg/L	1.0	34	27	206	124	139	44
Bicarbonate as HCO_3 in mg/L	1.0	34	33	251	150	167	52
Dissolved oxygen in mg/L	0.1	38	2.5	10.7	7.2	7.2	1.5
pH in standard units	0.1	38	6.1	8.6	7.7	7.8	0.5
Specific conductance in µs/cm	1.0	37	90	658	390	401	125
Water temperature in degrees C	0.1	39	12.6	30.5	22.5	23.0	5.1
Instantaneous discharge in cfs	0.1	42	6,870	959,000	329,820	172,500	331,600
Small stream stations with basins dominated by row crop agriculture and/or livestock production							
Alkalinity as $CaCO_3$ in mg/L	1.0	4	110	238	196	218	58
Bicarbonate as HCO_3 in mg/L	1.0	4	134	290	239	266	71
Dissolved oxygen in mg/L	0.1	15	6.6	13.9	9.5	9.1	1.8
pH in standard units	0.1	15	7.5	8.7	8.1	8.1	0.3
Specific conductance in µs/cm	1.0	15	259	1,210	683	659	324
Water temperature in degrees C	0.1	15	1.0	28.0	17.6	16.5	7.0
Instantaneous discharge in cfs	0.1	16	9.8	872	187	37.2	285
Small stream stations with basins dominated by row crop agriculture							
Alkalinity as $CaCO_3$ in mg/L	1.0	25	70	302	191	194	57
Bicarbonate as HCO_3 in mg/L	1.0	25	85	368	234	237	69
Dissolved oxygen in mg/L	0.1	33	3.6	12.8	8.7	8.5	2.0
pH in standard units	0.1	33	7.2	8.5	7.8	7.8	0.3
Specific conductance in µs/cm	1.0	32	240	837	521	537	137
Water temperature in degrees C	0.1	33	2.3	31.5	17.5	19.0	7.7
Instantaneous discharge in cfs	0.1	36	2.1	2,130	196	104	363
Small stream stations with basins dominated by urban land							
Alkalinity as $CaCO_3$ in mg/L	1.0	8	102	201	141	138	35
Bicarbonate as HCO_3 in mg/L	1.0	8	124	245	171	167	43
Dissolved oxygen in mg/L	0.1	9	3.2	9.2	6.9	7.6	1.9
pH in standard units	0.1	9	7.3	7.9	7.6	7.7	0.2
Specific conductance in µs/cm	1.0	9	316	934	558	485	214
Water temperature in degrees C	0.1	9	8.7	23.9	17.0	17.1	4.9
Instantaneous discharge in cfs	0.1	9	1.9	329	76	51	104
Small stream stations with basins dominated by undeveloped land							
Alkalinity as $CaCO_3$ in mg/L	1.0	5	20	81	49	51	23
Bicarbonate as HCO_3 in mg/L	1.0	5	24	99	60	62	28
Dissolved oxygen in mg/L	0.1	9	8.4	13.8	10.2	9.3	1.8
pH in standard units	0.1	9	6.8	8.5	7.9	8.2	0.6
Specific conductance in µs/cm	1.0	9	62	186	145	156	40
Water temperature in degrees C	0.1	9	2.2	23.4	13.8	14.9	6.9
Instantaneous discharge in cfs	0.1	9	51	473	203	217	121

Science and Technology, 1999; Carey and others, 1999; Alexander and others, 2000); that much of the NO_3 in the Mississippi River originates in the agriculturally dominated basins of the upper-Midwestern United States, and is transported without significant transformation or other loss to the Gulf of Mexico. Isotope ratio values could not be used to identify specific NO_3 sources in small streams or large rivers. The isotope results did show that in-stream transformations of NO_3 do not result in a significant (more than 15%) loss in N mass and do not significantly alter the isotope signal in large rivers. Hence, basins with large annual yields of NO_3 are likely to be the most significant sources of NO_3 to the Gulf of Mexico. Clearly, the rivers in the Mississippi basin with the highest annual NO_3 yields are those in the upper-midwest that are dominated by row crop agriculture and/or livestock production (Goolsby and others, 1999; Goolsby and Battaglin, 2000).

