

MAJOR IONS  
NUTRIENTS  
AND  
TRACE ELEMENTS



IN THE  
MISSISSIPPI RIVER  
NEAR THEBES, ILLINOIS  
JULY THROUGH SEPTEMBER  
1 . 9 . 9 . 3



Front cover—View of Highway 67, West Alton, Missouri  
(Srenco Photography, St. Louis, Mo.)

Back cover—View of Spirit of St. Louis Airport,  
Chesterfield, Mo. (Srenco Photography,  
St. Louis, Mo.)

Field Hydrologist making streamflow  
measurements (U.S. Geological Survey)

# MAJOR IONS, NUTRIENTS, AND TRACE ELEMENTS IN THE MISSISSIPPI RIVER NEAR THEBES, ILLINOIS, JULY THROUGH SEPTEMBER 1993

*By* Howard E. Taylor, Ronald C. Antweiler, Terry I. Brinton, David A. Roth, *and* John A. Moody

Floods in the Upper Mississippi River Basin, 1993

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U.S. GEOLOGICAL SURVEY CIRCULAR 1120-D

**U.S. DEPARTMENT OF THE INTERIOR**  
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## FOREWORD

During spring and summer 1993, record flooding inundated much of the upper Mississippi River Basin. The magnitude of the damages—in terms of property, disrupted business, and personal trauma—was unmatched by any other flood disaster in United States history. Property damage alone is expected to exceed \$10 billion. Damaged highways and submerged roads disrupted overland transportation throughout the flooded region. The Mississippi and the Missouri Rivers were closed to navigation before, during, and after the flooding. Millions of acres of productive farmland remained under water for weeks during the growing season. Rills and gullies in many tilled fields are the result of the severe erosion that occurred throughout the Midwestern United States farmbelt. The hydrologic effects of extended rainfall throughout the upper Midwestern United States were severe and widespread. The banks and channels of many rivers were severely eroded, and sediment was deposited over large areas of the basin's flood plain. Record flows submerged many areas that had not been affected by previous floods. Industrial and agricultural areas were inundated, which caused concern about the transport and fate of industrial chemicals, sewage effluent, and agricultural chemicals in the floodwaters. The extent and duration of the flooding caused numerous levees to fail. One failed levee on the Raccoon River in Des Moines, Iowa, led to flooding of the city's water treatment plant. As a result, the city was without drinking water for 19 days.

As the Nation's principal water-science agency, the U.S. Geological Survey (USGS) is in a unique position to provide an immediate assessment of some of the hydrological effects of the 1993 flood. The USGS maintains a hydrologic data network and conducts extensive water-resources investigations nationwide. Long-term data from this network and information on local and regional hydrology provide the basis for identifying and documenting the effects of the flooding. During the flood, the USGS provided continuous streamflow and related information to the National Weather Service (NWS), the U.S. Army Corps of Engineers, the Federal Emergency Management Agency (FEMA), and many State and local agencies as part of its role to provide basic information on the Nation's surface- and ground-water resources at thousands of locations across the United States. The NWS has used the data in forecasting floods and issuing flood warnings. The data have been used by the Corps of Engineers to operate water diversions, dams, locks, and levees. The FEMA and many State and local emergency management agencies have used USGS hydrologic data and NWS forecasts as part of the basis of their local flood-response activities. In addition, USGS hydrologists are conducting a series of investigations to document the effects of the flooding and to improve understanding of the related processes. The major initial findings from these studies will be reported in this Circular series as results become available.

U.S. Geological Survey Circular 1120, *Floods in the Upper Mississippi River Basin, 1993*, consists of individually published chapters that will document the effects of the 1993 flooding. The series includes data and findings on the magnitude and frequency of peak discharges; precipitation; water-quality characteristics, including nutrients and man-made contaminants; transport of sediment; assessment of sediment deposited on flood plains; effects of inundation on ground-water quality; flood-discharge volume; effects of reservoir storage on flood peaks; stream-channel scour at selected bridges; extent of flood-plain inundation; and documentation of geomorphologic changes.



Acting Director  
February 28, 1994

# Contents

Foreword.....	III
Abstract.....	1
Introduction.....	1
Study methods.....	3
Sample collection and processing procedures.....	3
Laboratory analysis techniques.....	4
Occurrence and transport of constituents.....	4
Occurrence of major ions, nutrients, and trace elements.....	4
Transport of constituents.....	6
Summary.....	7
References cited.....	7

## FIGURES

1. Map of the Mississippi River showing the location of sampling sites on the Mississippi River near Thebes, Illinois.....	2
2. Photograph showing the railroad bridge on the Mississippi River near Thebes, Illinois, and the monorail car with collapsible-bag sampler used to collect water-quality samples below the railroad bridge.....	3
3.–15. Graphs showing:	
3. Discharge, pH, alkalinity, specific conductance, and concentrations of dissolved chromium and vanadium in the Mississippi River near Thebes, Illinois, July through September 1993.....	9
4. Concentrations of dissolved nitrate, nitrite, ammonium ion, phosphate, dissolved organic carbon, and suspended sediment in the Mississippi River near Thebes, Illinois, July through September 1993.....	10
5. Concentrations of dissolved silica, sodium, potassium, calcium, magnesium, and strontium in the Mississippi River near Thebes, Illinois, July through September 1993.....	11
6. Concentrations of dissolved bicarbonate, carbonate, chloride, sulfate, fluoride, and bromide in the Mississippi River near Thebes, Illinois, July through September 1993.....	12
7. Concentrations of dissolved aluminum, mercury, lithium, molybdenum, nickel, and uranium in the Mississippi River near Thebes, Illinois, July through September 1993.....	13
8. Concentrations of dissolved boron, barium, beryllium, cobalt, copper, and arsenic in the Mississippi River near Thebes, Illinois, July through September 1993.....	14
9. pH and concentrations of dissolved sodium, barium, phosphate, mercury, and uranium as a function of discharge in the Mississippi River near Thebes, Illinois, July through September 1993.....	15
10. Loads of dissolved nitrate, nitrite, ammonium ion, phosphate, dissolved organic carbon, and suspended sediment in the Mississippi River near Thebes, July through September 1993.....	16
11. Loads of dissolved silica, sodium, potassium, calcium, magnesium, and strontium in the Mississippi River near Thebes, Illinois, July through September 1993.....	17
12. Loads of dissolved bicarbonate, carbonate, chloride, sulfate, fluoride, and bromide in the Mississippi River near Thebes, Illinois, July through September 1993.....	18
13. Loads of dissolved aluminum, iron, manganese, boron, barium, and beryllium in the Mississippi River near Thebes, Illinois, July through September 1993.....	19
14. Loads of dissolved arsenic, cobalt, chromium, copper, lithium, and molybdenum in the Mississippi River near Thebes, Illinois, July through September 1993.....	20
15. Loads of dissolved mercury, nickel, uranium, vanadium, cadmium, and zinc in the Mississippi River near Thebes, Illinois, July through September 1993.....	21

## TABLES

1. Stream discharge, major ions, pH, specific conductance, alkalinity, and suspended-sediment concentration data from the Mississippi River near Thebes, Illinois, July through September 1993 .....	4
2. Nutrient and dissolved organic carbon concentration data from the Mississippi River near Thebes, Illinois, July through September 1993 .....	5
3. Trace-element concentration data from the Mississippi River near Thebes, Illinois, July through September 1993.....	5

## CONVERSION FACTORS

Multiply	By	To obtain
cubic meter per second (m <sup>3</sup> /s)	35.31	cubic foot per second
kilograms per day (kg/d)	2.205	pounds per day
metric tons per day (t/d)	1.102	short tons per day
micrometer (μm)	0.00003937	inch
degree Celsius (°C)	1.8 x °C + 32	degree Fahrenheit

# Major Ions, Nutrients, and Trace Elements in the Mississippi River Near Thebes, Illinois, July Through September 1993

By Howard E. Taylor, Ronald C. Antweiler, Terry I. Brinton, David A. Roth, and John A. Moody

## Abstract

Extensive flooding in the upper Mississippi River Basin during summer 1993 had a significant effect on the water quality of the Mississippi River. To evaluate the change in temporal distribution and transport of dissolved constituents in the Mississippi River, six water samples were collected by a discharge-weighted method from July through September 1993 near Thebes, Illinois. Sampling at this location provided water-quality information from the upper Mississippi, the Missouri, and the Illinois River Basins.

Dissolved major constituents that were analyzed in each of the samples included bicarbonate, calcium (Ca), carbonate ( $\text{CO}_3$ ), chloride (Cl), dissolved organic carbon, magnesium (Mg), potassium (K), silica ( $\text{SiO}_2$ ), sodium (Na), and sulfate ( $\text{SO}_4$ ). Dissolved nutrients included ammonium ion ( $\text{NH}_4$ ), nitrate ( $\text{NO}_3$ ), nitrite ( $\text{NO}_2$ ), and orthophosphate ( $\text{PO}_4$ ). Dissolved trace elements included aluminum (Al), arsenic (As), barium (Ba), boron (B), beryllium (Be), bromide (Br), cadmium (Cd), chromium (Cr), cobalt, (Co), copper (Cu), fluoride (F), iron (Fe), lead, lithium (Li), manganese (Mn), mercury (Hg), molybdenum (Mo), nickel (Ni), strontium (Sr), thallium, uranium (U), vanadium (V), and zinc (Zn). Other physical properties of water that were measured included specific conductance, pH and suspended-sediment concentration (particle size, less than 63 micrometers).

Results of this study indicated that large quantities of dissolved constituents were transported through the river system. Generally, pH,

alkalinity, and specific conductance and the concentrations of B, Br, Ca, Cl, Cr, K, Li, Mg, Mo, Na,  $\text{SO}_4$ , Sr, U, and V increased as water discharge decreased, while concentrations of F, Hg, and suspended sediment sharply decreased as water discharge decreased after the crest of the flood. Concentrations of other constituents, such as Al, As, Ba, Be, Co, Cu, Ni,  $\text{NO}_3$ ,  $\text{NO}_2$ ,  $\text{NH}_4$ ,  $\text{PO}_4$ , and  $\text{SiO}_2$ , varied with time as discharge decreased after the crest of the flood.

For most constituents, the load transported during floods generally is much greater than that transported during low-flow conditions. However, for Cd, Cr, Fe, Mn, V, and Zn, loads increased substantially as water discharge decreased after the crest of the flood.

## INTRODUCTION

Extensive and persistent rainfall during summer 1993 (Wahl and others, 1993) in the Mississippi River Basin resulted in severe flooding of the Mississippi River and its tributaries. An area that includes southern Minnesota, southwestern Wisconsin, Iowa, western Illinois, northern Missouri, southern North Dakota, and eastern parts of South Dakota, Nebraska, and Kansas was affected by significant flooding from mid-June to early August. Peak discharges measured at 154 streamflow-gaging stations in this geographic area exceeded the 10-year recurrence interval; peak discharges at 46 streamflow-gaging stations exceeded the 100-year recurrence interval (Parrett and others, 1993). Record peak discharges were recorded at more than 40 of these gaging stations.

