

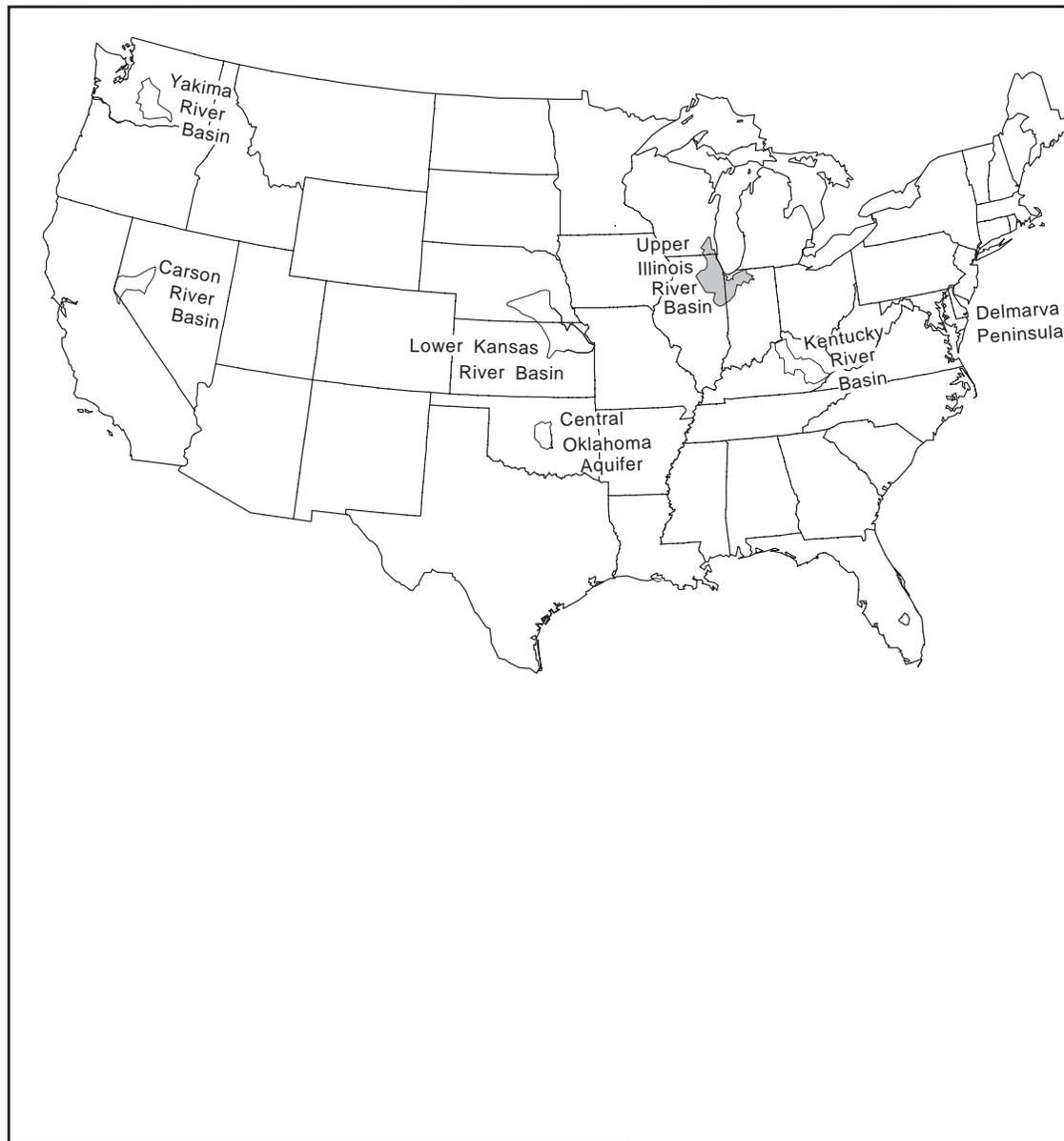
# SURFACE-WATER-QUALITY ASSESSMENT OF THE UPPER ILLINOIS RIVER BASIN IN ILLINOIS, INDIANA, AND WISCONSIN: MAJOR AND TRACE ELEMENTS IN WATER, SEDIMENT, AND BIOTA, 1978–90



U.S. GEOLOGICAL SURVEY  
Water-Resources Investigations Report 95-4045

# WATER-QUALITY ASSESSMENT OF THE UPPER ILLINOIS RIVER BASIN IN ILLINOIS, INDIANA, AND WISCONSIN: MAJOR AND TRACE ELEMENTS IN WATER, SEDIMENT, AND BIOTA, 1978–90

by Faith A. Fitzpatrick, Barbara C. Scudder, J. Kent Crawford, Arthur R. Schmidt, Jennifer B. Sieverling, and others



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CONVERSION FACTORS AND ABBREVIATED WATER-QUALITY UNITS

	Multiply	By	To obtain
	inch (in.)	25.4	millimeter
	mile (mi)	1.609	kilometer
	square mile (mi <sup>2</sup> )	2.590	square kilometer
	cubic foot per second (ft <sup>3</sup> /s)	0.02832	cubic meter per second
	ton per square mile (ton/mi <sup>2</sup> )	2.350	megagram per square kilometer

Temperature in degrees Fahrenheit (°C) as follows:

$$^{\circ}\text{F} = 1.8 \times ^{\circ}\text{C} + 32$$

**Abbreviated water-quality units used in this report:** Chemical concentrations and water temperature are given in metric units. Chemical concentration is given in milligrams per liter (mg/L), micrograms per liter (µg/L) micrograms per gram (µg/g), or milligrams per kilograms (mg/kg). Milligrams per liter is a unit expressing the concentration of chemical constituents in solution as mass (milligrams) of solute per unit volume (liter) of water. One thousand micrograms per liter is equivalent to one milligram per liter. For concentrations less than 7,000 mg/L, the numerical value is the same as for concentrations in parts per million. Micrograms per gram and milligrams per kilograms are in units expressing the concentration of chemical constituents in solution as mass (micrograms/milligrams) of constituent per unit mass (gram/kilogram) of a dry sample.

Some masses in this report are given in grams (g). Pore sizes of membrane filters and screen sizes of sieves are given in millimeters (mm).

# Surface-Water-Quality Assessment of the Upper Illinois River Basin in Illinois, Indiana, and Wisconsin: Major and Trace Elements in Water, Sediment, and Biota, 1978–90

By Faith A. Fitzpatrick, Barbara C. Scudder, J. Kent Crawford, Arthur R. Schmidt, and Jennifer B. Sieverling; *with contributions from* John A. Colman, Charles G. Crawford, and Daniel J. Sullivan

## Abstract

The distribution of 22 major and trace elements was examined in water, sediment, and biota in the upper Illinois River Basin in Illinois, Indiana, and Wisconsin as part of a pilot National Water-Quality Assessment project done by the U.S. Geological Survey from 1987 through 1990. The 22 elements are aluminum, antimony, arsenic, barium, beryllium, boron, cadmium, chromium, cobalt, copper, iron, lead, manganese, mercury, molybdenum, nickel, phosphorus, selenium, silver, strontium, vanadium, and zinc.

Concentrations of U.S. Environmental Protection Agency (USEPA) priority pollutants among the 22 elements were elevated in the Chicago area in all three aquatic components (water, sediment, and biota). Further, some of the priority pollutants also were found at elevated concentrations in biota in agricultural areas in the basin. Cadmium, chromium, copper, iron, lead, mercury, silver, and zinc concentrations in water exceeded USEPA acute or chronic water-quality criteria at several sites in the Chicago area. Correlations among concentrations of elements in water, sediment, and biota were found, but the correlation analysis was hindered by the large proportion of observations less than the minimum reporting level in water. Those sites where water-quality criteria were sometimes exceeded were not always the same sites where concentrations in biota were the largest. This relation

indicates that accumulation of these pollutants in biota is confounded by complex geochemical and biological processes that differ throughout the upper Illinois River Basin.

## INTRODUCTION

The upper Illinois River Basin was one of four surface-water basins selected by the U.S. Geological Survey (USGS) in 1986 for the pilot phase of the National Water-Quality Assessment (NAWQA) program. The NAWQA program was designed to (1) provide a nationally consistent description of current water-quality conditions for a large part of the Nation's water resources, (2) define long-term trends in water quality, and (3) identify, describe, and explain the major factors that affect observed water-quality conditions and trends (Cohen and others, 1988; Hirsch and others, 1988). Major and trace elements in water, sediment, and biota were identified as principal constituents to target because of their possible effects on aquatic and terrestrial life, and their relation to the transport and accumulation of priority pollutants. Assessment of element concentrations in water, sediment, and biota will be used to address seven NAWQA issues: (1) occurrence of trace elements in each component of the aquatic system, (2) spatial distribution of elements in each component, (3) temporal distributions, (4) background concentrations, (5) relations to different land uses, (6) bioavailability, and (7) development of a national data base.

The upper Illinois River Basin drains 10,949 mi<sup>2</sup> of northeastern Illinois, northwestern Indiana, and southeastern Wisconsin (fig. 1). The upper Illinois River Basin includes three principal streams: the Des Plaines, Kankakee, and Fox Rivers. The Des Plaines River flows south from Wisconsin and through the city and metropolitan area of Chicago, where it receives water from Lake Michigan by way of the North Shore Channel, the Chicago Sanitary and Ship Canal, and the Calumet Sag Channel. The Kankakee River originates in northern Indiana and flows west into Illinois to combine with the Des Plaines River. The confluence of the two rivers marks the head of the Illinois River. The Fox River flows south from Wisconsin along the western edge of the basin and joins the Illinois River near Ottawa, Ill.