In figure 12, the $\delta^{15}N$ and $\delta^{18}O$ of NO_3 values from large rivers are plotted along with the typical ranges of $\delta^{15}N$ and $\delta^{18}O$ of NO_3 values from various nitrogen sources. Plots of $\delta^{15}N$ versus $\delta^{18}O$ of NO_3 values have been used to show how NO_3 in environmental samples compares to NO_3 from various N sources and how denitrification can change isotope values (Clark and Fritz, 1997; Kendall, 1998). The $\delta^{15}N$ and $\delta^{18}O$ of NO_3 values suggest that in large rivers NO_3 comes from more than one source. All of the $\delta^{15}N$ of NO_3 values from large rivers are within the range of values expected from NO_3 formed by nitrification in soils. Some $\delta^{15}N$ of NO_3 values are within the range of values expected from other sources including animal waste and atmospheric nitrate. The higher $\delta^{18}O$ of NO_3 values at some stations suggest that atmospheric sources of NO_3 are also important. The source of atmospheric NO_3 in the Mississippi basin is likely a mixture of NO_3 volatilized from soils, the conversion of atmospheric N_2 to NO_3 by lightning, and NO_3 from anthropogenic sources such as industrial emissions or automobile exhaust (Kendall, 1998). NO_3-based fertilizers such as calcium nitrate also have higher $\delta^{18}O$ of NO_3 values than NO_3 formed after application of more commonly used (Terry and Kirby, 1999) ammonium-based fertilizers.

In figure 13, $\delta^{15}N$ and $\delta^{18}O$ the NO_3 values from small streams are plotted by dominant land-cover type with the ranges of values from various N sources. $\delta^{15}N$ and $\delta^{18}O$ of NO_3 values show more of a pattern of separation than values from large rivers. NO_3 from basins dominated by urban land has an isotopic signature that resembles atmospheric NO_3 or NO_3 fertilizer. NO_3 from basins dominated by undeveloped land also resembles atmospheric NO_3. NO_3 from basins dominated by row crops or row crops and/or livestock production are very similar isotopically, and resemble the isotopic signature of the large rivers (fig. 12).

Evidence for Transformation of Nitrogen in the Mississippi River

NO_3 isotope values from large rivers are within the range of value from the small streams. This relationship suggests that denitrification in the main stem Mississippi River is not transforming much NO_3 and not causing a significant shift in NO_3 isotope ratio values. In figure 14, the distribution of NO_2 plus NO_3 concentrations and isotope values from large rivers are plotted in boxplots. These plots can be compared with boxplots of small streams results (fig. 8). All NO_2 plus NO_3 concentrations from large rivers are less than the median concentrations from basins dominated by row crops or row crops and/or livestock production, but most are greater than concentrations from basins dominated by urban or undeveloped land. Most $\delta^{15}N$ of NO_3 values from large rivers are between +5‰ and +10‰—a similar range to values from basins dominated by row crops or row crops and/or livestock production, but generally greater than values from basins dominated by urban or undeveloped land. In contrast, most $\delta^{18}O$ of NO_3 values from large rivers are greater than +10‰, a similar range to values from basins dominated by urban land, but generally greater than values from basins dominated by row crops or row crops and/or livestock production.

Results of isotope (table 4), and nutrient (table 8), and major ion (table 10) analyses from the two Lagrangian sample sets were used (Battaglin and others, 2001) to determine whether simple mixing models can explain how NO_3 behaves in the Lower Mississippi River, and what transformations affect NO_3 in the river. The analysis suggests that a small fraction of the NO_3 present in the Upper Mississippi and Ohio Rivers is lost between their confluence and the Gulf of Mexico. However, mixing of water from the Upper Mississippi and Ohio Rivers can explain the measured isotope values in the Lower Mississippi River. This result suggests that denitrification or other