The effects of the extensive flooding on water quality of the Mississippi River are a major concern for the local and Federal agencies involved with pub-

lic water supplies. Goolsby and others (1993) studied the occurrence and transport of agricultural chemicals during the floods. They reported that large amounts of the herbicides atrazine, alachlor, cyanazine, and metolachlor, which had been recently applied to farm land throughout the Mississippi River Basin, were flushed into the river by runoff that resulted from the very high rainfall.

Flooding also can affect other naturally occurring and manmade water-quality constituents. Hem (1989) described an initial increase in concentration of dissolved constituents as discharge increases during the early stages of a flood, which is presumably caused by the accumulation of solutes in the wave front. As the flood crest is reached, concentrations begin to decrease because of dilution by the large volume of flood water. After the crest, concentrations would continue to decrease with the additional dilution of flood water. As base flow is approached, concentrations increase to pre-flood levels.

The sources of chemical constituents have a substantial effect on the quality of flood waters. The concentrations of nonpoint-source agricultural related constituents, such as nitrate, should respond similarly to that of herbicides, as reported by Goolsby and others (1993). Concentrations of point-source contaminants, such as those that originate from inundated industrial, municipal, or specific geochemically anomalous sites (such as lead and zinc mining areas) can fluctuate substantially with changes in discharge or the extent of local flooding.

This report summarizes information on the dissolved concentrations and transport of major ions, nutrients, and trace elements in the Mississippi River during the peak and recession stages of flooding from July through September 1993. Water samples were collected in the river near Thebes, Illinois (fig. 1) on July 16, 18, 20, and 28, August 16, and September 13, 1993. The site was selected for sampling because it is a long-term U.S. Geological Survey streamflow and water-quality measuring site where representative water samples can be readily collected on the upper Mississippi River downstream from all major tributaries. Because the river did not overflow its banks in this reach, the site was ideal for collecting samples that integrated all water-quality characteristics from upstream flood-affected areas. In addition, water-quality data that were collected near this site in 1991 as part of earlier research studies by the Geological Survey were available for comparison.



**Figure 1.** Location of sampling sites on the Mississippi River near Thebes, Illinois.

Dissolved major ions for which concentrations were determined in water from the samples included bicarbonate ( $\text{HCO}_3$ ), calcium (Ca), carbonate ( $\text{CO}_3$ ), chloride (Cl), dissolved organic carbon (DOC), magnesium (Mg), potassium (K), silica ( $\text{SiO}_2$ ), sodium (Na), and sulfate ( $\text{SO}_4$ ). Dissolved nutrient concentrations determined included ammonium ion ( $\text{NH}_4$ ), nitrate ( $\text{NO}_3$ ), nitrite ( $\text{NO}_2$ ), and orthophosphate ( $\text{PO}_4$ ). Dissolved trace-element concentrations analyzed included aluminum (Al), arsenic (As), barium (Ba), beryllium (Be), boron (B), bromide (Br), cad-

mium (Cd), chromium (Cr), cobalt (Co), copper (Cu), fluoride (F), iron (Fe), lead (Pb), lithium (Li), manganese (Mn), mercury (Hg), molybdenum (Mo), nickel (Ni), strontium (Sr), thallium (Tl), uranium (U), vanadium (V), and zinc (Zn). Other physical properties of water that were measured included specific conductance, pH, and suspended-sediment concentration [particle size, less than 63 micrometers ( $\mu\text{m}$ )].

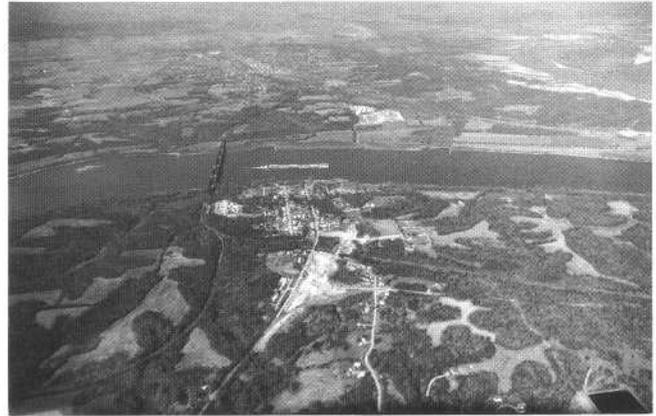
## STUDY METHODS

### Sample Collection and Processing Procedures

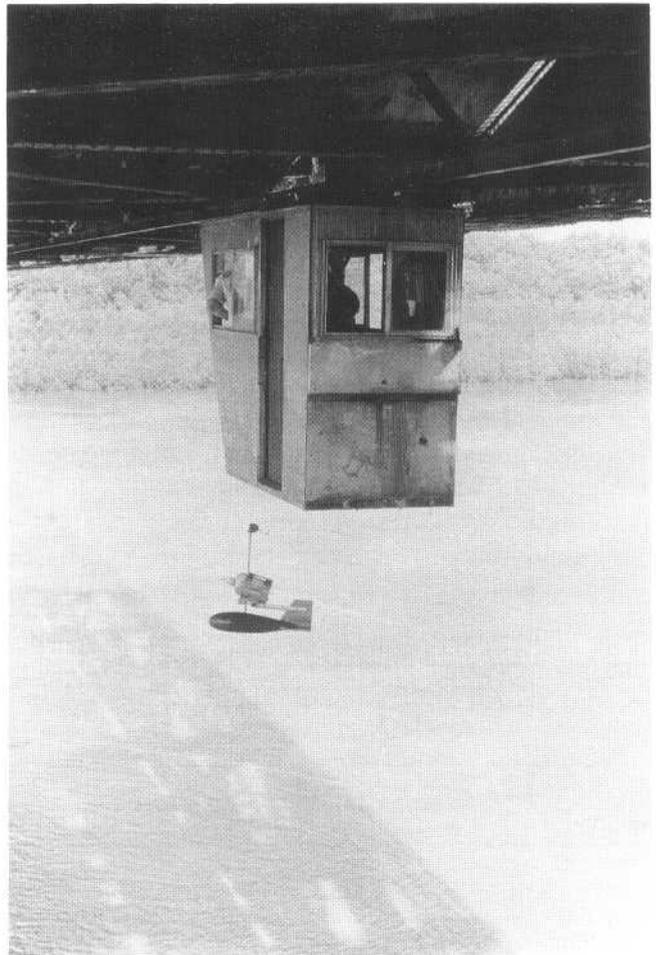
All samples were collected from a monorail car suspended below the railroad bridge near Thebes, Illinois (fig. 2). The water sample of July 16, 1993, consisted of 4 liters (L) of water that was collected at each of 10 points across the river by using the equal-discharge increment method described by Guy and Norman (1982); estimates of discharge were calculated from preflood discharge measurements. Samples collected on subsequent dates were based on the 10 equal-discharge increment method and discharge measurements made during the flood; the discharge measurements were adjusted for changes in measured river stage.

Samples were collected by using a collapsible-bag sampler with a Teflon nozzle, identical to that described by Moody and Meade (1992), attached to a 136-kilogram Columbus sounding weight. Teflon sample bags were used with the sampler to minimize trace-element contamination of the water sample. A previous study (Moody and Meade, in press) has shown that a representative sample of fine-grained suspended sediment (particle size, less than 63  $\mu\text{m}$ ) can be collected by sampling at the mid-depth of the river. For this reason, each of the samples was collected by rapidly lowering the sampler to approximately one-half the total depth of the river and holding it stationary at that depth until 4 L of sample was collected, at which time the sampler was rapidly retrieved. Samples collected at alternating discharge increment locations were composited by using a procedure similar to that described by Leenheer and others (1989). The samplers were composited into two separate Teflon-coated stainless steel churn splitters from which subsamples were removed in a uniform manner. Comparison of the separately composited samples permitted an evaluation of sampling precision.

Subsamples for trace-element analyses were immediately filtered through a 0.4- $\mu\text{m}$  Nuclepore



A



B

**Figure 2.** Railroad bridge on the Mississippi River near Thebes, Illinois (A), and the monorail car with collapsible-bag sampler used to collect water-quality samples below railroad bridge (B). Photographs by R.H. Meade, U.S. Geological Survey.

membrane by using ultra-clean techniques and followed by the addition of ultra-high purity nitric acid

for preservation (Taylor and others, 1990). An additional aliquot of this filtered subsample was preserved with a mixture of nitric acid and potassium dichromate specifically for a Hg determination. Other subsamples for DOC and nutrient analyses were pressure-filtered through a 0.45- $\mu\text{m}$  silver membrane filter and transported chilled to the laboratory for immediate analysis. Subsamples for alkalinity and anions were filtered through a 0.45- $\mu\text{m}$  cartridge filter, immediately chilled, and then transported to the laboratory. Field measurements for pH and specific conductance were made on water from an unfiltered subsample.

### Laboratory Analysis Techniques

Water samples were analyzed for dissolved constituents in the laboratory by a variety of techniques. Major cations (Ca, Mg, Na), Fe, and  $\text{SiO}_2$  were determined by an inductively coupled plasma-atomic emission spectrometric procedure described by Garbarino and Taylor (1979). Trace elements, which include Al, As, B, Ba, Be, Cd, Co, Cr, Cu, Li, Mn, Mo, Ni, Pb, Sr, Tl, U, V, and Zn, were analyzed by an inductively coupled plasma-mass spectrometric technique described by Taylor (1989) and Taylor and Garbarino (1992). Ultra-trace concentrations of Hg were determined by a cold-vapor atomic fluorescence method described by Godden and Stockwell (1989). Potassium concentration was determined by an atomic absorption spectrometric procedure, as dis-

cussed by Fishman and Friedman (1985). Major and minor anions, which include Br, Cl, F, and  $\text{SO}_4$ , were measured by a modified ion chromatographic technique similar to that described by Fishman and Friedman (1985). Alkalinity concentrations, which were used for the computation of  $\text{HCO}_3$  and  $\text{CO}_3$ , were determined by an automated Gran's titration procedure, as outlined by Kramer (1982). Dissolved organic carbon was measured by a method described by Menzel and Vaccaro (1964). Suspended-sediment concentrations were measured by filtration followed by gravimetric determination, as described by Moody and Meade (1992). Nutrients, including  $\text{NH}_4$ ,  $\text{NO}_2$ ,  $\text{NO}_3$ , and  $\text{PO}_4$ , were determined by using a methodology developed by Antweiler and others (1993).