The upper Illinois River Basin receives numerous anthropogenic inputs of major and trace elements from municipal and industrial point sources, urban and agricultural runoff, and atmospheric deposition. The urban and industrial areas in and around Chicago substantially affected the aquatic ecosystem of the upper Illinois River as early as 1900, when the flow of industrial and domestic wastes was redirected from Lake Michigan, Chicago's water supply, to the upper Illinois River system (Forbes and Richardson, 1913, 1919; Richardson, 1928). By 1912, fish and mussels were virtually absent from streams in and downstream from the Chicago area (Forbes and Richardson, 1913).

The deterioration in the quality of water in the upper Illinois River after 1900 has been due to the complex interaction of several factors: depletion of dissolved oxygen by large concentrations of organic matter in wastewater from Chicago (Forbes and Richardson, 1913; Mathis and Cummings, 1970), increased turbidity combined with loss of aquatic vegetation in backwater areas (Sparks, 1984), conversion of land in the basin from forest and prairie to agriculture (Forbes and Richardson, 1919), and construction of navigation dams for maintenance of water levels (Sparks, 1984). The additional effects of trace elements on the decline in quality of the upper Illinois River are unknown; however, changes in trace-element concentrations are suspected to have had some effect on the biological diversity of the upper Illinois River (Mathis and Cummings, 1970).

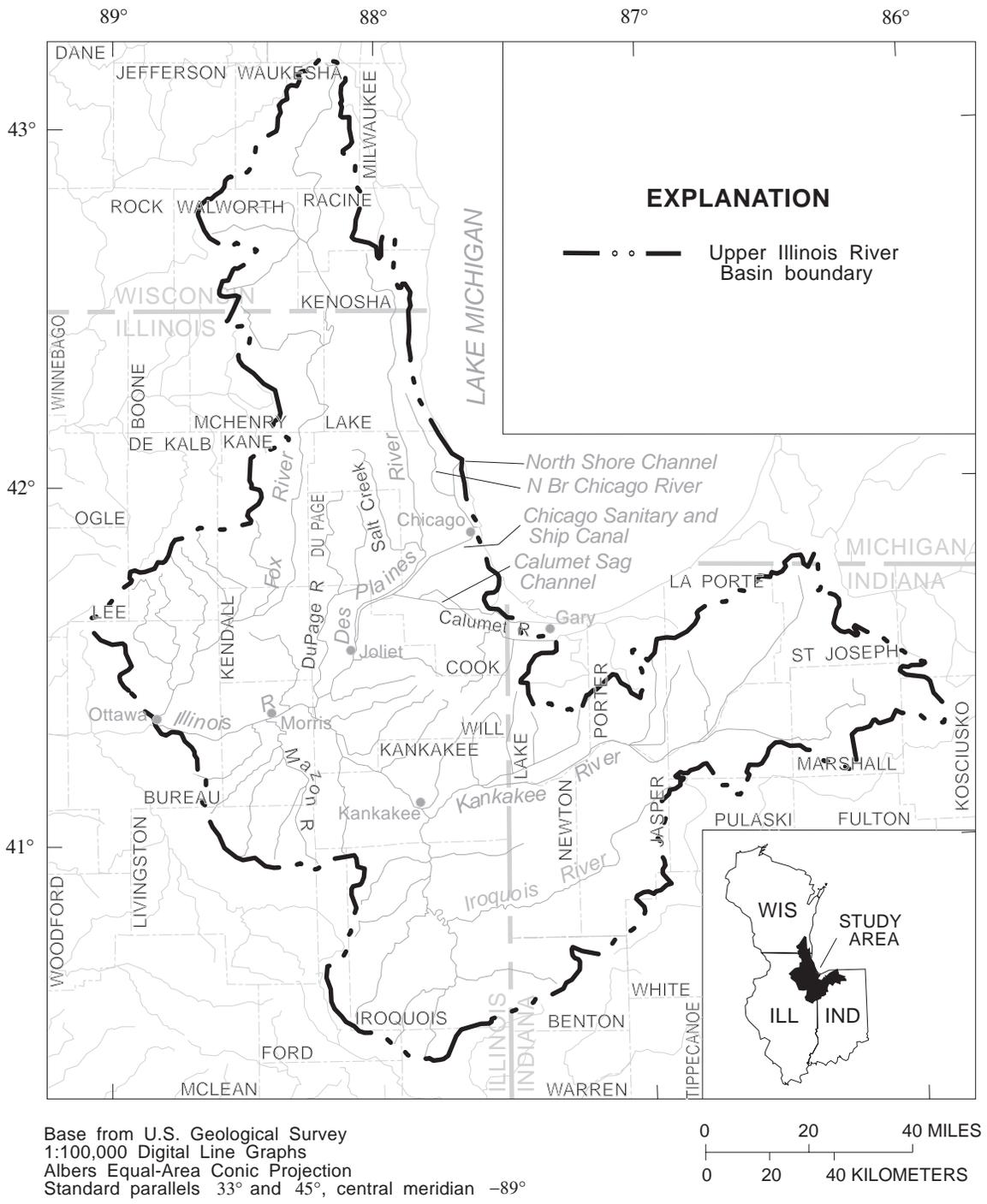
A variety of institutions have collected large amounts of data on the concentration of trace elements in water, sediment, and biota in streams in the upper Illinois River Basin since the early surveys of changes in the biota of the upper Illinois River after the opening of the Chicago Sanitary and Ship Canal (Forbes and Richardson, 1913, 1919; Richardson, 1928; Steffeck and Striegl, 1989). These institutions include Federal and State research and regulatory agencies, universities, regional planning commissions, and municipal wastewater-reclamation facilities. Results from some of these surveys were used in the design and planning of the upper Illinois River Basin NAWQA program.

## Purpose and Scope

This report describes the distribution of major and trace elements in water, suspended and streambed sediment, and biota in streams of the upper Illinois River Basin from April 1978 through August 1990. The major objectives of this report are twofold. First, the report describes concentrations of major and trace elements in three components (water, sediment, and biota) of the aquatic environment in streams of the upper Illinois River Basin. Second, the report describes the relations between trace-element concentrations in water, sediment, and biota so that the effects and fates of trace elements throughout the food chain can be more completely understood.

Sources of chemical data used in this report included samples collected and analyzed during the NAWQA pilot study of the upper Illinois River Basin from synoptic sites and fixed-sampling sites from 1987 through 1990 and from the Illinois Environmental Protection Agency (IEPA) Ambient Water-Quality Monitoring Network from 1978 through 1990.

Included in the report are summary statistics; calculated loads and yields; descriptions of seasonal variations and trends; correlations among concentrations of trace elements; correlations among concentrations in water, sediment, and biota; and correlations among subbasins in the upper Illinois River Basin. In addition, element concentrations are compared to background concentrations and water-quality criteria. The 22 elements examined in this report are aluminum, antimony, arsenic, barium, beryllium, boron, cadmium, chromium, cobalt, copper, iron, lead, manganese, mercury, molybdenum, nickel, phosphorus, selenium,



**Figure 1.** Location of the upper Illinois River Basin.

silver, strontium, vanadium, and zinc. Other chemical constituents and physical properties are referred to throughout the discussion where they relate to element concentrations.

## Acknowledgments

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- U.S. Fish and Wildlife Service (La Crosse, Wis.)—Collection and identification of fish species in 1990

## Sources of Major and Trace Elements

Element concentrations in water, sediment, and biota in streams in the upper Illinois River Basin reflect a combination of the geochemistry of the surficial deposits in the basin, stream morphology, and land-use practices. Principal background sources of trace elements in streams in the upper Illinois River Basin are rocks, soils, and plant litter. Anthropogenic sources include dry and wet deposition of atmospheric emissions, industrial and municipal discharges, and runoff from agricultural and urban areas. In many parts of the upper Illinois River Basin, inputs from anthropogenic sources are many times greater than inputs from background sources.

## Background Sources

In the upper Illinois River Basin, background concentrations are not synonymous with natural or pristine conditions because virtually all of the upper Illinois River Basin is affected by human activities. In previous studies of the upper Illinois River Basin, background sites for collections of streambed sediment were defined as sites upstream from any known point-source discharge and with a population density less than 1,000 people per square mile within a 3-mi radius

of the collection site (John A. Colman, U.S. Geological Survey, written commun., 1989). Kelly and Hite (1984, p. 10) defined background as those sites “judged unimpacted by point or nonpoint discharge with the exception of agricultural nonpoint inputs.” In this report, the term “background concentrations” refers to concentrations that are minimally affected by anthropogenic sources.

Elements are released from rocks and soils through chemical and biological weathering (Leckie and James, 1974; Mattigod and Page, 1983, p. 358). Analysis of bulk chemistry of geologic materials can indicate potential sources of trace elements (table 1; all tables in back of report). Mineralogy and weathering intensity control the release of these elements into stream water (Leckie and James, 1974; Drever, 1988). In addition to directly affecting the trace-element chemistry of a stream, geologic material also affects other geochemical properties, such as pH and hardness, that indirectly affect trace-element chemistry (Drever, 1988).

Release of carbonate from weathering of limestone and dolomite typically increases pH, hardness, and alkalinity. Streams in the upper Illinois River Basin have eroded through soils and unconsolidated deposits into carbonate-rich bedrock in many areas. These rocks are mainly composed of dolomite interbedded with lesser amounts of limestone, sandstone, shale, and coal (Willman and others, 1975; Mades, 1987). Downcutting by the Illinois River and the lower Fox River has exposed limestone and dolomite of Ordovician and Silurian age and shale, limestone, and coal of Pennsylvanian age (Willman, 1973; Willman and others, 1975; Mades, 1987). Dolomite of Silurian age is exposed in deep quarries near Chicago; along the valleys of the lower Des Plaines, lower Kankakee, lower Du Page, and lower Fox Rivers; and in the excavated channel of the Chicago Sanitary and Ship Canal (Willman, 1973; Willman and others, 1975; Gross and Berg, 1981; Mades, 1987). Limestone, shale, and sandstone of Mississippian and Devonian age crop out along the Iroquois River and some of its tributaries (Willman and others, 1975; Mades, 1987).