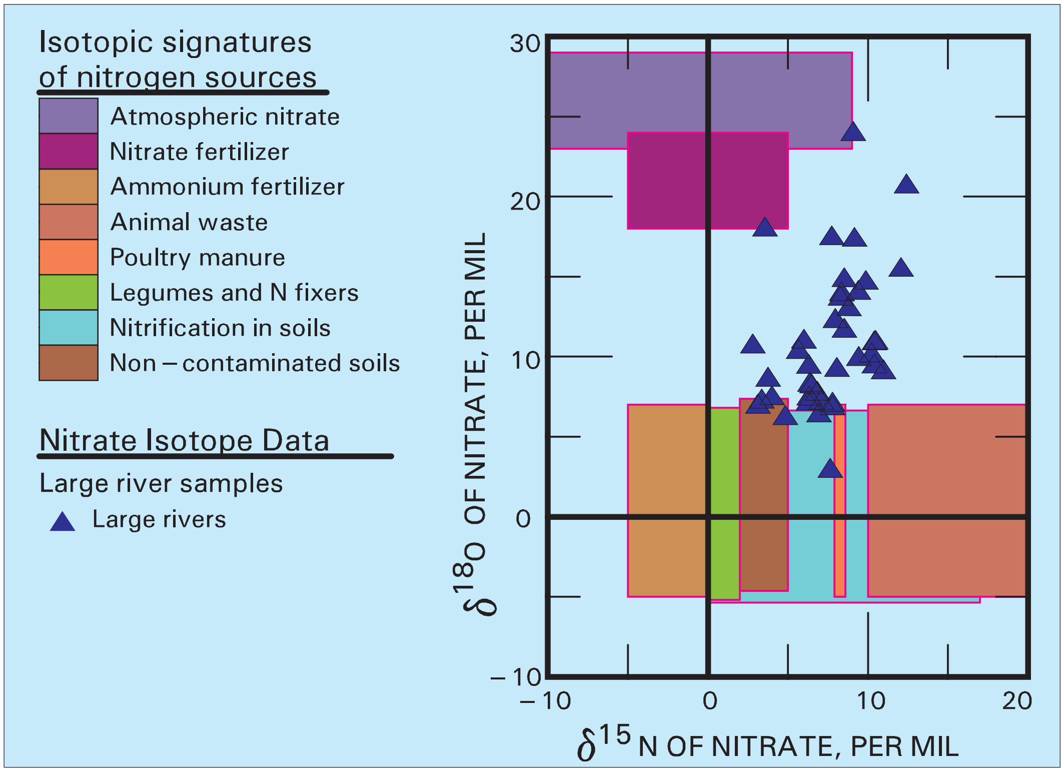

Figure 12. Typical ranges of $\delta^{15}N$ and $\delta^{18}O$ of NO_3 values for various N sources and measured values from large river stations, 1997–1998 (modified from Kendall, 1998, figure 16.9).

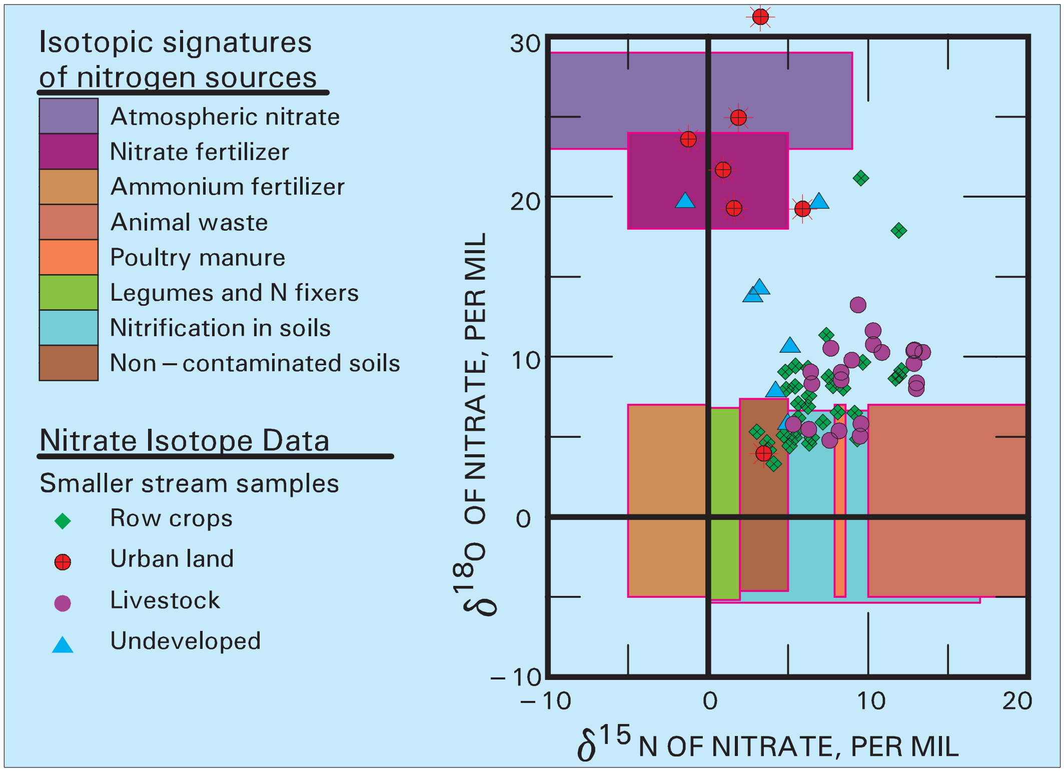

Figure 13. Typical ranges of $\delta^{15}N$ and $\delta^{18}O$ of NO_3 for various N sources and measured values from small stream stations, 1997–1998 (modified from Kendall, 1998, figure 16.9).