### OCCURRENCE AND TRANSPORT OF CONSTITUENTS

#### Occurrence of Major Ions, Nutrients, and Trace Elements

Concentrations of major ions, nutrients, and trace elements determined from water samples collected in the Mississippi River near Thebes, Illinois, from July through September 1993 are listed in tables 1 through 3, respectively; other physical properties of water measured, which include pH, specific conductance, discharge, and suspended-sediment concentration, also are listed in table 1. Concentrations of some trace elements, such as Cd, Cr, Fe, Mn, Pb, Tl,

**Table 1.** Stream discharge, major ions, pH, specific conductance, alkalinity, and suspended-sediment concentration data from the Mississippi River near Thebes, Illinois, July through September 1993

[Constituent concentrations, in milligrams per liter, except as noted;  $\mu\text{S}/\text{cm}$ , microsiemens per centimeter at 25 degrees Celsius;  $\text{m}^3/\text{s}$ , cubic meters per second;  $\mu\text{eq}/\text{L}$ , microequivalents per liter; <, less than;  $\mu\text{m}$ , micrometers]

Constituent	Sampling dates					
	July 16	July 18	July 20	July 28	August 16	September 13
Discharge ( $\text{m}^3/\text{s}$ ) <sup>1</sup> .....	23,500	23,700	24,900	24,600	21,800	13,900
Bicarbonate.....	136	141	143	161	174	194
Calcium.....	39.5	39.4	41.2	45.9	48.9	51.0
Carbonate.....	.18	.23	.2	.23	.54	.85
Chloride.....	8.6	9.0	8.9	9.3	10.6	13.3
Magnesium.....	11.1	11.2	11.5	13.2	14.4	16.6
Potassium.....	3.9	3.8	3.9	4.3	4.5	4.4
Silica.....	10.3	10.3	10.9	11.8	10.8	11.6
Sodium.....	6.1	6.0	6.1	6.9	8.3	12.0
Sulfate.....	25.2	25.4	24.9	31.6	35.0	40.2
pH (standard units).....	7.46	7.55	7.5	7.49	7.83	7.98
Specific conductance ( $\mu\text{S}/\text{cm}$ ).....	323	330	323	379	408	486
Alkalinity ( $\mu\text{eq}/\text{L}$ ).....	2,233	2,313	2,358	2,649	2,864	3,207
Suspended sediment (<63 $\mu\text{m}$ ).....	320	308	288	174	140	180

<sup>1</sup>Interpolated from discharges measured every other day.

**Table 2.** Nutrient and dissolved organic carbon concentration data from the Mississippi River near Thebes, Illinois, July through September 1993

[Constituent concentrations, in milligrams per liter]

Constituent	Sampling dates					
	July 16	July 18	July 20	July 28	August 16	September 13
Ammonium.....	0.016	0.011	0.011	0.009	0.011	0.017
Nitrate.....	10.2	9.9	8.5	10.1	7.3	10.2
Nitrite.....	.09	.04	.05	.09	.10	.06
Orthophosphate.....	.37	.25	.27	.29	.27	.44
Dissolved organic carbon (as C).....	4.92	4.99	5.02	4.88	5.04	4.73

**Table 3.** Trace-element concentration data from the Mississippi River near Thebes, Illinois, July through September 1993

[Constituent concentrations, in micrograms per liter; <, less than; -, not measured]

Constituent	Sampling dates					
	July 16	July 18	July 20	July 28	August 16	September 13
Aluminum.....	6.7	5.0	4.0	4.6	8.4	7.6
Arsenic.....	<2.4	2.8	2.6	3.2	3.1	<2.4
Barium.....	72	80	84	94	96	89
Beryllium.....	.38	.40	.43	.40	.58	.15
Boron.....	29	26	26	30	46	70
Bromide.....	6	5	5	7	8	10
Cadmium.....	<.1	<.1	<.1	<.1	<.1	.3
Chromium.....	<.2	<.2	<.2	<.2	1.0	9.9
Cobalt.....	1.5	1.7	1.6	2.0	2.2	1.7
Copper.....	1.8	1.7	1.5	1.6	2.0	1.2
Fluoride.....	96	83	81	77	-	67
Iron.....	6.0	<3	<3	<3	<3	3.6
Lead.....	<.06	<.06	<.06	<.06	<.06	<.06
Lithium.....	3.7	3.8	3.6	5.1	6.1	6.4
Manganese.....	<.06	<.06	<.06	<.06	.13	.50
Mercury.....	.013	.007	.007	.002	.002	.003
Molybdenum.....	1.6	1.2	1.4	1.6	1.8	2.7
Nickel.....	14	15	15	18	16	15
Strontium.....	119	128	124	148	156	158
Thallium.....	<.05	<.05	<.05	<.05	<.05	<.05
Uranium.....	1.3	1.1	1.2	1.7	2.0	2.8
Vanadium.....	<.07	<.07	<.07	<.07	4.3	30
Zinc.....	<.08	<.08	<.08	<.08	<.08	.75

V, and Zn, which are listed in table 3, are reported to be less than the detection limits for the analytical procedures used to determine the concentrations. Ion-balance analyses were performed on each sample; the results indicated that the percentage differences between the sum of anions and cations were less than  $\pm 1.5$  percent.

Graphs of concentrations of selected constituents during the period of flooding are shown in figures 3 through 8<sup>1</sup>. Preflood data on constituent concentrations at the sampling site were not available for comparative purposes in 1993; however, water-quality

data collected at the site in 1993 are compared with that collected at the same site in unpublished studies conducted in 1991.

Stream discharge shown in figure 3, increases to about 25,000 cubic meters per second ( $m^3/s$ ) in middle and late July and to about 28,000  $m^3/s$  in early August before steadily decreasing to 13,900  $m^3/s$  (the last sample collected). Several measurements, which include alkalinity, pH, specific conductance, and concentration of B, Ca, Cl, Cr,  $CO_3$ ,  $HCO_3$ , K, Li, Mg, Mo, Na,  $SO_4$ , Sr, and U, increase with time as the discharge decreases, which is probably the result of the lessening effects of simple dilution (Hem, 1989). Concentrations of other constituents, which include

<sup>1</sup>Figures 3 through 15 are found on pages 9 through 21.

Al, As, Ba, Be, Co, Cu, DOC, F, Hg, NH<sub>4</sub>, Ni, NO<sub>2</sub>, NO<sub>3</sub>, PO<sub>4</sub>, and SiO<sub>4</sub>, are variable with respect to stream discharge.

The relations among concentrations of selected constituents and stream discharge are shown in figure 9. Data points are connected in chronological order of sampling, with an arrow point to indicate the increase in sampling date.

The chronological sequence of sodium concentration as a function of stream discharge (fig. 9B) showed a counter-clockwise pattern, which was similar to that described by Toler (1965) for floods on Spring Creek, Georgia, for specific conductance. A similar pattern also was observed for B, Br, Ca, Cl, CO<sub>3</sub>, HCO<sub>3</sub>, K, Li, Mg, Mo, SO<sub>4</sub> (not shown in fig. 9), and U (fig. 9F). Toler attributed this pattern to a rapid influx of ground water with high dissolved-solids content into the stream after the crest of the flood had passed; this results in increased constituent concentrations in the stream as discharge decreases. The influx of ground water into the river, however, was clearly not the case in the 1993 Mississippi River flood data. The observation of increasing levels of standing water behind levees along the Mississippi, the Illinois, and the Missouri Rivers long after the September sampling date (R.H. Meade, U.S. Geological Survey, oral commun., 1993) indicated that the hydraulic gradient between the rivers and the water table in the adjacent flood plains was towards the flood plains; this prevented the influx of ground water into the river during the collection of the six samples.

The chronological sequence of DOC concentration (not shown in fig. 9) and pH (fig. 9A) as a function of stream discharge during the flood crest showed a variable trend with a generally clockwise pattern. The clockwise pattern is similar to that reported by Hendrickson and Krieger (1964) for constituent concentrations during floods in several Kentucky streams. They attributed this pattern to the rapid transport of soluble material that accumulated and was flushed from the soils of the drainage basin into the stream, followed by a lessening of the dilution effect after the flood crest.

Concentrations of other constituents show less distinct patterns. Barium (fig. 9C) and Sr (not shown in fig. 9) rapidly increase in concentration as discharge increases and then remain nearly constant as discharge decreases. Mercury (fig. 9E) rapidly decreases in concentration as discharge increases and remains constant as discharge decreases. Concentrations of other constitu-

ents, such as Al, Co, Cu, NH<sub>4</sub>, Ni, NO<sub>3</sub>, NO<sub>2</sub>, PO<sub>4</sub> (fig. 9D), and SiO<sub>2</sub>, are highly variable.

Because the sampling site near Thebes was specifically chosen due to its location below the confluences of the upper Mississippi with the Missouri and the Illinois Rivers, a possible explanation for changes in chemistry of flood waters at this site probably could be explained by the variable contributions of water from these rivers, which probably have substantially different dissolved chemical compositions, before and after the flood crest. Also it was noted (R.H. Meade, U.S. Geological Survey, oral commun., 1993) that levees along the rivers broke at several locations during the flood; this resulted in the inundation of large agricultural areas. As the flood crest began to recede, water from these inundated areas returned to the river. It is possible that soluble constituents in water, which probably originated from soils and other sources in the flood plain, changed in concentration in the mainstem of the river as these waters mixed.

## Transport of Constituents

Transport of constituents through the river system is a function of the concentration of the constituents and the volume of water that flowed in the river. In terms of load, transport is calculated as the product of the concentration and the river discharge, which yields units of metric tons per day or kilograms per day.

Instantaneous loads of DOC, NH<sub>4</sub>, NO<sub>3</sub>, NO<sub>2</sub>, PO<sub>4</sub>, and suspended sediment in metric tons per day are shown in figure 10. A gray line is included for comparative purposes against previously measured loads for each constituent calculated from samples collected on July 29, 1991, at a stream discharge of 4,390 m<sup>3</sup>/s. Similar patterns of an initial decrease in instantaneous loads before the flood crest followed by a slight increase to a maximum and either a gradual decrease or a stabilization of load with time are observed for each of the nutrients and DOC. In each case, all loads are substantially larger than those measured in July 1991. Suspended-sediment loads exponentially decrease with time as stream discharge decreases.

Loads of Ca, K, Mg, Na, Sr, and SiO<sub>2</sub> are shown in figure 11. Each of these constituents showed a similar pattern of load as a function of time, with the maximum in load at about the same time as the crest of the flood and followed by a decrease in loads as discharge decreases. Each constituent load

was substantially larger than the corresponding loads observed in July 1991. Loads of HCO<sub>3</sub>, Cl, SO<sub>4</sub>, and Br (figs. 12A, C, D, F); B, Ba, and Be (figs. 13D–F); As, Co, Cu, Li, and Mo (figs. 14A, B, D–F); and Ni and U (figs. 15B, C) show patterns that are similar to those in figure 11 and are substantially larger than loads in July 1991.

Carbonate (fig. 12B); Al, Fe, and Mn (figs. 13A–C); Cr (fig. 14C); and Hg, V, Cd, and Zn (figs. 15A, D–F) show variable patterns of load as a function of time. As indicated by the open circles in figures 13B and C, 14A and C, and 15D, E and F, concentrations of some of these constituents were at the detection limit for the analytical procedure used to determine the concentrations. In some cases, concentrations of Mn (fig. 13C), Cr (fig. 14C), and V (fig. 15D) were at the detection limits when the samples were collected at the highest observed discharge. After July 28, 1993, loads of these constituents increased rapidly. Similar patterns are observed for Fe (fig. 13B) and Zn (fig. 15F), although no similar pattern was observed in loads transported in July 1991. Mercury (fig. 15A) represents the most unusual case because the load for Hg decreased sharply from July 16 to July 28, 1993, and nearly reached the magnitude of loads observed in July 1991, which indicates the possibility that elevated quantities of dissolved Hg were flushed from agricultural and (or) industrial sources during the 1993 flood.