Typical concentrations of elements in carbonate rocks, sandstone, and shales are listed in table 1. These concentrations reflect averages for the United States. No data are available for rocks in the upper Illinois River Basin alone; however, consistent information is available for

background stream concentrations in Illinois, as well as data collected nationwide for soil concentrations. Statewide background distributions that reflect Illinois geology have been identified by Kelly and Hite (1984). Aluminum and iron are abundant in rocks; copper, vanadium, and zinc are less abundant but still common in rocks (Moore and Ramamoorthy, 1984; City of Chicago and Illinois Environmental Protection Agency, 1985) (table 1). Strontium concentrations are typically larger in carbonate rocks than in other rock types (table 1) (City of Chicago and Illinois Environmental Protection Agency, 1985). Weathering of coal-bearing sedimentary rocks can release arsenic (Kelly and Hite, 1984). Beryllium is rare in crustal rocks (City of Chicago and Illinois Environmental Protection Agency, 1985; Hem, 1985).

Unconsolidated deposits blanket the bedrock surface and are variable in thickness and lithology. The surficial deposits are mainly glacial, glaciofluvial, or glaciolacustrine sediments that were deposited during the last glaciation (Willman and Frye, 1970; Lineback, 1979; Hansel and others, 1986). The mineralogy of the deposits and soils reflects the underlying bedrock in the vicinity (table 1); thus, these deposits also are carbonate rich. The most abundant type of glacial deposit in the upper Illinois River Basin is fine-grained till (Willman and Frye, 1970; Lineback, 1979). Major rivers in the basin generally flow through narrow bands of coarse-grained outwash and lacustrine deposits surrounded by silty and clayey glacial till. An exception is the Kankakee River, which flows through an areally extensive, coarse-grained outwash plain in Indiana (Hansel and others, 1986). The outwash plain consists of extensive sands covered in places by either eolian sand or organic-rich muck and peat. Because of this, the Kankakee River and its tributaries carry a greater sand load than other major rivers in the basin (Gross and Berg, 1981). The Iroquois River subbasin contains mainly glaciolacustrine deposits (Lineback, 1979; U.S. Department of Agriculture, Soil Conservation Service and Purdue University Agricultural Experiment Station, 1982).

Ground water from shallow bedrock aquifers contributes to the base flow of the major streams in the basin, although the volume of ground-water contribution has not been quantified. Extensive aquifers in the Ordovician and Silurian bedrock are known to contribute to the base flow of the Fox River in Kane County (Fitzpatrick and others, 1992). Ground water from bedrock is probably contributing to other stream

reaches as well, in contact with bedrock. The geochemistry of rocks in the aquifer is reflected in the geochemistry of the ground water. In the upper Illinois River Basin, accessory feldspar in sandstone may be the source of barium in ground water (Gilkeson and others, 1983). Sand and gravel aquifers are not as extensive as the bedrock aquifers; nevertheless, they also contribute to the base flow of streams where they are not hydraulically separated from the streambed by fine-grained glacial till, lacustrine deposits, or fine-grained alluvium.

Vegetation can change the geochemistry of soils by concentrating some elements and depleting others. Leaves and forest material, for example, can contain significant amounts of manganese, which may affect the manganese concentrations in streams (Hem, 1964, p. B2–B3; Bobo and Renn, 1980) (table 1). Plant litter and animal feces release phosphorus (Striegl and Cowan, 1987). Humic acids from plants can affect the pH of soils, which alters the solubility and release mechanism of some elements.

Clay minerals in fine-grained sediment, which are transported by the streams and deposited in pools, serve as media for adsorption of trace elements. Organic material also accumulates in these pools and may concentrate trace elements. Flood plain deposits and backwater sediments also may be resuspended during high flow and renew the source of fine-grained material available for trace-element adsorption. Background concentrations of selected elements in water and streambed sediments in the middle Illinois River and three nonindustrial tributaries are shown in table 1. Background concentrations of elements were larger in streambed sediment than in water; however, they were similar to concentrations of the elements in soils and surficial material (table 1). For example, concentration of arsenic in streambed sediments (2–14 mg/kg) did not differ substantially from background concentrations reported for precultural sediments from North American lakes (0.6–11 mg/kg) (Förstner and Wittman, 1979).

### **Anthropogenic Sources**

Elements from anthropogenic sources are transported directly to the stream environment through point-source discharge and indirectly through dry and wet atmospheric deposition and surface runoff. Significant human contributions of elements to streams in the upper Illinois River

Basin began in the 1870's and were caused by the growth and expansion of agriculture in the basin and by growth and expansion of industrial and urban areas in and near Chicago, Ill., and Gary, Ind. Navigational dams were constructed on the Des Plaines, Kankakee, Fox, and Illinois Rivers, which caused large volumes of fine-grained sediment to accumulate (U.S. Army Corps of Engineers, Chicago District, 1987).

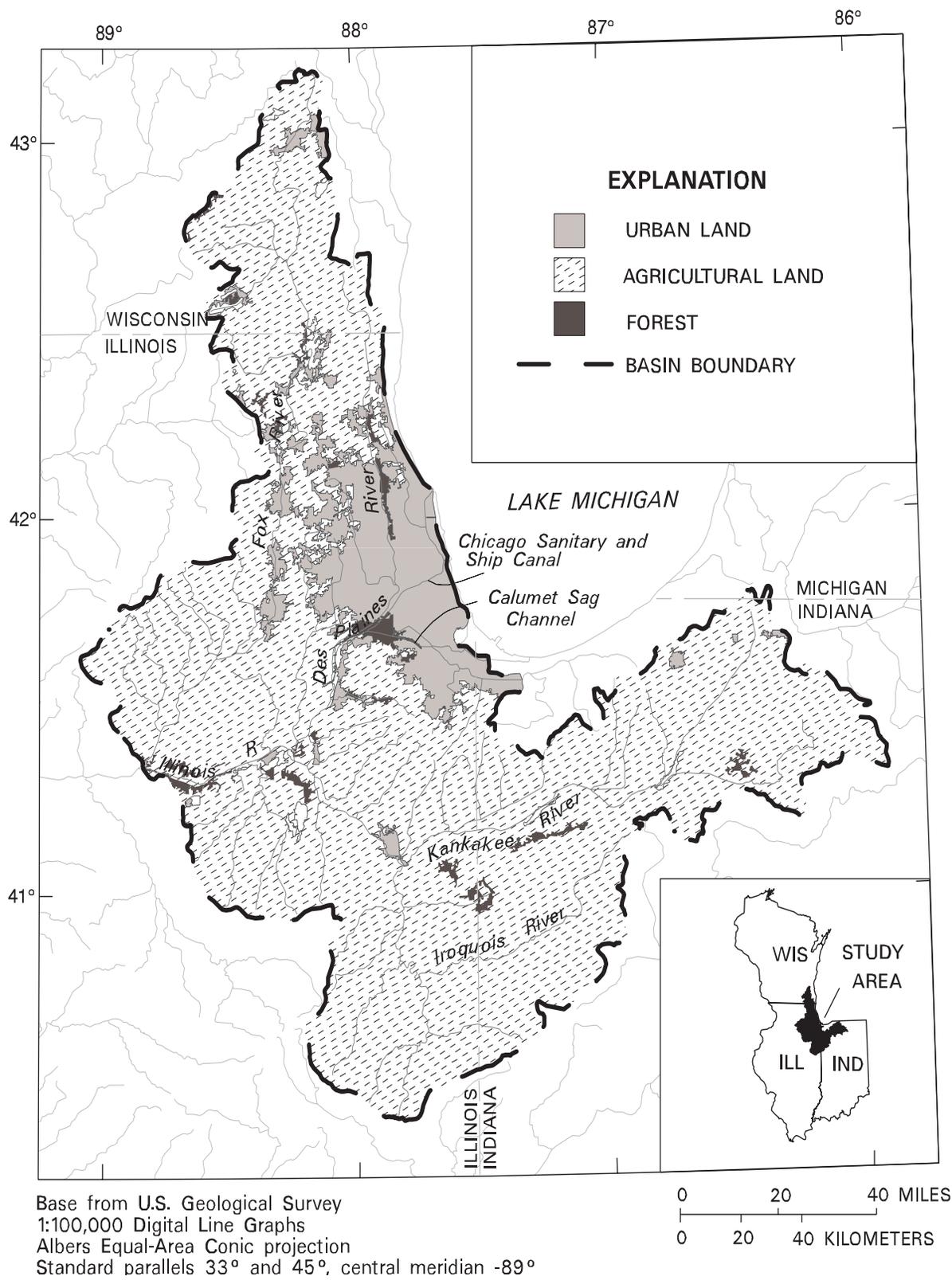
Urban areas contribute trace elements to streams in the upper Illinois River Basin through atmospheric deposition, point-source discharges, and nonpoint-source runoff (Mathis, 1976). Urban land in the basin (fig. 2) is estimated to be about 8 percent industrial, 59 percent residential, 19 percent commercial, and 15 percent undetermined urban land. The area drained by the Calumet River system contains some of the most heavily industrialized land in the Nation; petroleum refining and steel manufacturing are the dominant industries (City of Chicago and Illinois Environmental Protection Agency, 1989). Previous studies of streams near urban areas have concluded that, in general, elevated concentrations of copper, iron, mercury, and zinc are associated with urban activities (Leed and Belanger, 1981; Kelly and Hite, 1984). Cadmium, chromium, copper, iron, lead, nickel, and zinc concentrations were all significantly larger in bottom sediments of the Illinois River than in bottom sediments of the nonindustrial-area streams, and chromium, cobalt, copper, and lead concentrations were elevated in Illinois River water (Mathis and Cummings, 1970).