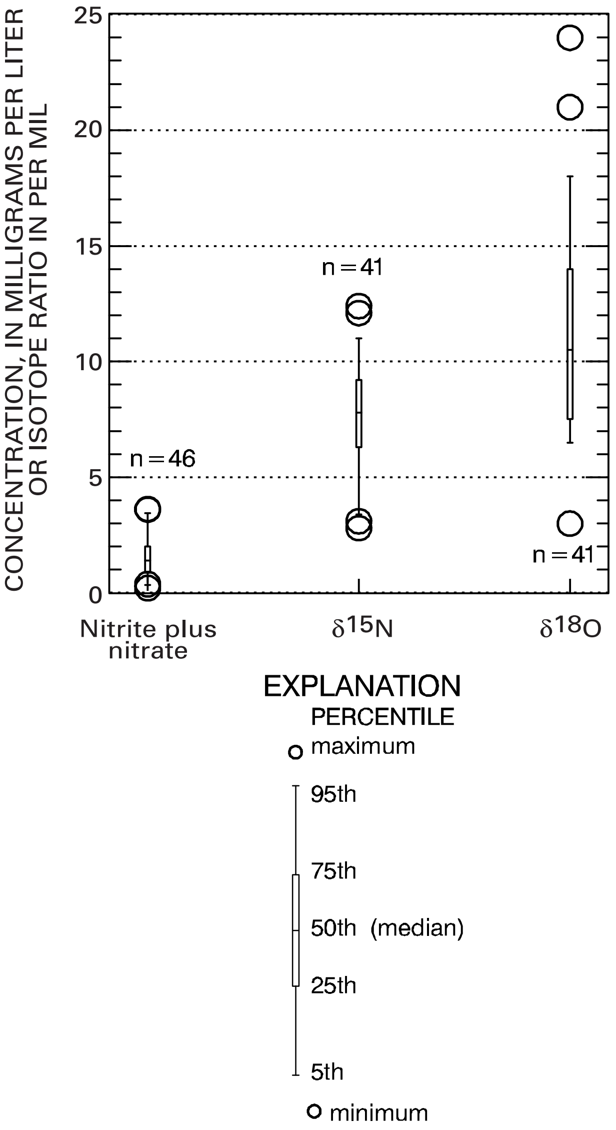

Figure 14. $\delta^{15}N$ and $\delta^{18}O$ of NO_3 values and NO_2 plus NO_3 concentrations from large river stations.

transformations that favor one isotope over the other do not occur to a large degree in the ~1,100 kilometers of river between the confluence and the Lower Mississippi stations. Assimilation by benthic or suspended algae or exchange of river water with ground water that has a lighter $\delta^{15}N$ of NO_3 isotopic signature are plausible explanations for this result (Battaglin and others, 2001).

CONCLUSIONS

Identification of sources of nitrate (NO_3) and mechanisms and rates of NO_3 removal in the Missisippi River help to understand the effects of upstream activities on development of the Gulf of Mexico hypoxic zone. Results from isotopic analyses of about 120 water and suspended sediment samples collected in 1997 and 1998 from 24 locations in the Mississippi River Basin during this pilot study are tabulated and analyzed in this report. This was a pilot study with a relatively small number of sampled collected in a very large study area.

Distinct $\delta^{15}N$ and $\delta^{18}O$ of NO_3 isotope ratio values were measured in smaller streams that have relatively uniform nitrogen (N) sources of in their drainage basins (fig. 8). Most $\delta^{15}N$ of NO_3 values from basins dominated by urban or undeveloped land are less than +5‰, while most values from basins dominated by row crop or row crops and/or livestock production are greater than +5‰. $\delta^{18}O$ of NO_3 values are also distinctive. Most values from basins dominated by urban or undeveloped land greater than +10‰, while most values from basins dominated by row crops or row crops and/or livestock production are less than +10‰. The distinctiveness of $\delta^{15}N$ and $\delta^{18}O$ of NO_3 values from the small basins is likely limited by the lack of uniformity of land-cover within those basins. Separating row crop agriculture from livestock production and finding uniformly urban or undeveloped basins in the agriculturally dominated midwestern States was particularly difficult.