## SUMMARY

Major constituents, such as Ca, Cl, K, Mg, Na, and SO<sub>4</sub>; physical properties, such as alkalinity, pH, and specific conductance; and some trace elements, such as B, Cr, Li, Mo, Sr, and U, in the Mississippi River near Thebes, Illinois, generally increased in concentration with time and as stream discharge generally decreased. Other constituents, which include Al, As, Ba, Be, Co, Cu, DOC, F, Hg, and SiO<sub>2</sub>, and nutrients, such as NO<sub>3</sub>, NO<sub>2</sub>, NH<sub>4</sub>, and PO<sub>4</sub>, showed either a general decrease in concentration with time (similar to suspended-sediment concentration) or variable changes in concentration, which indicates possible variable manmade sources of constituent contribution or tributary mixing interactions that were independent of simple dilution effects.

Most constituents, except pH and DOC, demonstrated a counter-clockwise pattern of concentration chronologically with discharge; this possibly

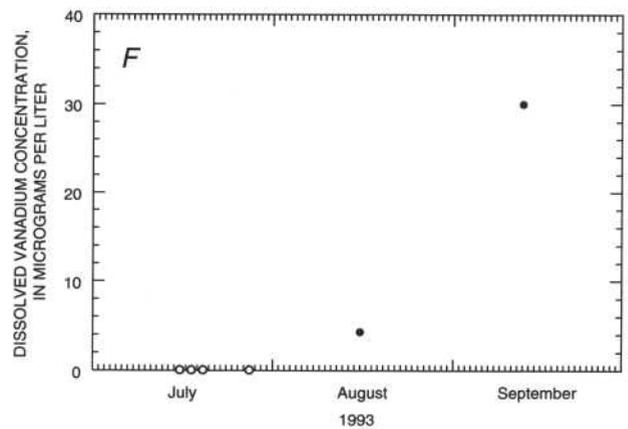
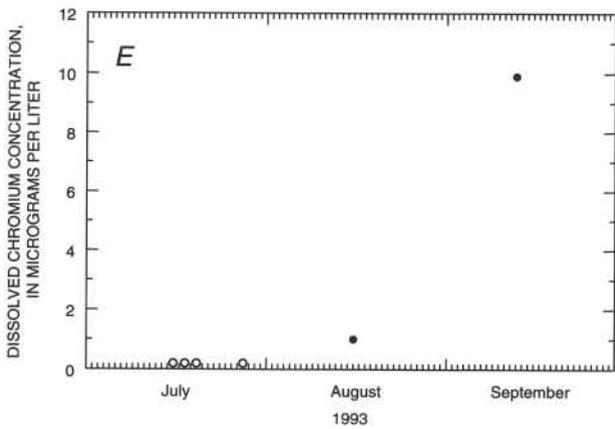
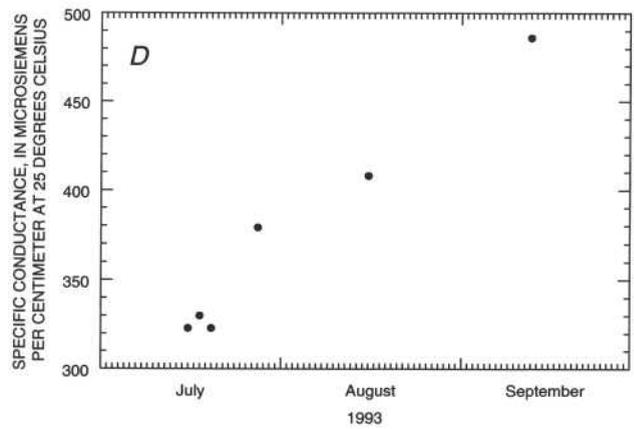
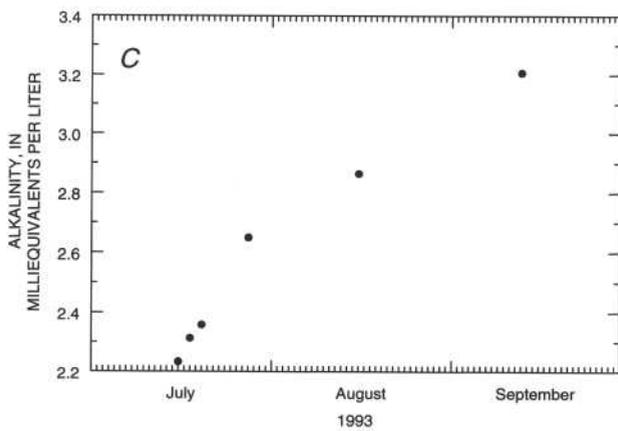
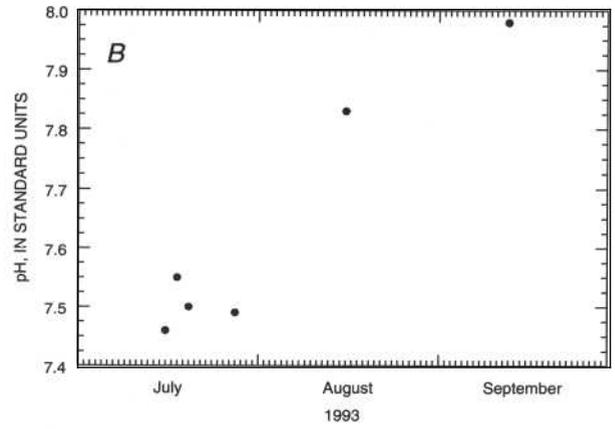
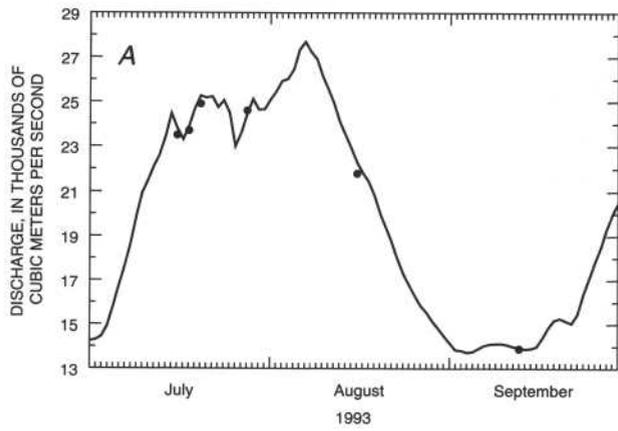
indicates major changes in chemical composition as a result of variable contributions of water from upstream tributaries.

The loads of most constituents, as functions of time and discharge, generally decreased. Loads of most constituents generally were much larger during flood conditions than during lower flow conditions. Loads of some constituents, which include Cd, Cr, Fe, Mn, V, and Zn, varied with time as stream discharge decreased.

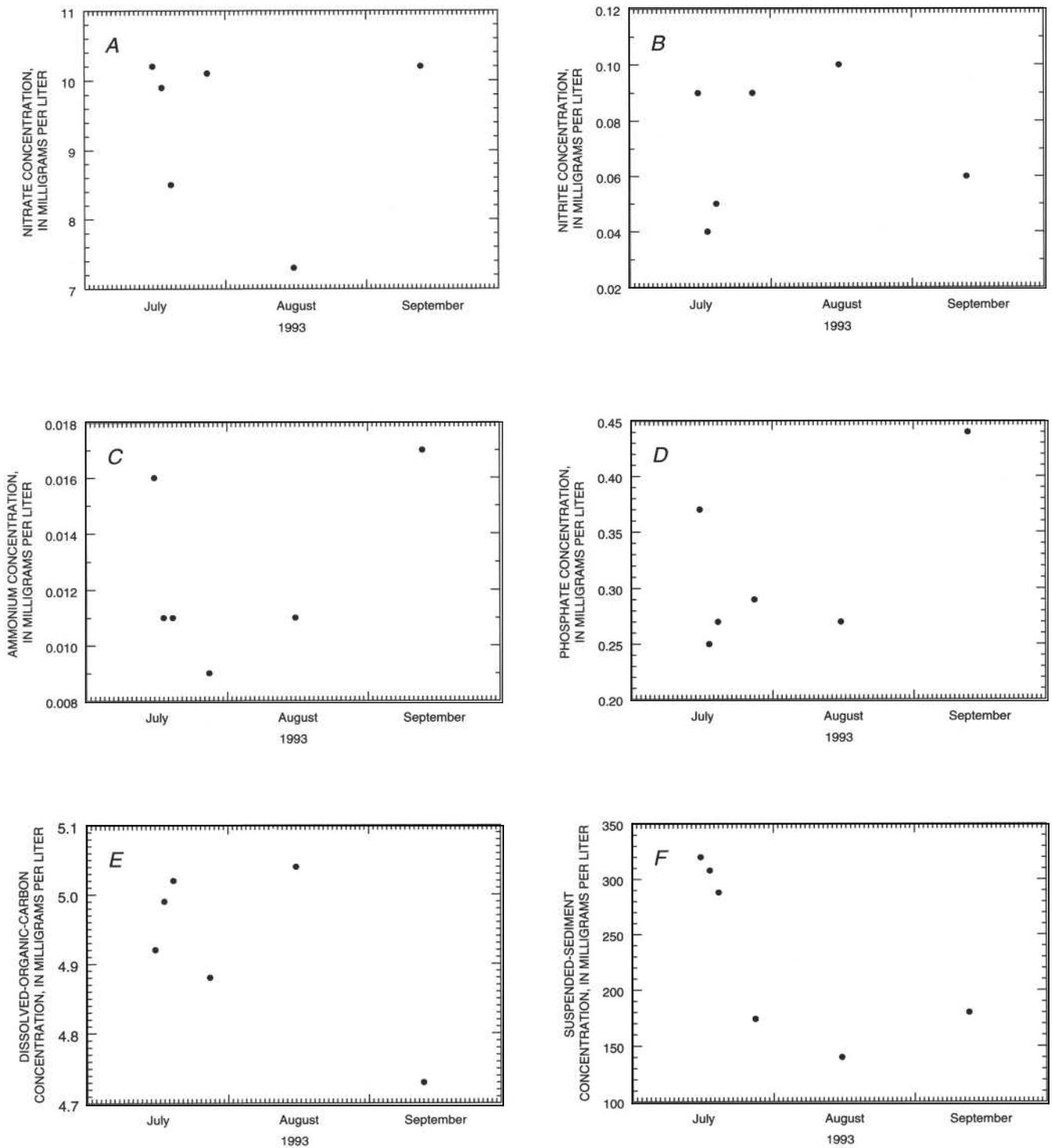
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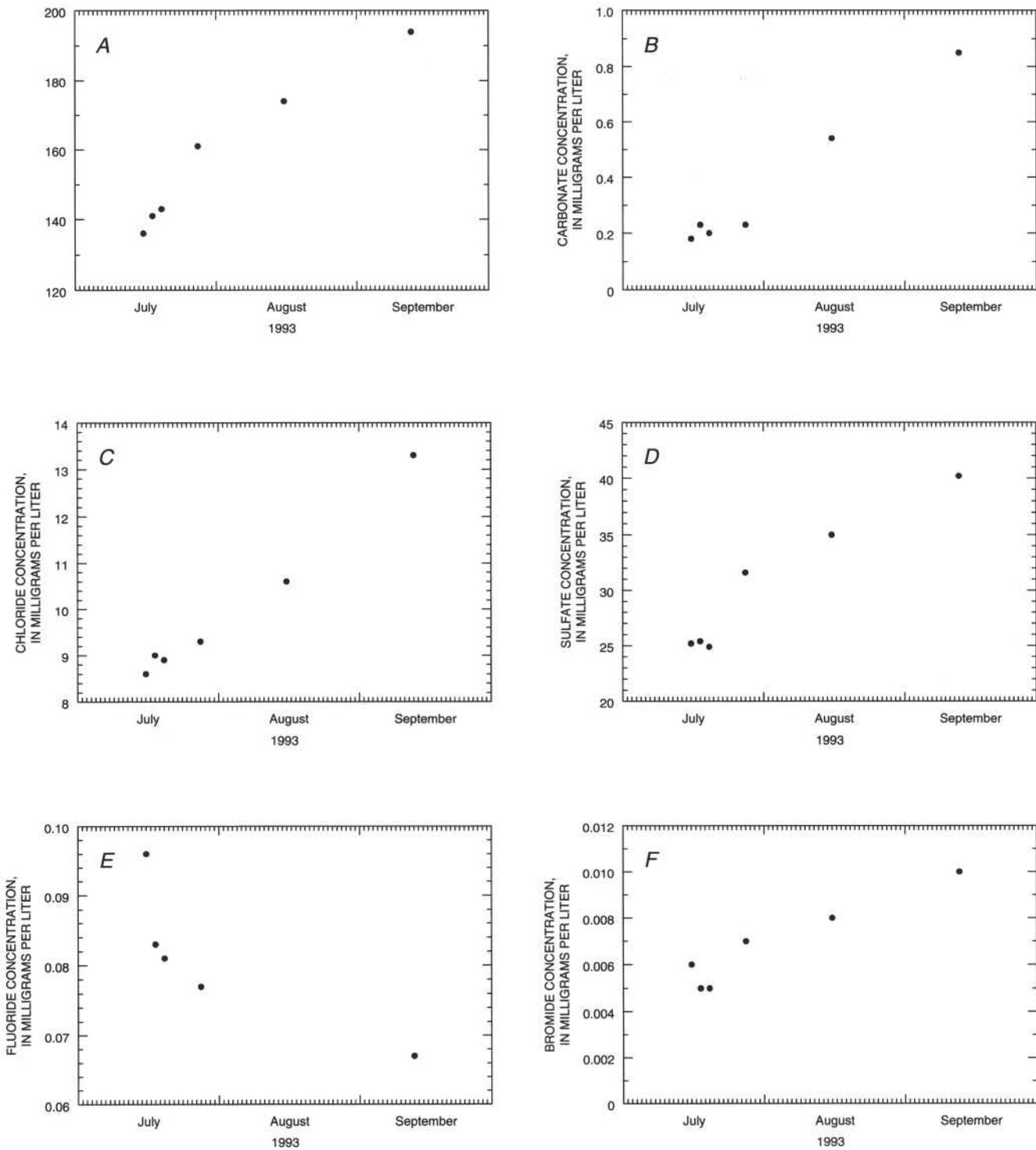