Base flows of most streams in the Chicago area consist partly of industrial or municipal effluent or both. Streams and their tributaries where stream quality is particularly affected by effluent from point discharges include the Des Plaines River, the tributaries that flow along the shore of Lake Michigan through inner Chicago, the Chicago Sanitary and Ship Canal, the Calumet River system, and the Du Page River. Examples of point-source discharges include effluent from wastewater-treatment plants (fig. 3), manufacturing plants and other industries (fig. 4), chemical spills, and sewer outfalls. Few streams in the upper Illinois River Basin do not receive some kind of point discharge. Wastewater-treatment plants remove some of the elements from sewage, but some element concentrations are commonly elevated in wastewater from the treatment plants relative to background concentrations (table 2) (Williams and others, 1974). Copper, chromium, nickel, and zinc

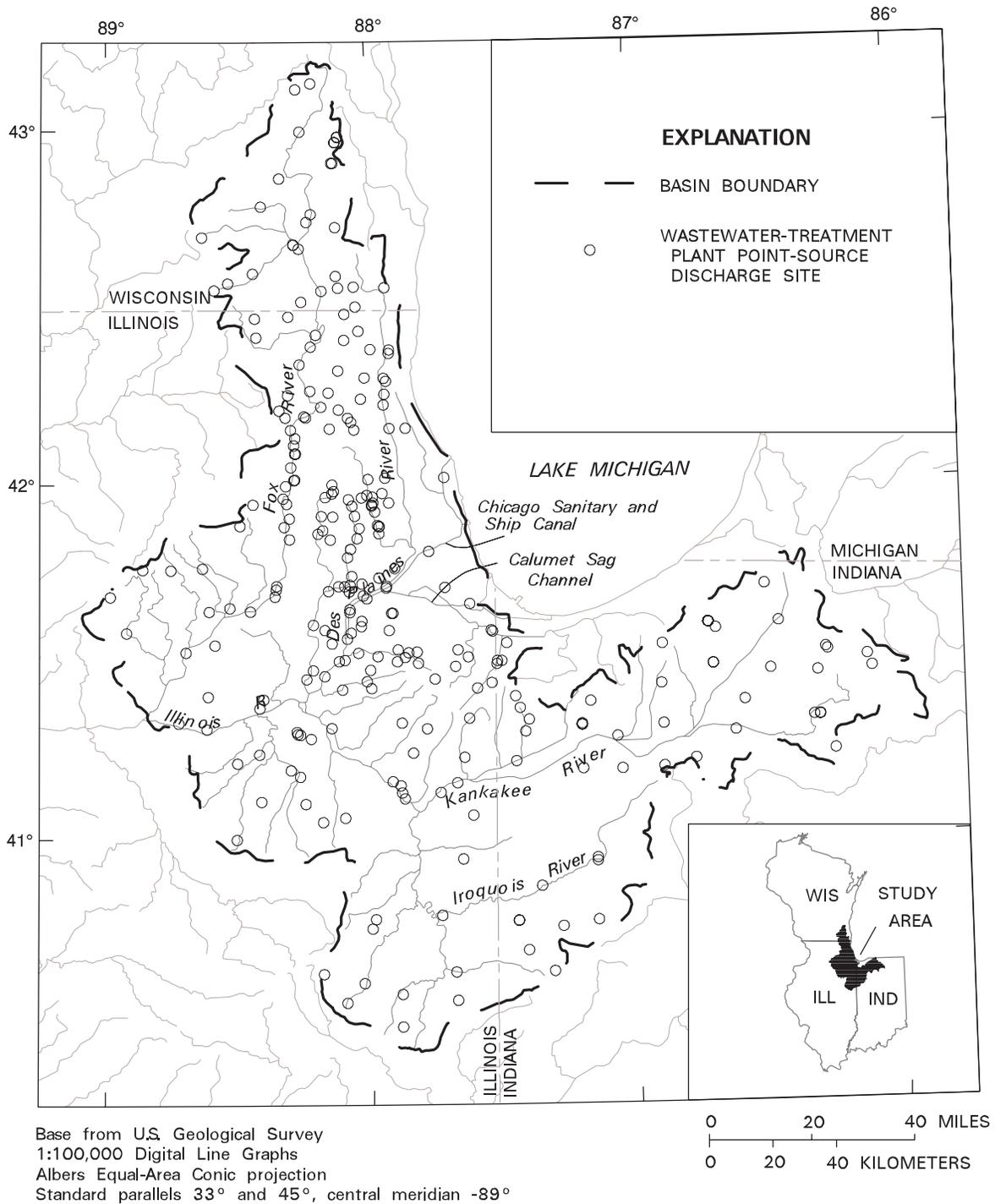
are common trace elements supplied by domestic sewage (Williams and others, 1974). Effluent from iron and steel manufacturing plants can contain copper, chromium, lead, and nickel (Förstner and Wittman, 1979; Salomons and Förstner, 1984). Effluent from other metal industries, including nonferrous primary producers, electroplating industries, and ferrochrome industries, commonly includes copper, chromium, lead, nickel, silver, and zinc (Kelly and Hite, 1981, 1984; Moore and Ramamoorthy, 1984). Ground-wood pulping processes release barium, chromium, and zinc (Rickert and others, 1977; Kelly and Hite, 1981; City of Chicago and Illinois Environmental Protection Agency, 1985). Lead and cadmium are released from battery-manufacturing plants (Kelly and Hite, 1981, 1984; Moore and Ramamoorthy, 1984).

Several possible disposal methods of the elements and related compounds complicate the direct relation of the amounts of elements released by industries and the amounts that arrive in streams in the Chicago area. Industrial wastes are disposed of through air emissions, water discharges, wastewater-treatment plants, landfills, and offsite transfers (table 3). In the Chicago metropolitan area, most of the elements are disposed of primarily through offsite transfers and secondly through land disposals. Offsite transfer means that the waste was disposed of somewhere outside of the Chicago area. Only a small percentage of the total amount released is discharged directly to streams, air, or a wastewater-treatment plant.

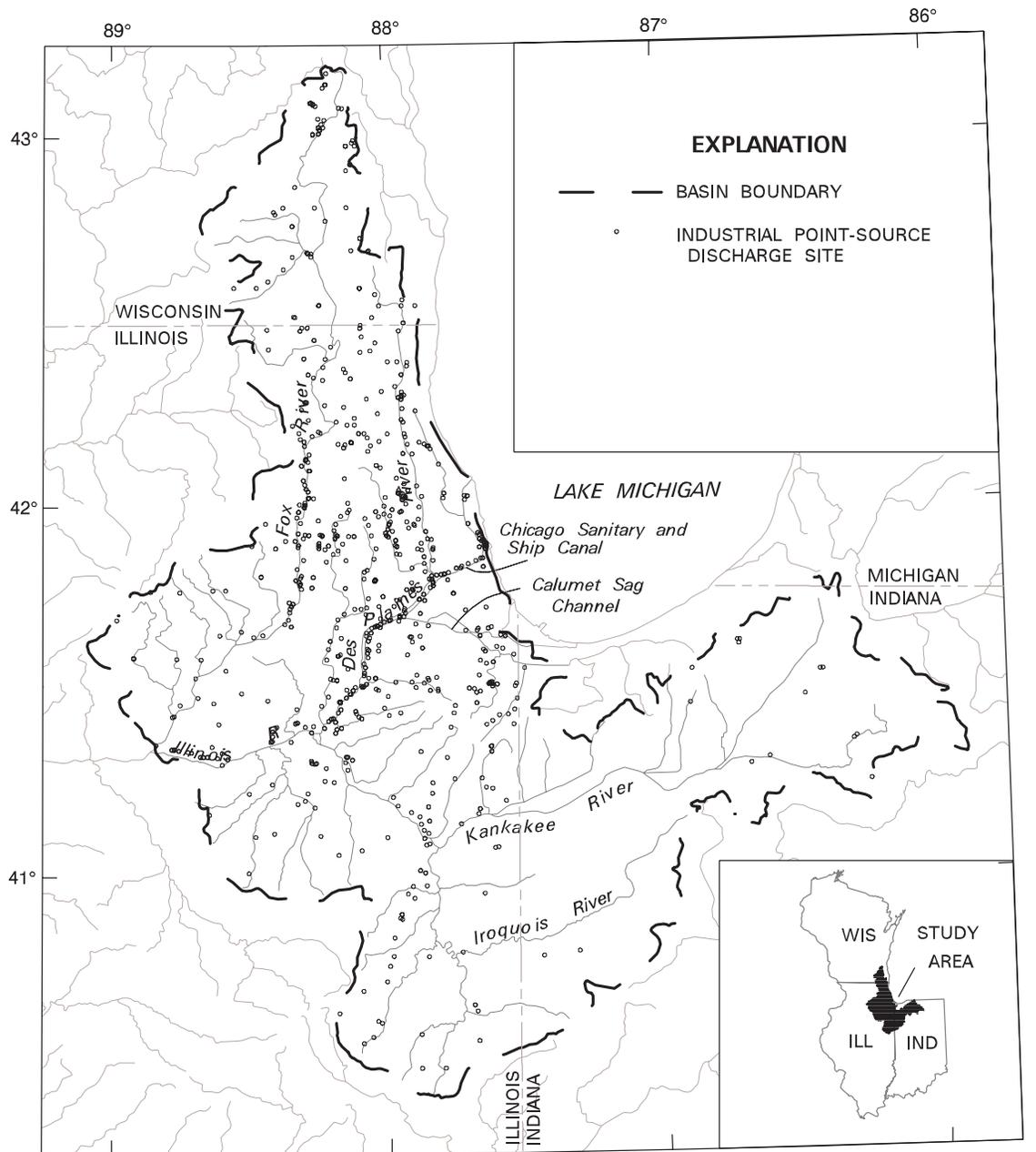
Sources that contribute elements to the atmosphere in the Chicago metropolitan area include devices that burn fossil fuels, metallurgical coke manufacturing ovens, iron and steel manufacturing facilities, waste incinerators, and cement manufacturing plants (Winchester and Nifong, 1971). Fossil-fuel combustion releases a variety of trace elements, including aluminum, arsenic, barium, cadmium, chromium, cobalt, iron, lead, mercury, molybdenum, nickel, selenium, vanadium, and zinc (Winchester and Nifong, 1971; Kagey and Wixson, 1983, p. 473–475; Kelly and Hite, 1984; Moore and Ramamoorthy, 1984; City of Chicago and Illinois Environmental Protection Agency, 1985). Metallurgical coke manufacturing ovens and other metal producers emit aluminum, cadmium, chromium, copper, iron, lead, and zinc into the atmosphere (Winchester and Nifong, 1971;



**Figure 2.** Land use in the upper Illinois River Basin.



**Figure 3.** Locations of wastewater-treatment plants in the upper Illinois River Basin. (Locations compiled from the Illinois State Water Use data base, John LaTour, U.S. Geological Survey, written commun., 1988; and from the Industrial Facilities Discharge data base, Phillip Taylor, U.S. Environmental Protection Agency, oral commun., 1988.)