There was considerable temporal and spatial variation in $\delta^{15}N$ and $\delta^{13}C$ of POM values at stations across the Mississippi Basin. $\delta^{15}N$ of POM values from basins dominated by urban or undeveloped land also tended to be less than +5‰, while most values from basins dominated by row crops or row crops and/or livestock production are greater than +5‰.

There is some indication of seasonal- or discharge-related variability in the isotope results from a given station. $\delta^{15}N$ and $\delta^{18}O$ of NO_3 values tend to increase from spring to fall as discharge and NO_3 concentrations decrease. $\delta^{15}N$ of POM values also tend to increase from spring to fall. More data is needed to determine if these shifts are the result of a change in the source of water, NO_3, and POM or are evidence for transformation of NO_3 during late-summer months.

In part because of the small number of samples, the isotope data from large rivers could not be used to identify the proportions of NO_3 that originated from various N sources within the basin. However, the data do confirm that NO_3 from major tributaries accumulates in the Mississippi River and is not significantly altered by transformations such as denitrification as it is transported to the Gulf of Mexico. The ranges of NO_3 and particulate organic material (POM) isotope values from large rivers are generally narrower and near the middle of the ranges of measurements from all stations.

Suggestions for Future Research

This pilot study, with comparatively large and complex basins, showed that source differentiation and transformation characterization in small streams and larger rivers is possible with a multi-isotope approach. However, because of the limited number of samples and sampling stations, it was not always possible to sort out the difference between seasonal (or flow related) changes in NO_3 sources and changes in isotope values resulting from NO_3 transformations. A time-series plot of the POM data from the Yazoo River station (fig. 15) highlights this point. At this station (and several others on large rivers) POM samples were collected more frequently as part of a related study (Kendall and others, 2001). In figure 15, all isotope ratio values from POM samples collected at this station are plotted as open circles and those that have matching NO_3 isotope data (collected for this study) are plotted as filled circles. Clearly there is temporal pattern to the $\delta^{15}N$ and $\delta^{13}C$ of POM values that is not well represented by the four samples collected and analyzed for this study.

We suggest that more isotope data be collected in the Mississippi Basin. This effort should focus on building a long-term baseline of data at few locations and then detailed temporal data at a few stations. Collection of additional Lagrangian data sets is also recommended. This should involve sampling of other significant rivers in the Mississippi basins (for example, the Illinois River and Red River) that were not sampled in this study. Cost is always a limiting factor in study design. Newly available equipment, and resulting simplifications in sample processing and analysis will reduce the per sample cost of isotope analysis. These will aid our understanding of the dynamics of delivery and transformation of NO_3 in the Mississippi River basin. The data may also show how changes in cultural practices, such as use of agricultural best management practices affect delivery of NO_3 to streams of the midwestern United States.

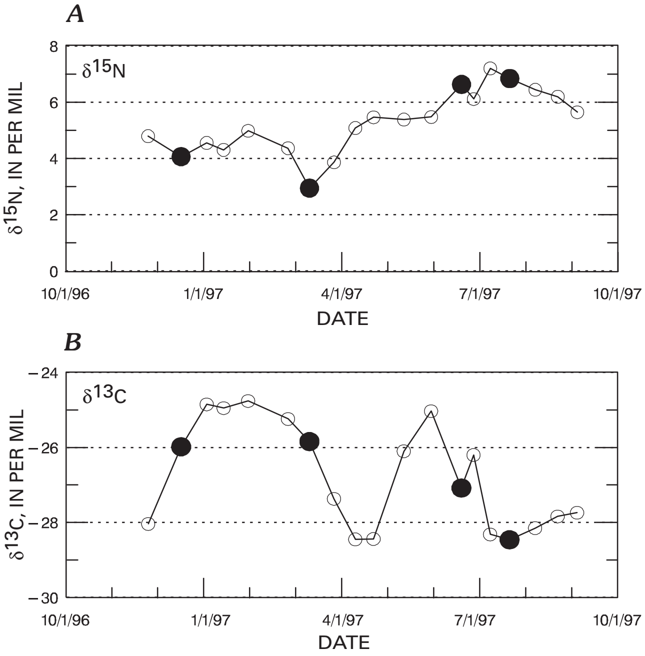

Figure 15. Particulate organic material data time series for the Yazoo River in 1997 (open circles are all data and filled circles are data collected for this study); (*A*) $\delta^{15}N$, and (*B*) $\delta^{13}C$.