**Figure 3.** Discharge (A), pH (B), alkalinity (C), specific conductance (D), and concentrations of dissolved chromium (E) and vanadium (F) in the Mississippi River near Thebes, Illinois, July through September 1993. Open circles denote values at the analytical detection limit for the constituent.

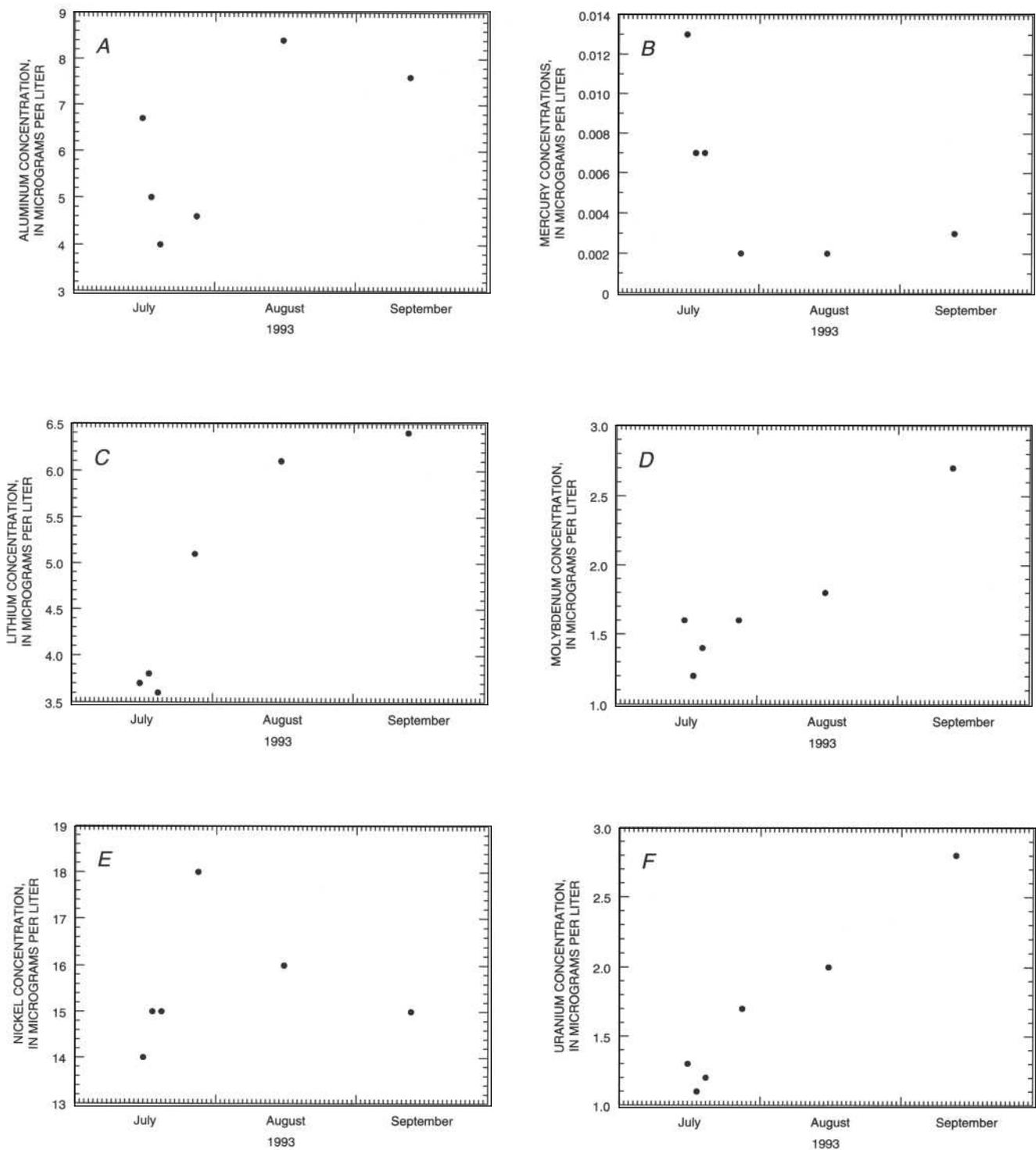


**Figure 4.** Concentrations of dissolved nitrate (A), nitrite (B), ammonium ion (C), phosphate (D), dissolved organic carbon (E), and suspended sediment (F) in the Mississippi River near Thebes, Illinois, July through September 1993.