Base from U.S. Geological Survey  
 1:100,000 Digital Line Graphs  
 Albers Equal-Area Conic projection  
 Standard parallels 33° and 45°, central meridian -89°

0 20 40 MILES  
 0 20 40 KILOMETERS

**Figure 4.** Locations of industrial point-source discharges to stream water in the upper Illinois River Basin. (Locations compiled from the Illinois State Water Use data base, John LaTour, U.S. Geological Survey, written commun., 1988; and from the Industrial Facilities Discharge data base, Phillip Taylor, U.S. Environmental Protection Agency, oral commun., 1988.)

Moore and Ramamoorthy, 1984). Iron and steel manufacturing releases atmospheric emissions of aluminum, arsenic, cadmium, copper, iron, lead, manganese, nickel, and zinc (Winchester and Nifong, 1971; Kelly and Hite, 1981, 1984; Moore and Ramamoorthy, 1984). Waste incineration releases mercury, nickel, and zinc (Moore and Ramamoorthy, 1984). Cement manufacturing plants and refractory brick producers release aluminum, chromium, and iron (Winchester and Nifong, 1971; Moore and Ramamoorthy, 1984).

Runoff from urban areas commonly contains residues from gasoline, motor oil, tires, brake linings, galvanized metal, nails, painted surfaces, pesticides, and fertilizers (Moore and Ramamoorthy, 1984; Striegl and Cowan, 1987). Arsenic, chromium, copper, iron, mercury, and phosphate are associated with runoff from urban areas (Leed and Belanger, 1981; Kelly and Hite, 1981, 1984; Moore and Ramamoorthy, 1984). Traffic-related sources contribute copper, lead, and zinc to urban runoff (Striegl and Cowan, 1987). Building materials commonly release zinc (Kelly and Hite, 1984).

Runoff from urban and agricultural areas alike can be affected by fertilizers and pesticides, which may release arsenic, copper, mercury, phosphorus, and zinc (Richardson and others, 1978; Kelly and Hite, 1981, 1984; Moore and Ramamoorthy, 1984). Agricultural land, which accounts for approximately 75 percent of the basin, mainly consists of cropland; the principal crops produced are corn and soybeans (Anderson and others, 1976; Feagas and others, 1983) (fig. 4). Methylmercury acetate and methoxyethyl mercury acetate were previously used on corn, but these pesticides are now banned. Sodium arsenate was used as an insecticide, but its use has been discontinued (Berg, 1976; Kelly and Hite, 1981; Sine, 1992). Sodium arsenite is used as a fungicide, herbicide, and insecticide, but its use decreased before the 1970's because of its extreme toxicity and solubility (Berg, 1976).

Runoff from coal-mined areas can have elevated concentrations of arsenic, boron, iron, manganese, and zinc (Kelly and Hite, 1981, 1984; Brabets, 1984; Moore and Ramamoorthy, 1984). Coal has been mined by surface and subsurface methods in the southwestern part of the upper Illinois River Basin. The coal-mining district extends from the confluence of the Kankakee and Des Plaines Rivers southwest along the valley of the Illinois River to the basin boundary, and

south of the Illinois River in the Mazon River Basin (Smith, 1968). Previous studies have shown that large concentrations of aluminum, iron, manganese, and zinc were found in samples from streams downstream from coal-mining areas in other parts of Illinois, particularly in acidic environments (Brabets, 1984). In-place neutralization, however, greatly reduces metal concentrations in mine runoff (Brabets, 1984), especially in the upper Illinois River Basin where limestone is abundant.

## Geochemistry of Major and Trace Elements

The 22 elements examined in this report are present in major and trace amounts in surface water. Normally, major elements are defined as elements that are present in water at concentrations of greater than 1 mg/L (Hem, 1985). Of the 22 elements, major elements include boron and three metals: aluminum, iron, and manganese. The remaining 18 elements generally are present at concentrations less than 1 mg/L in water and are considered minor or trace elements. Most of the 18 trace elements are metals; exceptions are antimony, arsenic, and selenium. Lead and mercury are generally referred to as heavy metals in the literature, although many authors use the terms heavy metals and trace elements interchangeably. Minor, or trace, elements also may be present at concentrations greater than 1 mg/L as a result of weathering of ore-bearing rocks and sediments, discharge of industrial and municipal effluents, urban and agricultural runoff, and atmospheric deposition.

Concentrations of elements in the water and sediment depend not only on the sources of the elements but also on the complex interaction of chemical and biological processes in the stream that receives the elements (Williams and others, 1974). These processes affect the speciation and the partitioning of an element in the aquatic environment.

The species of these elements affect their availability and toxicity to humans and aquatic life (Batley, 1983). Speciation refers to the distribution between chemical species and includes the valence or oxidation state of an element. Speciation is affected by hydrogen ion activity, oxidizing or reducing conditions, temperature, alkalinity, hardness, chlorinity, complexation with other compounds, and biochemical activity.

Elements can be partitioned among the dissolved or particulate phases in differing amounts,

depending on a variety of factors including hydrogen ion activity, oxidizing or reducing conditions, adsorption to hydrous oxides, concentration of organic matter, biological activity, hydraulic energy, and the nature of the substrate (Williams and others, 1974; Elder, 1988; Horowitz, 1991). In general, antimony, arsenic, barium, boron, molybdenum, selenium, and strontium are found in the dissolved phase, whereas aluminum, chromium, iron, lead, mercury, vanadium, and zinc are mainly found in the particulate phase. Cadmium, cobalt, copper, manganese, and nickel are commonly found in both phases (Horowitz, 1991).

Elements may transfer from one phase to another through changes in precipitation/dissolution, sorption/desorption, electrostatic attraction, hydrogen ion activity and ionic strength of the solution, concentration of complex-forming ligands, and diagenesis of particulates over time (O'Connor and Kester, 1975; Förstner and Salomons, 1983). The strength of electrostatic attraction depends on particle or ligand composition, concentration, and absorptive properties; solution properties of hydrogen ion activity and oxidation-reduction reactions; and the composition, concentration, and reactivity of the ions in solution.

Streambed sediments in the upper Illinois River are known to be enriched with heavy metals compared to water (Mathis, 1976). For example, Presley and others (1980) found that greater than 87 percent of the total metal load carried in the lower Mississippi River is transported in the sediment load. Some metals that are adsorbed onto particulate matter in the bottom material may be desorbed back into the water column, depending on the chemical composition of the water; bottom sediments also can be resuspended by high streamflow and wave action in shallow backwater areas.

Dissolved species of trace elements are of particular concern because they are more readily incorporated into potable water supplies than particulate species are. Dissolved species have a strong sorption affinity toward three types of materials: organic detritus, clay-mineral particles, and iron-manganese oxide coatings (Elder, 1988). These materials can be transported in suspension, or they can settle and accumulate on the stream bottom.

Elements can be adsorbed onto organic ligands, iron or manganese hydroxides or oxides, and clay minerals through ion exchange, or they can precipitate as solid mineral phases (Förstner and Salomons, 1983). Physical adsorption occurs at external

surfaces, inner surfaces, or pores of particulates or colloids (Förstner and Salomons, 1983). Adsorption generally occurs faster than mineral dissolution and precipitation (Stumm and Morgan, 1981; Drever, 1988). Rates of adsorption may be greatly affected by small fluctuations in hydrogen ion activity (Förstner and Salomons, 1983). If pH is lowered, particle-surface charges and attractive forces are reduced, and surfaces can no longer hold positively charged metals (Michnowsky and others, 1982). Diurnal fluctuations in photosynthetic activity, which in turn affect pH, can cause substantial changes in dissolved element concentrations (Fuller and Davis, 1989). In addition to pH fluctuations, magnesium ions in solution interfere with adsorption of other trace elements by competing with them for the same adsorptive sites (O'Connor and Kester, 1975).

The adsorption capacities of elements are dependent on the reactivity and solubility of each element and particulate characteristics such as substrate source and thermodynamic instability, particle size, surface area, and surface charge. In general, lead has the largest binding capacity of all the trace elements, followed by copper; cadmium has the weakest binding capacity (Alberts and others, 1984). The adsorption affinity of lead can be attributed to its comparatively small hydrated radius and the adsorption preference of hydrolyzed species over divalent metal cations (Holden, 1989). Differences in characteristics of particulate matter and other environmental factors cause some differences in ranking the relative adsorption capacities of elements for iron and manganese oxides, organic ligands, and clay minerals (Collinson and Shimp, 1972; Leed and Belanger, 1981; Förstner and Salomons, 1983; Alberts and others, 1984; Bailey and Rada, 1984; Buhl and McConville, 1984; Johnson, 1986; Horowitz and Elrick, 1987; Holden, 1989).