REFERENCES CITED

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

Alexander, R.B., Smith, R.A., and Schwarz, G.E., 2000, Effect of stream channel size on the delivery of nitrogen to the Gulf of Mexico: Nature, v. 403, p. 758–761.

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

Battaglin, W.A., Kendall, C., Goolsby, D.A., and Boyer, L.L., 1997, Plan of study to determine if the isotopic ratios $\delta^{15}N$ and $\delta^{18}O$ can reveal the sources of nitrate discharged by the Mississippi River into the Gulf of Mexico: U.S. Geological Survey Open-File Report 97–230, 18 p.

Battaglin, W.A., Kendall, C., Chang, C.C.Y., Silva, S.R., and Campbell, D.H., 2001, Chemical and isotopic evidence of nitrogen transformation in the Mississippi River, 1997–98: Hydrologic Processes, v. 15, no. 7, p. 1285–1300.

Böhlke, J.K. and Denver, J.M., 1995, Combined use of groundwater dating, chemical, and isotopic analyses to resolve the history and fate of nitrate contamination in two agricultural watersheds, Atlantic coastal plain, Maryland: Water Resources Research, v. 31, no. 9, p. 2319–2339.

Böttcher, J., Strebel, O., Voerkelius, S., and Schmidt, H.L., 1990, Using isotope fractionation of nitrate-nitrogen and nitrate-oxygen for evaluation of microbial denitrification in a sandy aquifer: Journal of Hydrology, v. 114, p. 413–424.

Broshears, R.E., Clark, G.M., and Jobson, H.E., 2001, Simulation of discharge and transport of nitrate and selected herbicides in the Mississippi River Basin: Hydrologic Processes v. 15, no. 8, p.???????.

Burkart, M.R., and James, D.E., 1999, Agricultural-nitrogen contributions to hypoxia in the Gulf of Mexico: Journal of Environmental Quality, v. 28, p. 850–859.

Carey, A.E., Pennock, J.R., Lehrter, J.C., Lyons, W.B., Schroeder, W.W., and Bonzongo, J-C., 1999, The role of the Mississippi River in Gulf of Mexico hypoxia. University of Alabama Environment Institute Report No. 70, 100 p.

Chang, C.C.Y., Langston, J., Riggs, M., Campbell, D.H., Silva, S.R., and Kendall, C., 1999, A method of nitrate collection for $\delta^{15}N$ and $\delta^{18}O$ analysis from water with low nitrate concentrations: Canadian Journal of Fishery and Aquatic Science, v. 56, p. 1856–1864.

Clark, I. and Fritz, P., 1997, Environmental Isotopes in Hydrogeology: Boca Raton, Fla., CRC Press LLC, 328 p.

Council for Agricultural Science and Technology, 1999, Gulf of Mexico Hypoxia Land and sea interactions: Task Force Report No. 134, 44 p.

Dole, R.B., 1909, The quality of surface waters in the United States: Part 1—Analysis of waters east of the one hundredth meridian: U.S. Geological Survey Water-Supply Paper 236, 123 p.

Cravotta, C.A., 1995, Use of stable isotopes of carbon, nitrogen, and sulfur to identify sources of nitrogen in surface waters in the Lower Susquehanna River Basin, Pennsylvania: U.S. Geological Survey Open-File Report 94–510, 103 p.

Diaz, R.J., and Rosenberg, R., 1995, Marine benthic hypoxia—A review of its ecological effects and the behavioral responses of benthic macrofauna: Oceanography and Marine Biology—An Annual Review, v. 33, p. 245–303.

Dole, R.B., 1909, The quality of surface waters in the United States. Part I. Analysis of waters east of the one hundredth meridian: U.S. Geological Survey Water-Supply Paper 236.

Dunn, D. D., 1996, Trends in nutrient inflows to the Gulf of Mexico from streams draining the conterminous United States, 1972–93: U.S. Geological Survey Water-Resources Investigations Report 96–4113, 60 p.

Feigin, A., Shearer, G., Kohl, D.H., and Commoner, B., 1974, The amount of nitrogen-15 content of nitrate in soil profiles from two central Illinois fields in a corn-soybean rotation: Soil Science Society of America Proceedings, v. 38, p. 465–471.

Fishman, M.J., and Friedman, L.C., 1989, Methods for determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A1, 545 p.