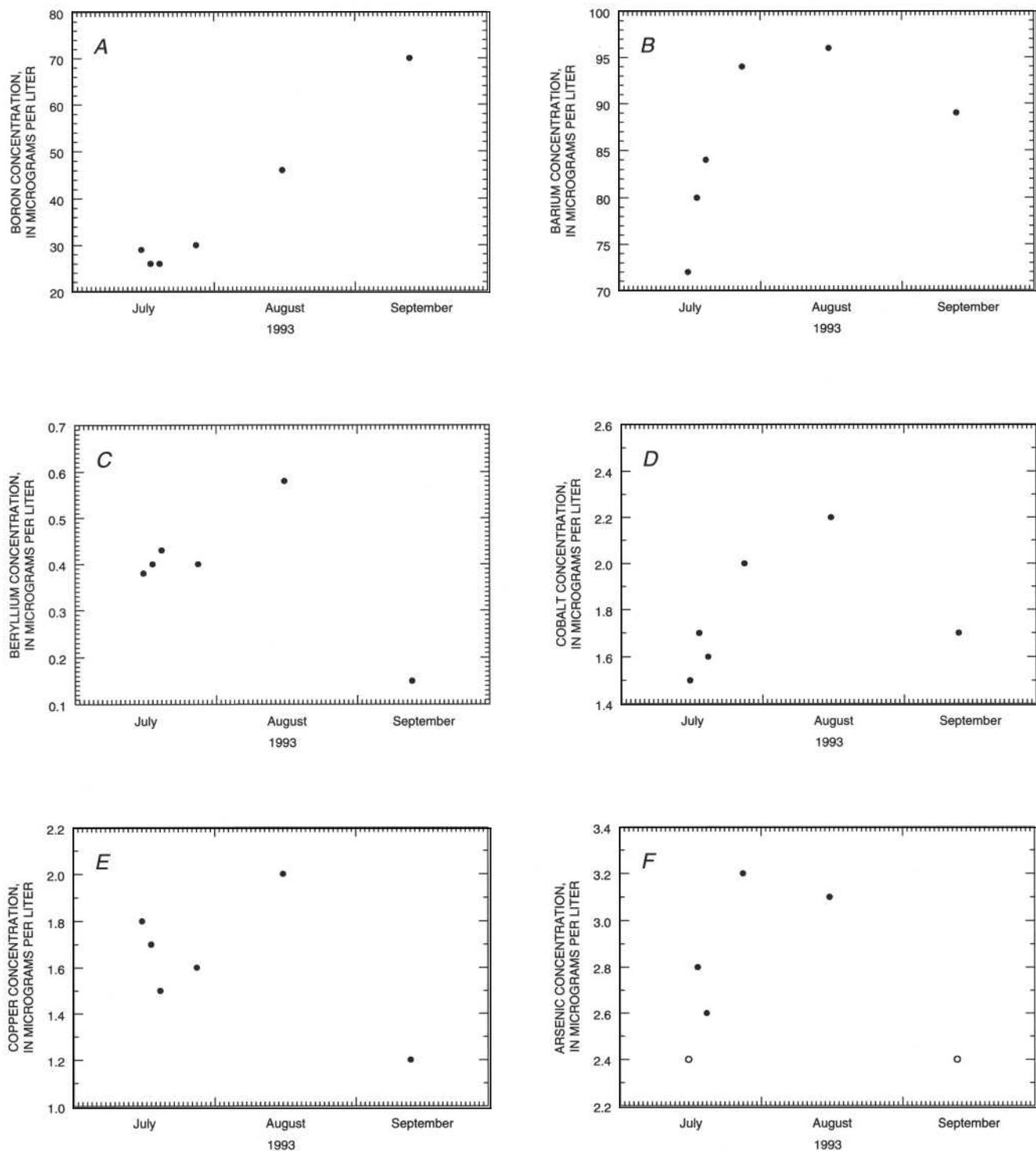




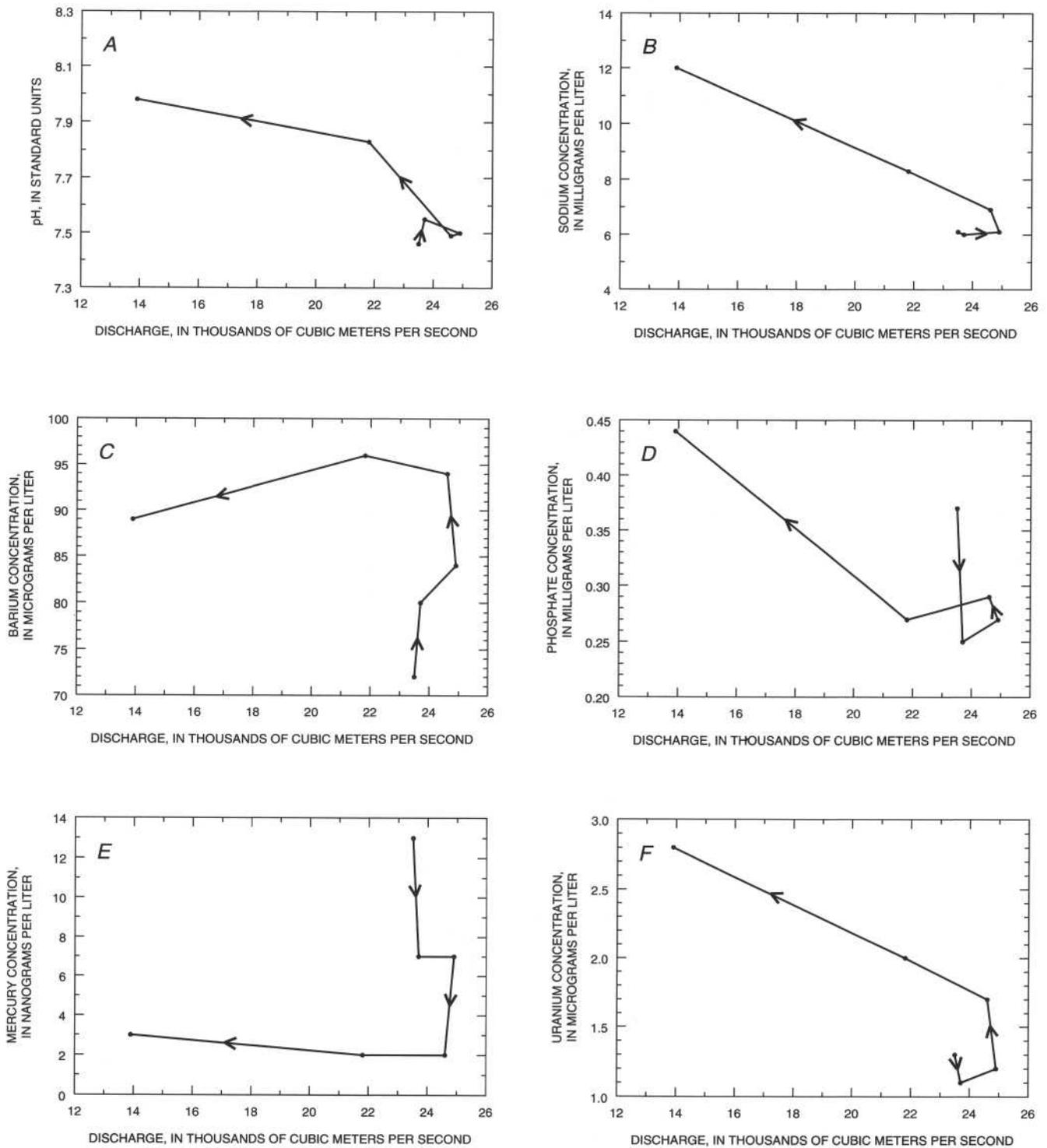
**Figure 6.** Concentrations of dissolved bicarbonate (A), carbonate (B), chloride (C), sulfate (D), fluoride (E), and bromide (F) in the Mississippi River near Thebes, Illinois, July through September 1993.



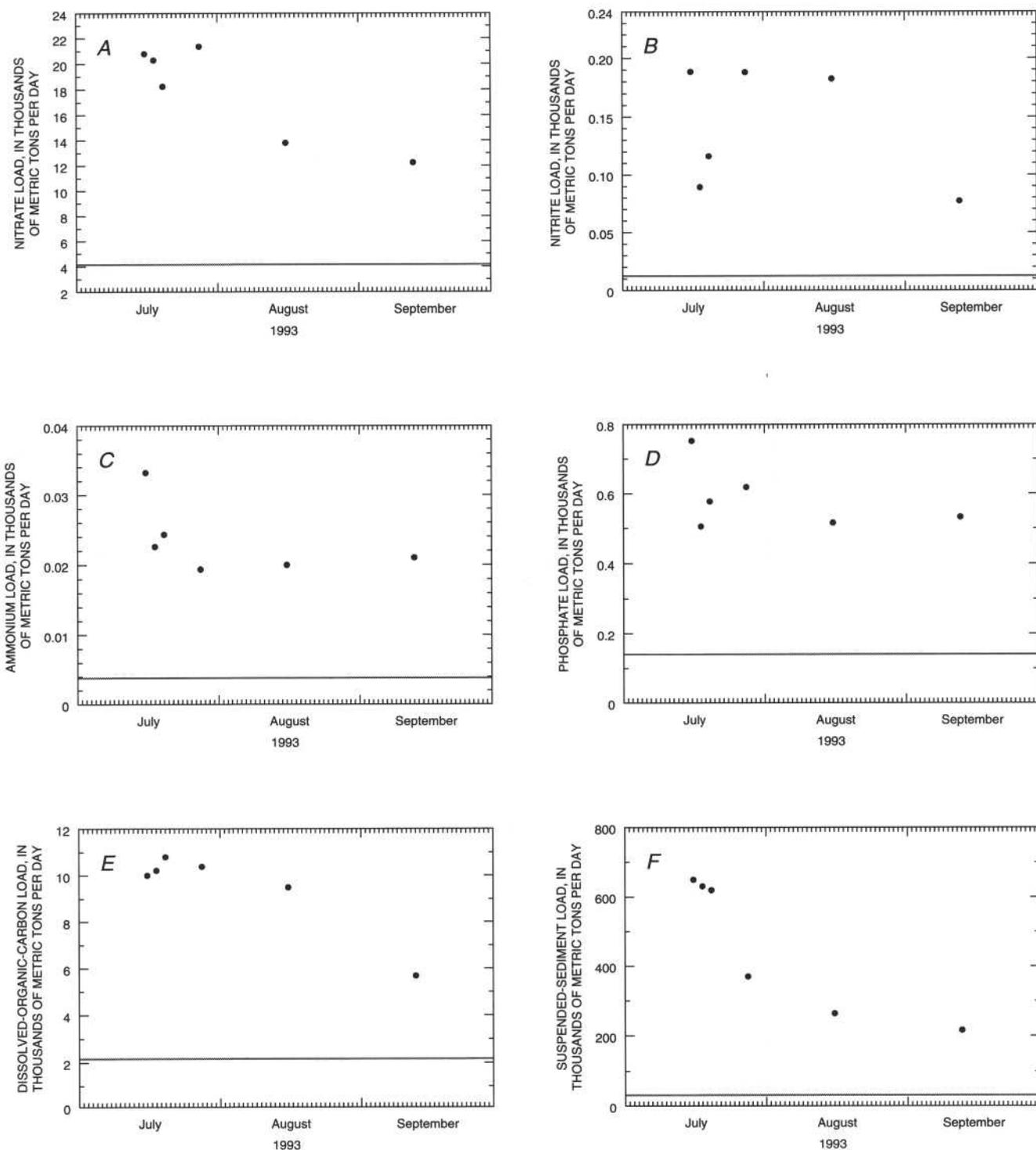
**Figure 7.** Concentrations of dissolved aluminum (A), mercury (B), lithium (C), molybdenum (D), nickel (E), and uranium (F) in the Mississippi River near Thebes, Illinois, July through September 1993.