Precipitation of element compounds can result from changes in conditions of pH, oxidation potential, and concentrations of precipitating compounds and elements (Förstner and Salomons, 1983). Precipitation also depends on the solubilities of the trace elements involved. Precipitation of element compounds can occur when waters from different sources mix, such as when two rivers with different water and sediment chemistry join or when ground water under reducing conditions comes in contact with oxidized surface water.

## Fate and Effects of Major and Trace Elements on Aquatic Biota

The complex interaction of physical, chemical, and biological processes that affect the speciation, and partitioning of elements can have profound effects on the availability of elements to biota, or bioavailability, as well as on their bioaccumulation and toxicity (Batley, 1983). The geochemistry of elements in sediment and in water greatly affects their bioavailability. Most elements in the aquatic environment exist for only a short time in the dissolved phase, the most important phase for uptake of elements by biota. Instead, elements are generally bound to particulates or organic and inorganic compounds and so are less bioavailable (Rand and Petrocelli, 1985; Elder, 1988; Luoma, 1989). Recent research has indicated that cadmium, copper, nickel, lead, and zinc in sediments may not be available to biota if acid volatile sulfide concentrations are sufficient to bind these elements (Ankley and others, 1992). Biota, however, may alter the species of an element, and thereby its bioavailability, through methylation, chelation, complexation, absorption, oxidation, and reduction (Förstner and Salomons, 1983; Smies, 1983). Elements that are known to undergo methylation include arsenic, mercury, selenium, and lead (Demayo and others, 1982; Smies, 1983; Moore and Ramamoorthy, 1984; Eisler, 1987, 1988a, 1988b). Although direct measurement of the amount of an element that is bioavailable is not currently possible, measurement of bioaccumulation of most elements is relatively straightforward (Luoma and Carter, 1991).

Biological uptake may be from elements that are dissolved in water, from suspended sediment to which elements are adsorbed, from elements bound to bottom material, or from consumption of other organisms. Although uptake from the particulate phase is less efficient than from the dissolved phase, the concentration of elements in the particulate phase is larger and, therefore, can be very important (Luoma, 1989). Uptake from the dissolved or particulate phases can occur in a variety of ways. Adsorption, the binding of an element to a surface, can be especially large for bacteria and diatoms because of their large surface-to-volume ratio. Adsorption may be followed by absorption, the movement of an element across cell membranes into the organism (Spacie and Hamelink, 1985). Submerged aquatic plants, such as pondweed, can absorb elements from water and from streambed sediments (Sculthorpe, 1967). Uptake of elements

into plant roots and subsequent transfer to stems and leaves can remobilize bound trace elements buried below the streambed surface, elements that were previously unavailable to other biota (Buhl and McConville, 1984). Invertebrates and fish can take up trace elements by absorption from water, ingestion of food and suspended particulates that contain trace elements, or adsorption of elements onto gill or other body surfaces. This uptake may be followed by diffusion through gills and linings of the gut and mouth of aquatic invertebrates and fish (Luoma, 1983; Rand and Petrocelli, 1985; Clements, 1991). Invertebrates can also be important in remobilizing trace elements back into the water column, where they would then be available for uptake by other organisms (Reynoldson, 1987).

Bioaccumulation of trace elements refers to their incorporation into the tissues of biota. Bioaccumulation can result in toxic effects such as decreased reproduction, mutations, or ultimately death. Important biotic factors affecting bioaccumulation and toxicity include the type and species of organism, as well as its age, sex, health, reproductive cycle, parasitism, acclimation, and a variety of internal biological processes (Phillips, 1980; Sprague, 1985; Cain and Luoma, 1990). After uptake, elements can be transported to another location in the body for storage or to organs that will either metabolize or eliminate the element. Elements may accumulate to different concentrations in various tissues, such as the liver, kidney, gills, and skin or cuticle. The liver is the primary site for metabolism of contaminants, and the kidney and liver are the main organs responsible for elimination of contaminants. Biota are able to regulate internal concentrations of some elements at small to moderate concentrations through uptake and elimination. The rate of elimination of trace elements from biota can be very important in reducing bioaccumulation and toxicity (Guthrie, 1980; Matthews, 1980; Rand and Petrocelli, 1985).

Toxicity to trace metals can range from sublethal effects, such as a decrease in growth, to acute effects, including death. Organometals, mainly alkyl metals such as methylmercury, are more toxic than most other forms of elements because they are lipid soluble, are easily mobilized through the food chain, and tend to bioaccumulate more. Although inorganic mercury in aquatic systems has not been shown to be toxic, microorganisms are capable of transforming it to methyl mercury compounds that are

highly biologically mobile and toxic (Eisler, 1987). Many trace elements are essential nutrients for most organisms at small concentrations but may be toxic at excessive concentrations. Elements of this type include cobalt, copper, chromium, iron, manganese, nickel, molybdenum, selenium, tin, and zinc. Cadmium, mercury, and lead are nonnutritive and can be toxic at very small environmental concentrations (Donaldson, 1980; Batley, 1983; Leland and Kuwabara, 1985; Eisler, 1988b). Arsenic may be nutritionally essential or beneficial in small doses (Eisler, 1988a).

Trace elements in water and bottom material can biomagnify, or increase in concentration, at higher levels of organization in the food chain, even though they may have entered the aquatic system at subtoxic levels. Biomagnification can proceed from primary producers (such as diatoms) to benthic and filter-feeding organisms to fish and, eventually, to humans. Once bound in aquatic plant tissues, accumulated elements can be transferred to other organisms through grazing or released to the aquatic environment through microbial decomposition of plant tissues (Buhl and McConville, 1984). Organisms that feed on the grazers may continue to bioaccumulate concentrations of the elements. Examples of the effects of biomagnification include (1) methylmercury poisoning in humans, in Minamata, Japan, from consumption of contaminated shellfish (Takeuchi, 1972; Förstner and Wittman, 1979); (2) itai-itai disease in humans living in Toyama Prefecture, Japan, from consumption of rice irrigated with cadmium-rich water (Friberg and others, 1974); (3) large concentrations of mercury in fish in Sweden and America, from industrial effluent and atmospheric deposition (Saha and McKinley, 1975); and (4) reproductive problems in aquatic birds at Kesterson National Wildlife Refuge in California, from accumulation of selenium (Ohlendorf, 1986; Presser and Ohlendorf, 1987).

### **Criteria and Guidelines for Element Concentrations in Water, Sediment, and Biota**

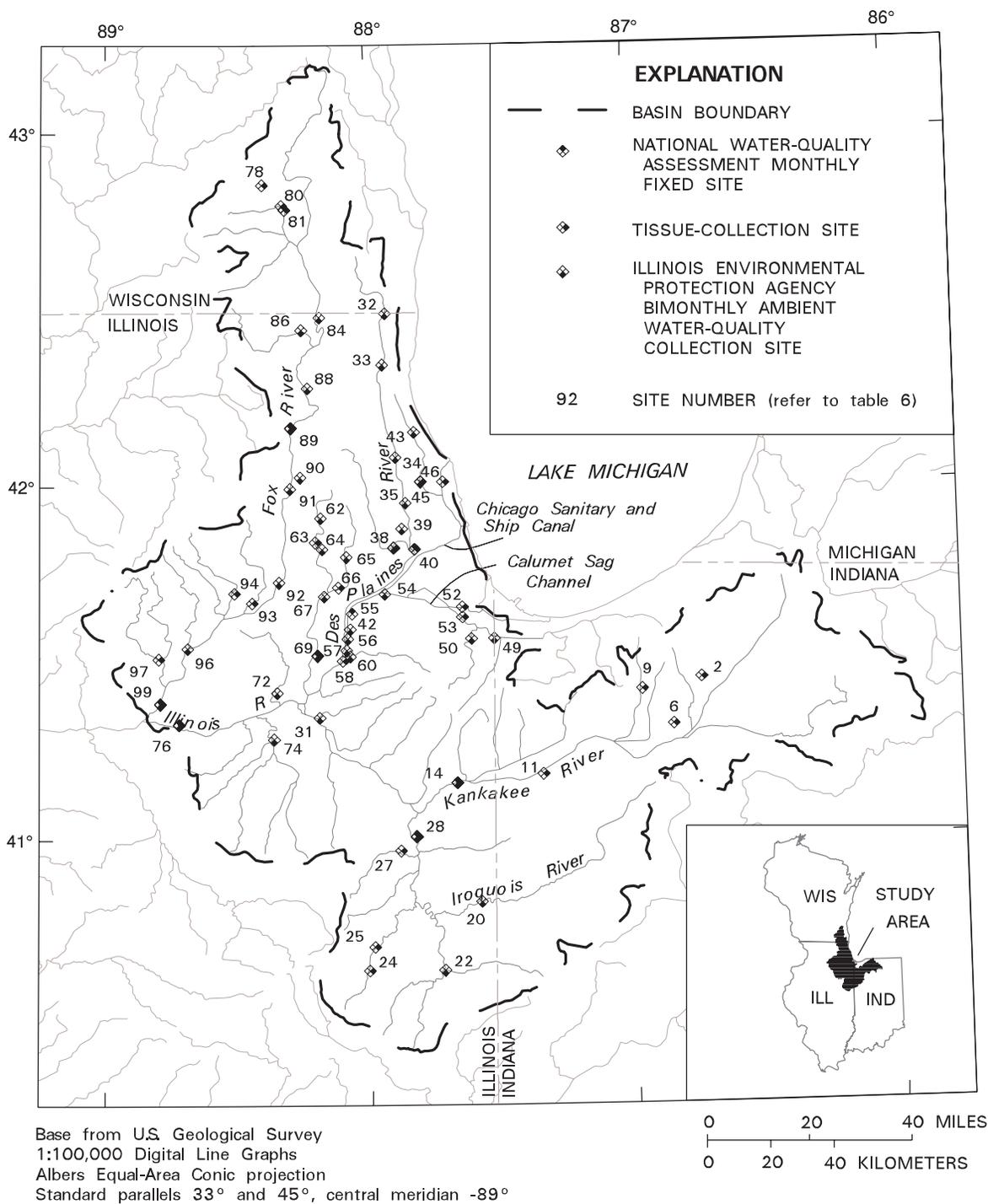
Of the 22 elements examined in this study, 12 are listed as priority pollutants by the U.S. Environmental Protection Agency (USEPA): antimony, arsenic, cadmium, beryllium, chromium, copper, lead, mercury, nickel, selenium, silver, and zinc (U.S. Environmental Protection Agency, 1986). Freshwater acute and chronic water-quality criteria,