Fogel, M.L., and Cifuentes, L.A., 1993, Isotope fractionation during primary production, *in*, M. Engel and S. Macko, eds., Organic geochemistry: New York, Plenum Press, p. 73–98.

Goni, M.A., Ruttenberg, K.C., and Eglinton, T.I., 1998, A reassessment of the sources and importance of land-derived organic matter in surface sediments from the Gulf of Mexico: Geochimica et Cosmochimica Acta, v. 62, p. 3055–3057.

Goolsby, D. A., and Battaglin, W. A., 2000, Nitrogen in the Mississippi Basin—Estimating sources and predicting flux to the Gulf of Mexico: U.S. Geological Survey Fact Sheet 135–00, 6 p.

Goolsby, D. A., and Battaglin, W. A., 2001, Long-term changes in concentrations and flux of nitrogen in the Mississippi River basin, USA: Hydrologic Processes, v. 15, no. 7, p. 1209–1226.

Goolsby, D.A., Battaglin, W.A., Lawrence, G.B., Artz, R.S., Aulenbach, B.T., Hooper, R.P., Keeney, D.R., and Stensland, G.J., 1999, Flux and sources of nutrients in the Mississippi-Atchafalaya River Basin—Topic E Report for the Integrated Assessment on Hypoxia in the Gulf of Mexico: NOAA Coastal Ocean Program Decision Analysis Series No. 17. NOAA Coastal Ocean Program, Silver Spring, Md., 130 p.

Heaton, T.H.E., 1986, Isotopic studies of nitrogen pollution in the hydrosphere and atmosphere: a review: Chemical Geology (Isotope Geoscience Section), v. 59, p. 87–102.

Helsel, D.R., and Hirsch, R.M., 1992, Statistical Methods in Water Resources: New York, Elsevier, 522 p.

Hubner, H., 1986, Isotope effects of nitrogen in the soil and biosphere, *in* P. Fritz and J. Fontes, eds., Handbook of Environmental Isotope Geochemistry, v. 2b, The terrestrial environment: Elsevier, p. 361–425.

Iman, R.L., and Conover, W.J., 1983, A modern approach to statistics: New York, John Wiley & Sons, 497 p.

Kellman, L., and Hillaire-Marcel, C., 1998, Nitrate cycling in streams—Using natural abundances of $NO_3 - \delta^{15}n$ to measure in-situ denitrification: Biogeochemistry, v. 43, p. 273–292.

Kendall, C., and Grimm, E., 1990, Combustion tube method for measurements of nitrogen isotope ratios using calcium oxide for total removal of carbon dioxide and water: Analytical Chemistry, v. 62, p. 526–529.

Kendall, C., Campbell, D.H., Burns, D.A., Shanley, J.B., Silva, S.R., and Chang, C.C.Y., 1995, Tracing sources of nitrate in snowmelt runoff using the oxygen and nitrogen isotopic compositions of nitrate, *in* Biogeochemistry of seasonally snow-covered catchments: International Association of Hydrological Sciences Publication No. 228, p. 339–347.

Kendall, C., 1998. Tracing nitrogen sources and cycling in catchments, *in* Kendall, C., and McDonnell, J.J., eds, Isotope-tracers in catchment hydrology, The Netherlands, Elsevier, p. 534–569.

Kendall, C., Silva, S.R., and Kelly, V.J., 2001, Carbon and nitrogen isotopic compositions of particulate organic matter in four large river systems across the United States, Hydrologic Processes, v. 15, no. 8, p.

Kohl, D.H., Shearer, G.B., and Commoner, B., 1971, Fertilizer nitrogen—Contribution to nitrate in surface water in a corn belt watershed: Science, v. 174, p. 1331–1334.

Kreitler, C.W., 1975, Determining the sources of nitrate in ground water by nitrogen isotope studies: Austin, University of Texas, Bureau of Economic Geology, Report of Investigations No. 83, 57 p.

Leighton, M.O., 1907, Pollution of Illinois and Mississippi Rivers by Chicago sewage—A digest of the testimony taken in the case of the State of Missouri v. the State of Illinois and the Sanitary District of Chicago: U.S. Geological Survey Water-Supply and Irrigation Paper no. 194, 369 p.

Mannion, A.M., 1995, Agriculture and Environmental change—Temporal and spatial dimensions: Chichester, John Wiley & Sons, 405 p.

McPhee, 1989, The control of nature: New York, Farrar, Straus and Giroux, 272 p.