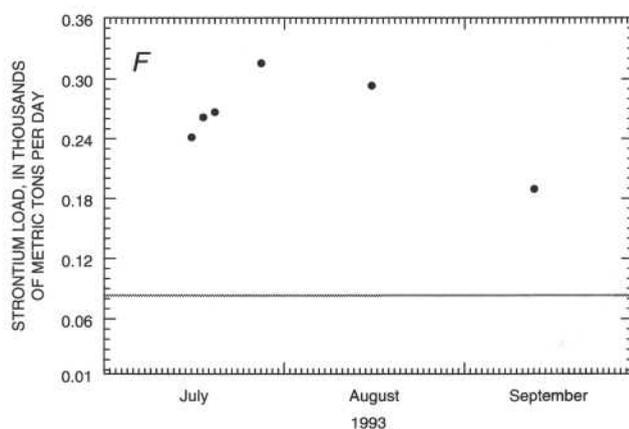
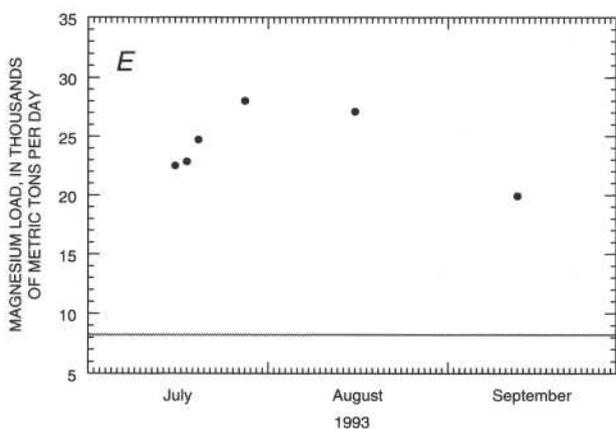
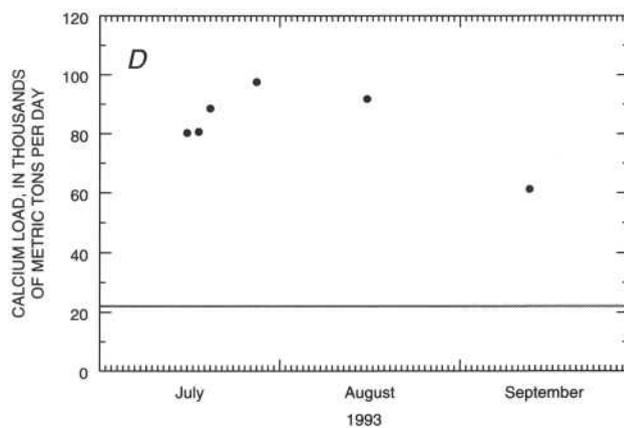
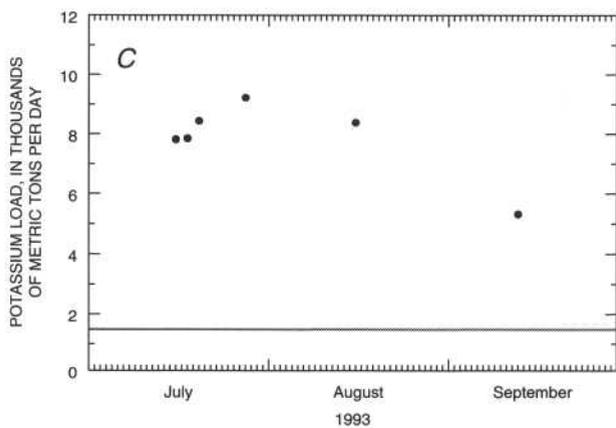
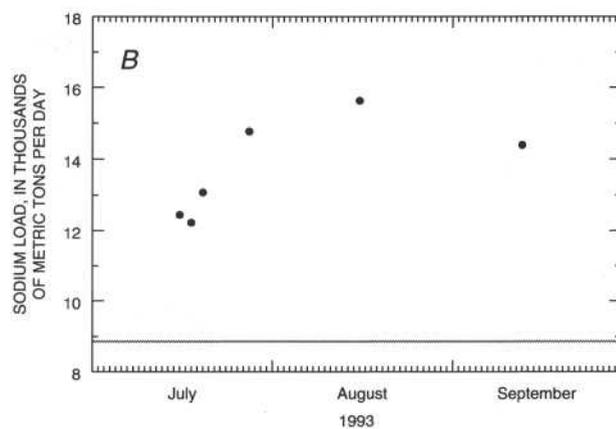
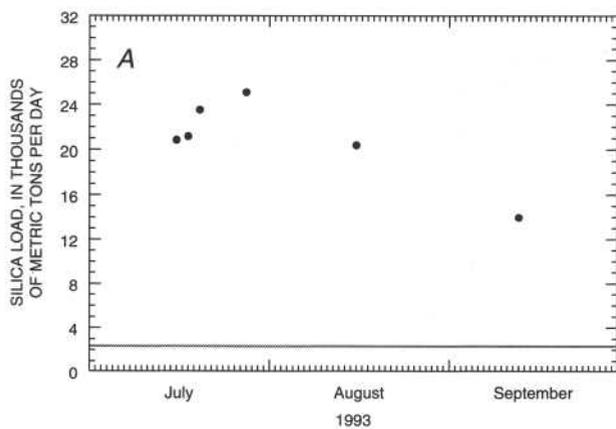
**Figure 8.** Concentrations of dissolved boron (A), barium (B), beryllium (C), cobalt (D), copper (E), and arsenic (F) in the Mississippi River near Thebes, Illinois, July through September 1993. Open circles denote values at the analytical detection limit for the constituent.



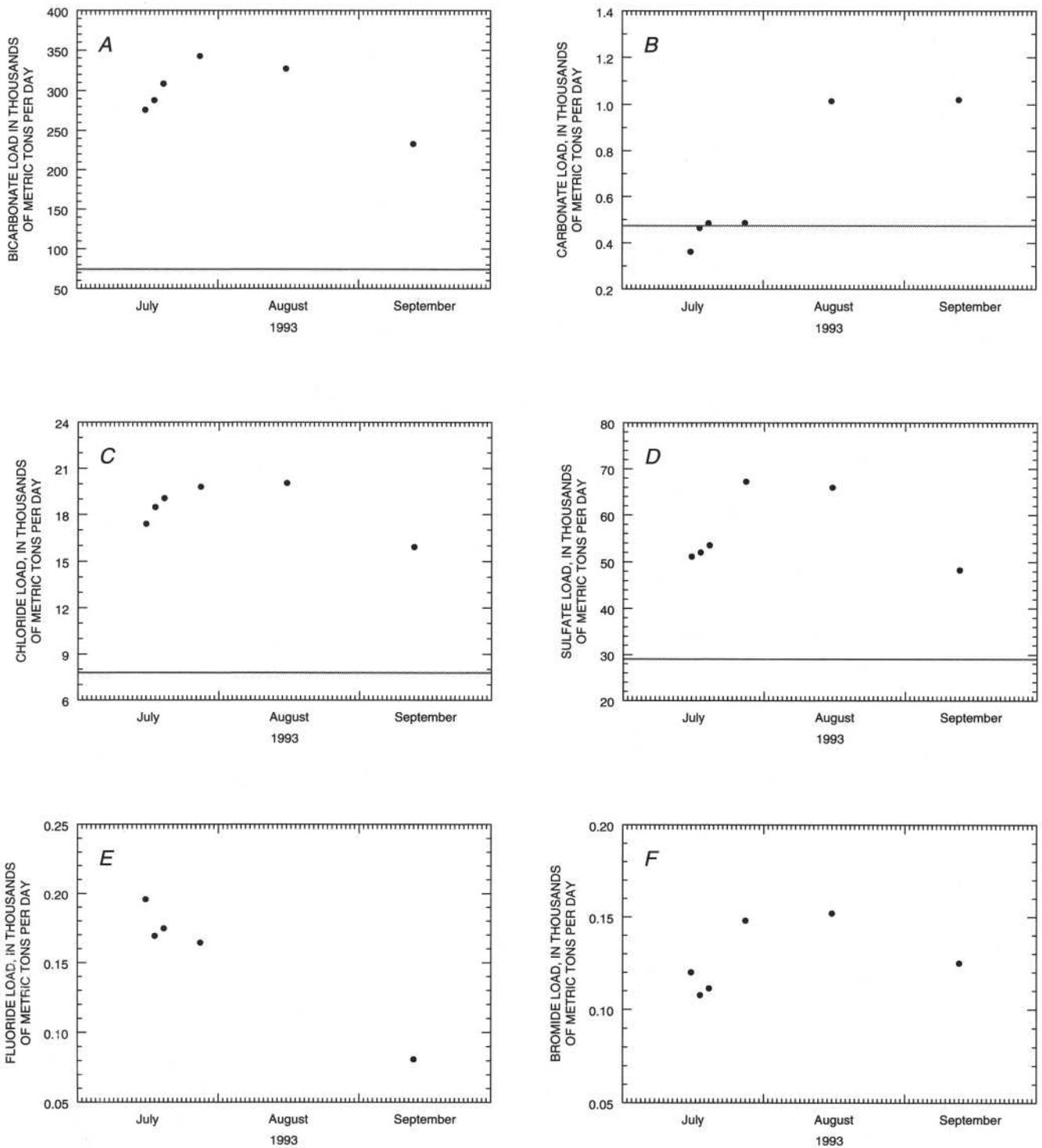
**Figure 9.** pH (A) and concentrations of dissolved sodium (B), barium (C), phosphate (D), mercury (E), and uranium (F) as a function of discharge in the Mississippi River near Thebes, Illinois, July through September 1993. Arrow indicates chronology of sampling dates.



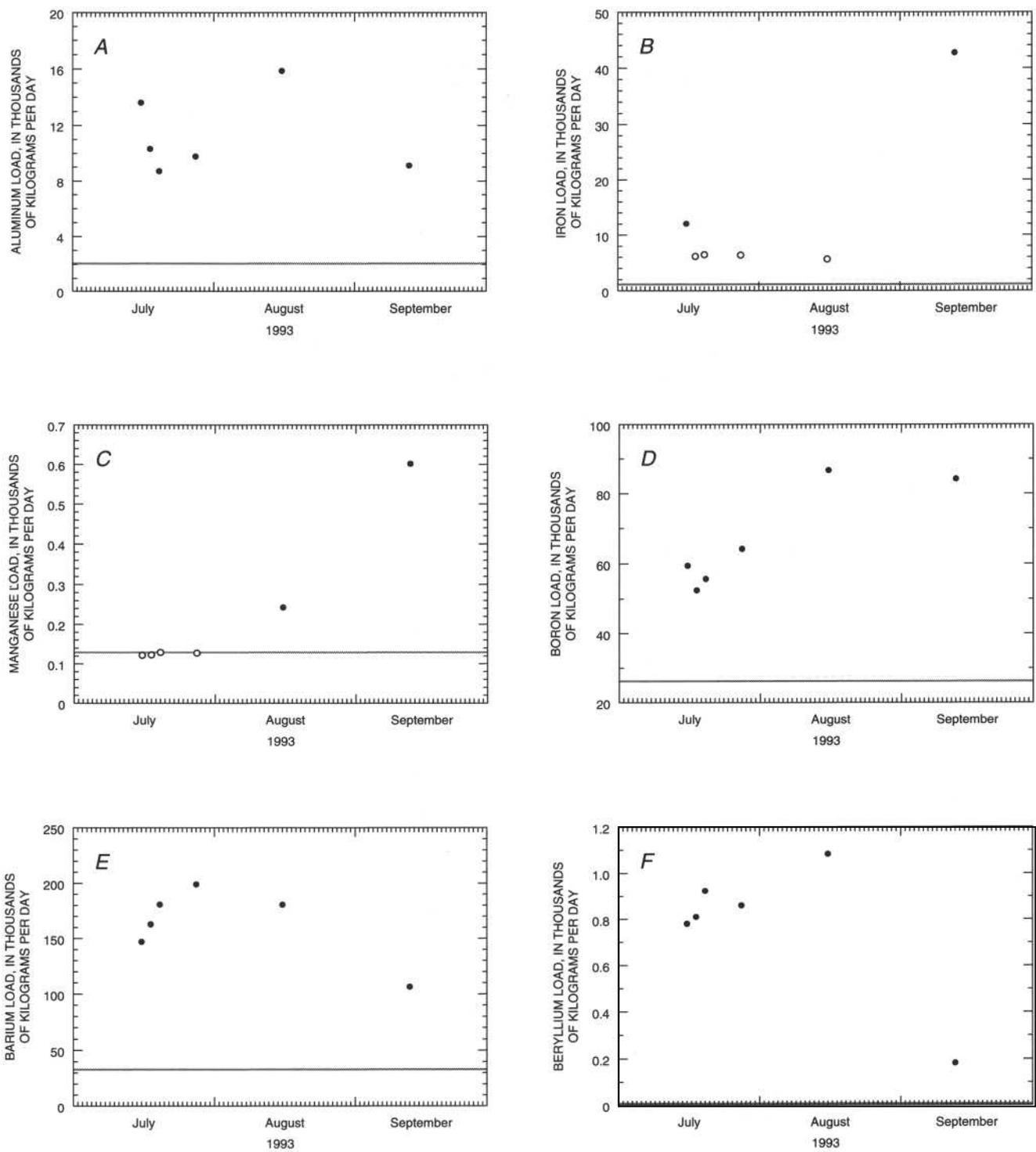
**Figure 10.** Loads of dissolved nitrate (A), nitrite (B), ammonium ion (C), phosphate (D), dissolved organic carbon (E), and suspended sediment (F) in the Mississippi River near Thebes, Illinois, July through September 1993. Gray lines indicate typical values measured on July 26, 1991.