fish-consumption advisory levels, and Maximum Contaminant Levels established by USEPA for these elements in drinking water are listed in table 4. Barium, iron, and manganese, although not considered priority pollutants, are addressed in some partial criteria for drinking water, freshwater chronic levels, and fish consumption. Arsenic(V), arsenic(III), chromium(VI), and chromium(III) are addressed by separate freshwater acute and chronic water-quality criteria based on valence. In addition, arsenic and beryllium are known carcinogens. Criteria for six elements in water are dependent on hardness, because increases in hardness reduce the toxicity of these elements (City of Chicago and Illinois Environmental Protection Agency, 1985; U.S. Environmental Protection Agency, 1986). Criteria in table 4 are based on a hardness of 100 mg/L. Hardness of stream water from the upper Illinois River Basin ranges from approximately 100 to 480 mg/L. Standards were established by the USEPA for the maximum acceptable concentrations of trace elements in unfiltered water.

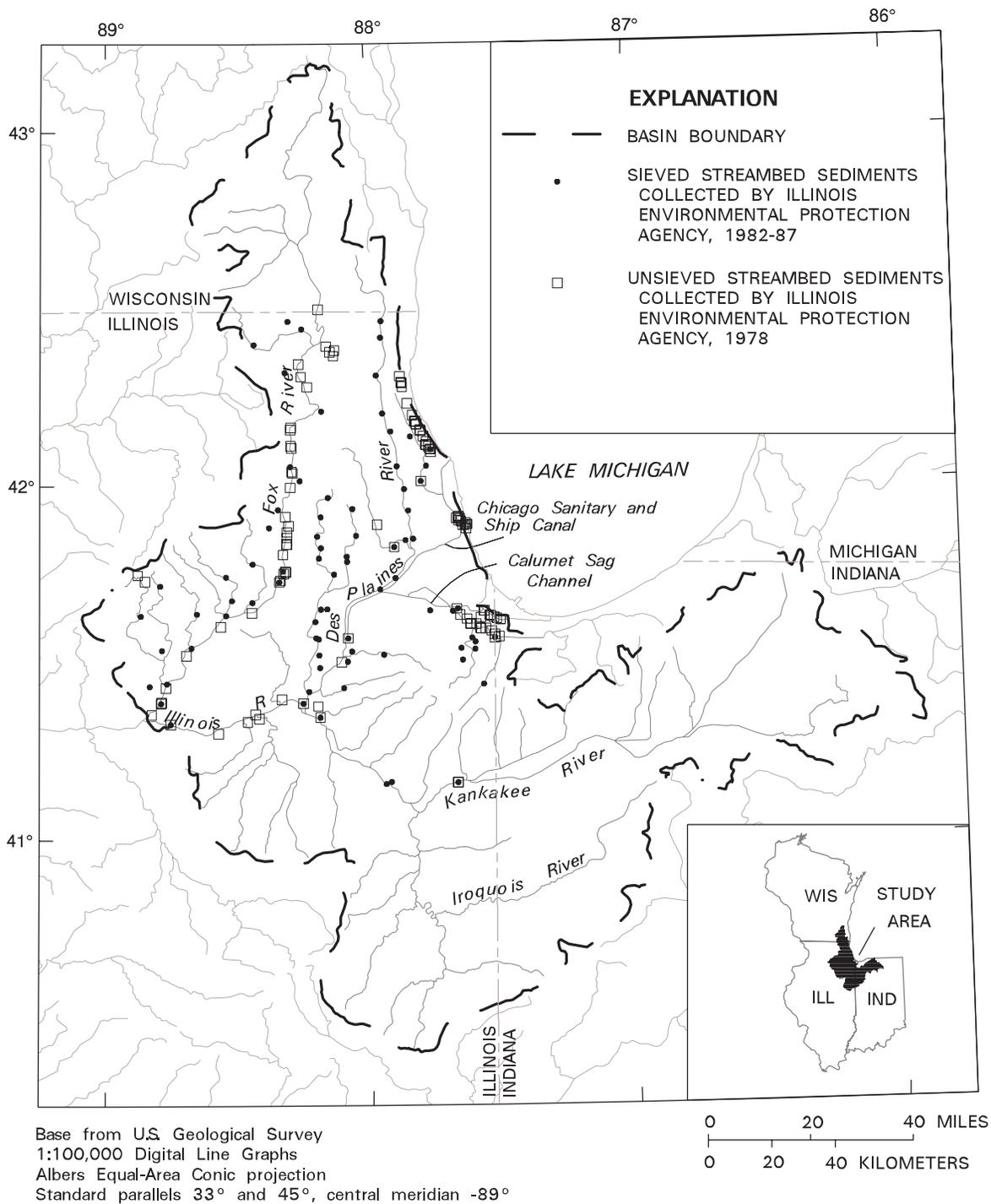
Although no sediment criteria have been accepted by USEPA at this time, two guidelines are frequently used to evaluate concentrations of the priority pollutants in sediments (table 5). The USEPA (1977) established guidelines for the classification of Great Lakes Harbor sediments that are used for evaluating the amount of pollution before dredging and cleanup. In addition, the Ontario Ministry of Environment and Energy established guidelines for the protection and management of aquatic sediments in Ontario (Persaud and others, 1993).

## **DESIGN OF THE ILLINOIS ENVIRONMENTAL PROTECTION AGENCY AND NATIONAL WATER-QUALITY ASSESSMENT PROGRAMS FOR MAJOR AND TRACE ELEMENTS IN WATER, SEDIMENT, AND BIOTA**

Data included in this report are from water, sediment, and biological samples collected by the USGS NAWQA program and the IEPA. Details about the design of the IEPA and NAWQA sampling programs are given in the following sections. Site characteristics are listed in table 6, and site locations are shown in figures 5 and 6.



**Figure 5.** Locations of sites sampled for major and trace elements in water and biota in the upper Illinois River Basin, 1978–90.



**Figure 6.** Locations of sites sampled for major and trace elements in streambed sediments in the upper Illinois River Basin, 1978–90.

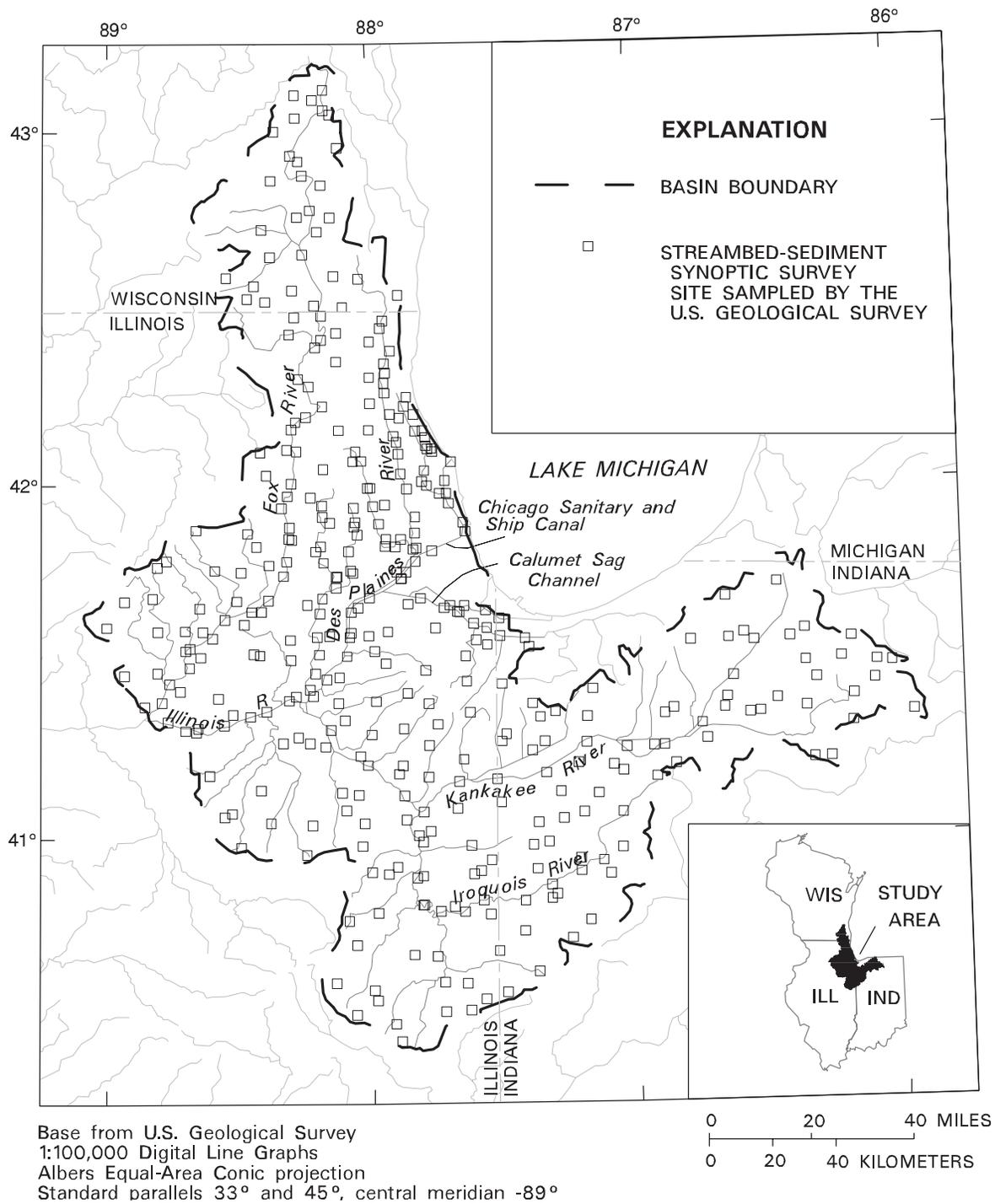


Figure 6. Continued.