Meade, R.H., 1995, Setting—Geology, hydrology, sediments, and engineering of the Mississippi River, *in* R.H. Meade, ed., Contaminants in the Mississippi River, 1987–92: U.S. Geological Survey Circular 1133, p. 13–30.

Meade, R.H., and Stevens, H.H., Jr., 1990, Strategies and equipment for sampling suspended sediment and associated with toxic chemicals in large rivers—with emphasis on the Mississippi River: Science of the Total Environment, v. 97/98, p. 125–135.

Moody, J.A., 1993, Evaluation of the Lagrangian scheme for sampling the Mississippi River during 1987–1990: U.S. Geological Survey Water-Resources Investigations Report 93–4042, 31 p.

NASQAN, 2001, National Stream Quality Accounting Network home page. Accessed 1/2001 at http://water.usgs.gov/nasqan/.

NAWQA, 2001, National Water Quality Assessment program. Accessed 1/2001 at http://water.usgs.gov/nawqa/.

National Agricultural Statistics Service, 1999, U.S. Department of Agriculture: National Agricultural Statistics Service Historical Data. Accessed 7/99 at URL http://www.usda.gov/nass/pubs/histdata.htm.

Onstad, G.D., Canfield, D.E., Quay, P.D., and Hedges, J.I., 2000, Sources of particulate organic matter in rivers from the continental USA—Lignin phenol and stable carbon isotope compositions: Geochimica et Cosmochimica Acta, v. 64, no. 20, p. 3439–3546.

Palmer, A.W., ca. 1903, Chemical Survey of the Waters of Illinois: Report for the years 1897–1902, University of Illinois, 254 p.

Rabalais, N. N., Turner, R. E., Justic, D., Dortch, Q., Wiseman, W. J., and Gupta, B. K. S., 1996, Nutrient changes in the Mississippi River and System responses on the adjacent continental shelf: Estuaries, v. 19, no. 2b, p. 386–407.

Rabalais, N. N., Turner, R. E., Justic, D., Dortch, Q., and Wiseman, W. J., 1999, Characterization of hypoxia: topic 1 report for the integrated assessment on hypoxia in the Gulf of Mexico: NOAA Coastal Ocean Program, NOAA Coastal Ocean Program Decision Analysis, Silver Spring, Md., Series no. 15, 167 p.

Shelton, L. R., 1994, Field guide for collecting and processing stream-water samples for the National Water-Quality Assessment program: U.S. Geological Survey Open-File Report 94–539, 57 p.

Showers, W.J., Eisenstein, D.M., Paerl, H., and Rudek, J., 1990, Stable isotope tracers of nitrogen sources to the Neuse River, North Carolina: Raleigh, North Carolina Water Resources Research Institute, Completion Report no. 253, 28 p.

Silva, S.R., Kendall, C., Wilkison, D.H., Ziegler, A.C., Chang, C.C.Y., and Avanzino, R.J., 2000, A new method for collection of nitrate from fresh water and analysis of its nitrogen and oxygen isotope ratios: Journal of Hydrology, v. 228, p. 22–36.

Terry, D.L., and Kirby, B.J., 1999, Commercial fertilizers 1999—A summary of fertilizer use in the United States: Lexington, Ky., Association of American Plant Food Control Officials, Inc. and The Fertilizer Institute, 41 p.

Turner, R. E., and Rabalais, N. N., 1991, Changes in Mississippi River water quality this century—Implications for coastal food webs, BioScience, v. 41, p. 140–147.

U.S. Department of Agriculture, 1997, Agricultural resources and environmental indicators, 1996–97: Washington, D.C., U.S Department of Agriculture, Economic Research Service, Natural Resources and Environment Division, Agricultural Handbook no. 712.

U.S. Geological Survey, 2000, National land cover characterization project home page, accessed 3/2000 at http://edcwww.cr.usgs.gov/programs/lccp/nationallandcover.html.

Van der Leeden, F., Troise, L., and Dodd, D.K., 1990, The Water Encyclopedia: Chelsea, Mich., Lewis Publishers Inc., 181 p.

Voerkelius, S., and Schmidt, H.L., 1990, Natural oxygen and nitrogen isotope abundance of compounds involved in denitrification: Mitteilungen der Deut. Bodenkundlichen Gesselschaft, v. 60, p. 364–366.

Winter, T.C., Harvey, J.W., Franke, O.L., and Alley, W.M., 1998, Ground water and surface water—A single resource. U.S. Geological Survey Circular 1139, 70 p.