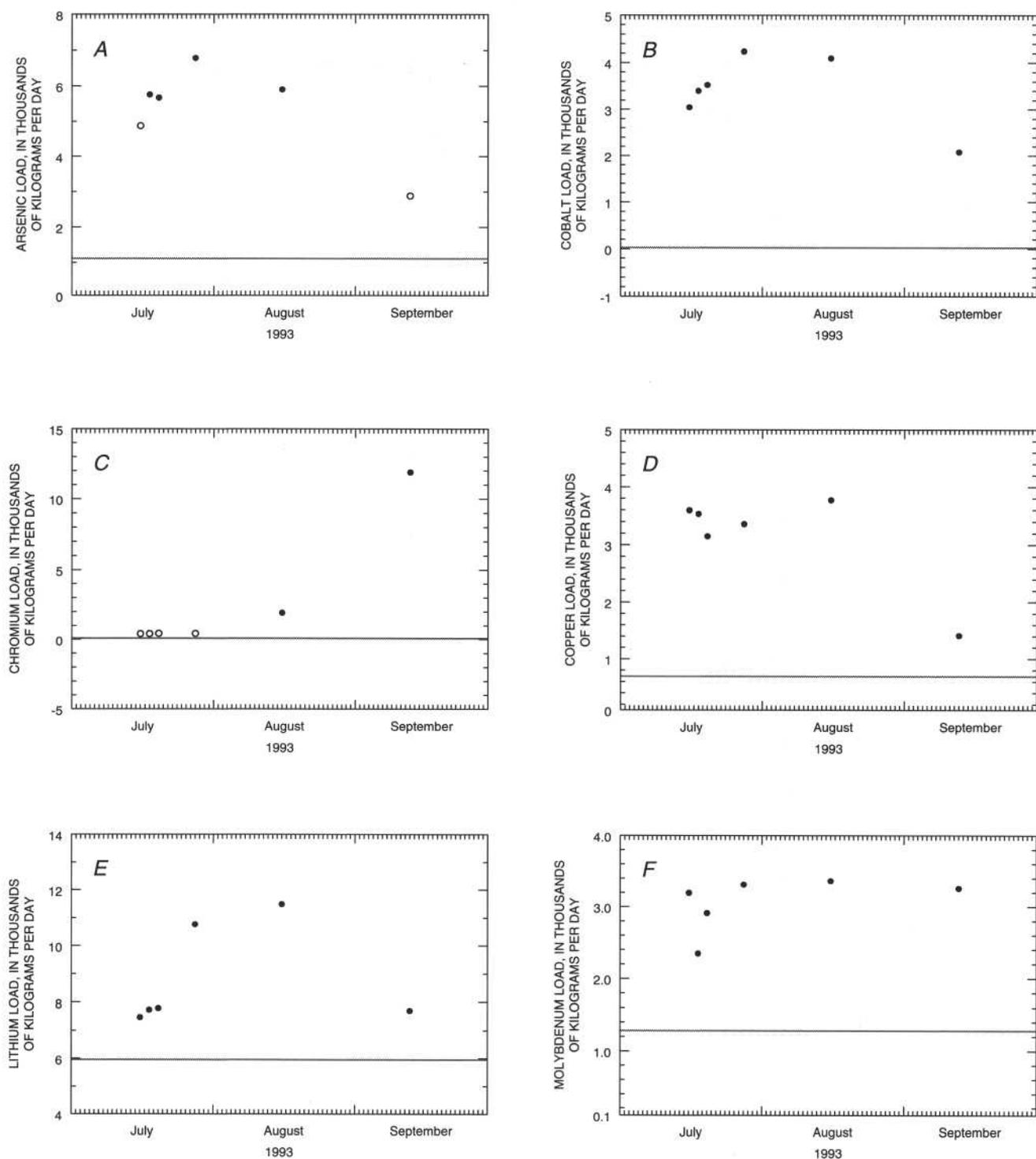
**Figure 11.** Loads of dissolved silica (A), sodium (B), potassium (C), calcium (D), magnesium (E), and strontium (F) in the Mississippi River near Thebes, Illinois, July through September 1993. Gray lines indicate typical values measured on July 26, 1991.



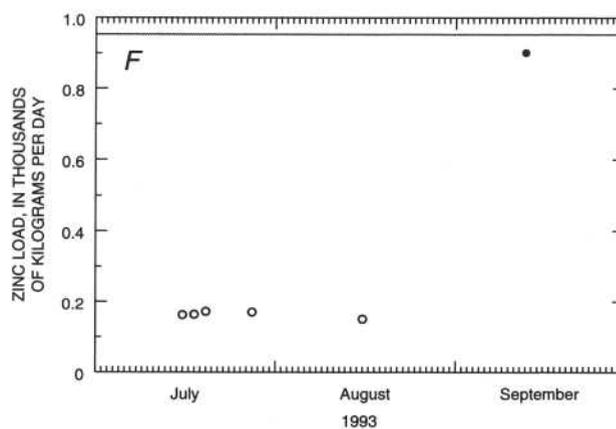
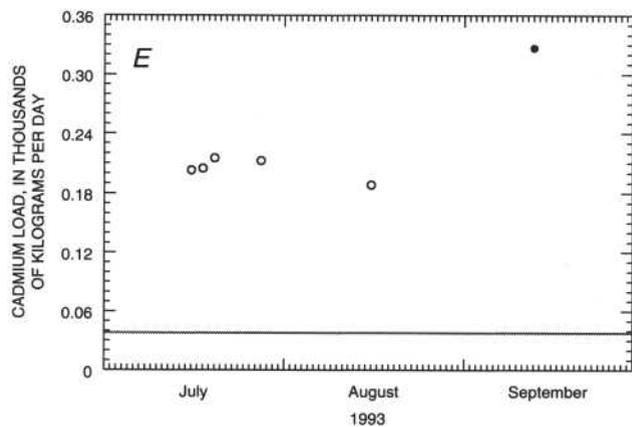
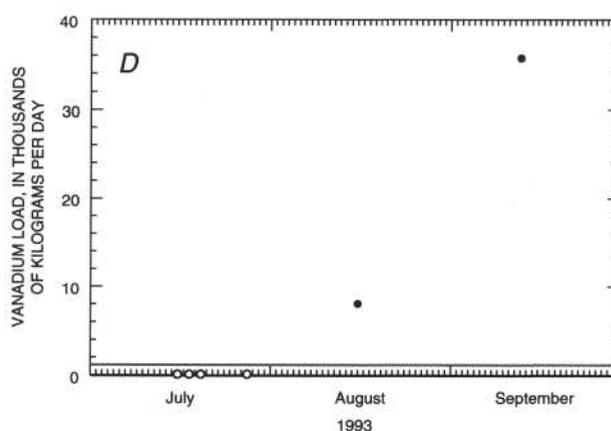
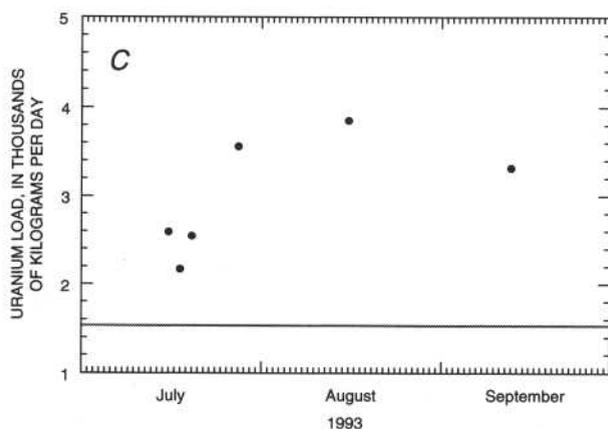
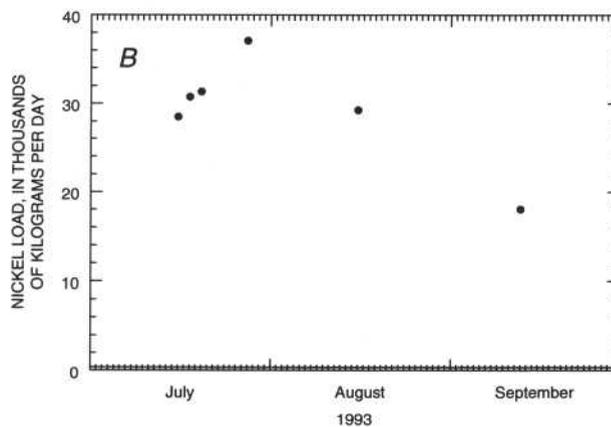
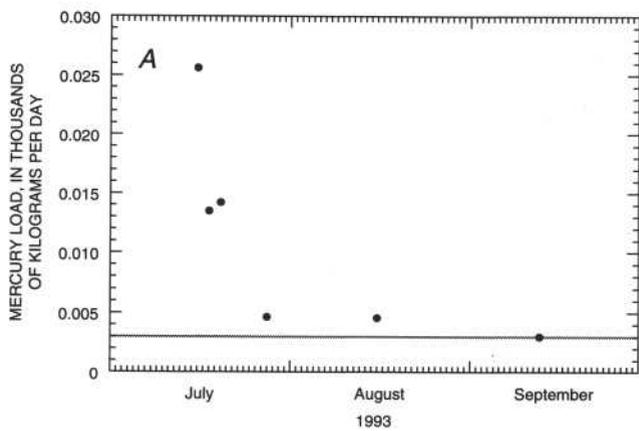
**Figure 12.** Loads of dissolved bicarbonate (A), carbonate (B), chloride (C), sulfate (D), fluoride (E), and bromide (F) in the Mississippi River near Thebes, Illinois, July through September 1993. Gray lines indicate typical values measured on July 26, 1991.



**Figure 13.** Loads of dissolved aluminum (A), iron (B), manganese (C), boron (D), barium (E), and beryllium (F) in the Mississippi River near Thebes, Illinois, July through September 1993. Open circles denote values at the analytical detection limit for the constituent. Gray lines indicate typical values measured on July 26, 1991.



**Figure 14.** Loads of dissolved arsenic (A), cobalt (B), chromium (C), copper (D), lithium (E), and molybdenum (F) in the Mississippi River near Thebes, Illinois, July through September 1993. Open circles denote values at the analytical detection limit for the constituent. Gray lines indicate typical values measured on July 26, 1991.



**Figure 15.** Loads of dissolved mercury (A), nickel (B), uranium (C), vanadium (D), cadmium (E), and zinc (F) in the Mississippi River near Thebes, Illinois, July through September 1993. Open circles denote values at the analytical detection limit for the constituent. Gray lines indicate typical values measured on July 26, 1991.