## Illinois Environmental Protection Agency

Since approximately 1978, the IEPA has collected water samples for analysis of dissolved and total recoverable concentrations of major and trace elements at 38 sites in the upper Illinois River Basin at 6-week intervals (fig. 5; table 6). These sites are part of the Illinois Ambient Water-Quality Monitoring Network and are on main-stem streams in Illinois (except for one site on the Illinois-Indiana State line). From 1987 through 1990, 6 of the 38 sites were sampled at 4-week intervals by the USGS as part of the NAWQA program. Samples were analyzed for 17 of the 22 elements discussed in this report; analysis for antimony, selenium, and molybdenum, and dissolved arsenic and mercury were not done.

Streambed-sediment data for major and trace elements were collected by the IEPA at 103 sites from approximately 1978 through 1987 (fig. 6). Although many elements in streambed sediments were analyzed for by the IEPA, only 10 elements were measured in nearly every sample: arsenic, cadmium, chromium, copper, iron, lead, manganese, mercury, phosphorus, and zinc. Most of the sediment-data sites are clustered along main-stem streams in the northern part of the Illinois part of the upper Illinois River Basin, including the Fox, Du Page, Des Plaines, North Branch Chicago, Calumet, and Illinois Rivers.

## National Water-Quality Assessment Program

Samples for dissolved and total recoverable concentrations of trace elements in water were collected monthly at the eight NAWQA fixed sites from 1987 through 1990. Suspended-sediment samples were collected bimonthly (table 6; fig. 5). Details about the sampling design and the quality-assurance results are given in Sullivan and Blanchard (1994). The fixed sites are all at established stream-flow-gaging stations and generally are near the mouths of major rivers. Two fixed sites are on the Fox River (sites 89 and 99), and one site each is on the Kankakee River (site 14), the Iroquois River (site 28), the Des Plaines River (site 40), the Chicago Sanitary and Ship Canal (site 55), the Du Page River (site 69), and the Illinois River (site 76). The sites were chosen to maximize the information obtained from calculating mass balances within the upper Illinois River Basin and to document the transport of constituents (Sullivan and Blanchard, 1994). Six of the eight fixed sites

(sites 14, 28, 69, 76, 89, and 99) were established IEPA sampling sites that the USGS sampled for the IEPA during 1987 through 1990.

Data from the total recoverable phase in water were available for all 22 trace elements. Samples for analysis of dissolved antimony and molybdenum were collected seasonally (four times a year) instead of monthly. Dissolved and total recoverable mercury data were few because of problems with sample contamination during processing. Only a few observations were available for selenium concentrations. Suspended-sediment samples were analyzed for 17 of the 22 elements examined in this report; barium, boron, mercury, selenium, and strontium were excluded.

Streambed-sediment samples were collected by the USGS during the fall of 1987 at 372 sites (fig. 6). Details about the sampling design are described in Colman and Sanzalone (1991). Of the 372 streambed-sediment sampling sites, 238 were on low-order (first- and second-order) streams that were randomly selected from a grid (with grid-element sides of 6.2 mi) placed over a basin map. The remaining 134 streambed-sediment sampling sites were on high-order (fourth-order or higher) streams. Data were available for all 22 elements discussed in this report. In addition, the samples also were analyzed for 35 other elements including total carbon, inorganic carbon, major cations, and rare earth elements (Colman and Sanzalone, 1991). In 1990, streambed-sediment samples were collected simultaneously with biota at the 25 tissue-sampling sites; however, lack of fine-grained sediments precluded element analysis at Mukwonago River (site 78) and Honey Creek (sites 80 and 81).

Samples of biological tissue were collected by the USGS at low streamflows at 15 and 25 sites during the summers of 1989 and 1990, respectively (fig. 5). Sampling locations for tissues were chosen on the basis of ecoregion (Omernik and Gallant, 1988), land use, historical data, and accessibility; sites included low- and high-order streams. To the extent possible, sites were coincident with fixed sites and streambed synoptic sites. Low-order stream sites included paired sites and other urban sites of interest. The paired sites were similar in size and drainage area to each other and were composed of one or more reference sites (sites selected to represent drainage basins that were either minimally affected or stable with regard to human activities) and one or more other

sites selected to represent agricultural or urban land uses. At least one set of paired sites was sampled in each of the three ecoregions: Central Corn Belt Plains, Southeastern Wisconsin Till Plains, and Southern Michigan/Northern Indiana Till Plains. Reference sites sampled in the Central Corn Belt Plains, the largest ecoregion were Big Rock Creek (site 94), Indian Creek (site 97), Langan Creek (site 27), and Spring Creek (site 24); the Mukwonago River (site 78) and Mill Creek (site 2) were selected as reference sites in the Southeastern Wisconsin Till Plains and the Southern Michigan/Northern Indiana Till Plains, respectively.

Organisms collected for tissue analysis were selected from the list of national target organisms for the NAWQA program (Crawford and Luoma, 1993). When organisms from the national target list could not be collected at a site, other organisms were substituted. The resulting mixture of tissue-sample types consisted of mollusks, fish livers, aquatic insects, aquatic plants, and crayfish. Of the 59 total samples analyzed in 1989 and 1990, 33 (56 percent) were fish livers. Of the 33 samples of fish livers collected, 23 were from the common carp (*Cyprinus carpio*).

## METHODS

### Field and Laboratory Methods

Field and laboratory methods are briefly described below. Details about field and laboratory techniques can be found in the references listed in the following sections.

#### Water

Water samples were collected by the IEPA by use of equal width increments and equal transit rate (Illinois Environmental Protection Agency, 1987c). Water samples collected by the IEPA were analyzed at the IEPA Laboratories in Chicago and Champaign, Ill., for dissolved and total recoverable<sup>1</sup> concentrations for 17 of the 22 elements. Samples analyzed for dissolved constituents had been passed through a 0.45- $\mu\text{m}$ -pore-size filter. Samples were preserved with nitric acid and digested with hydrochloric acid (Illinois Environmental Protection Agency, 1987d) (table B1), except those analyzed for mercury. Laboratory methods include inductively coupled

plasma-atomic emission spectrometry, gas flame atomic absorption spectroscopy, direct atomic absorption, or atomic absorption spectroscopy (table B1). Minimum reporting levels are listed in Table B1.

Water samples were also collected as part of the NAWQA program, again by use of equal width increments and equal transit rate (Sullivan and Blanchard, 1994). Samples were analyzed by the IEPA laboratories listed above except that concentrations of dissolved antimony and molybdenum were determined by the USGS National Water-Quality Laboratory in Colorado (NWQL).

The NWQL periodically analyzed water samples to document discrepancies between the IEPA Laboratory and NWQL because of differences in analytical methods. Reported concentrations for both dissolved and total recoverable phases differ between the two laboratories from 0 to about 200 percent, neither laboratory reporting consistently larger or smaller values than the other (Troy Stinson, U.S. Geological Survey, oral commun., 1991). Thus, for consistency, only the results from IEPA laboratories are used in this report for the dissolved and total recoverable phases. Some samples were analyzed by the NWQL for quality assurance according to methods described by Fishman and Friedman (1989) and Matraw and others (1989).

It must be mentioned here that a potential problem is, however, inherent in the interpretation of dissolved concentrations of certain trace elements. Recent studies indicate that the standard accepted protocol used by many agencies for collecting and analyzing trace element data, especially the dissolved component, results in higher potential for sample contamination than newer, ultraclean techniques do (Windom and others, 1991). Thus, in this report, results from the analyses of these dissolved

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<sup>1</sup>Total recoverable concentration of an element in water is an operational definition and is dependent on the extraction method used to isolate the element (Horowitz, 1991). Comparison of total and dissolved element concentrations from different studies is difficult because of the different methods used for filtering, extraction, or identification. The dissolved phase of water is defined operationally as any substance that passes through a 0.45- $\mu\text{m}$ -pore-size filter (Hem, 1985). This phase includes small particulates such as metal hydroxides, aluminosilicates, and organic matter; colloids; and ions in solution. The operational definition was not a problem in this study because filtering methods were similar in the IEPA and NAWQA programs and only data from the IEPA laboratories were used in this report.

constituents are included, but discussion of the implications of the results is kept to a minimum because of the known potential problems with the data. Therefore, caution was used in the interpretation of the following dissolved constituents: arsenic, beryllium, cadmium, chromium, copper, lead, mercury, and zinc (D.A. Rickert, U.S. Geological Survey, written commun., 1991; Windom and others, 1991). The USGS also has reported that dissolved boron concentrations may reflect significant sample contamination (D.A. Rickert, U.S. Geological Survey, written commun., 1991).

### **Suspended and Streambed Sediment**

Suspended-sediment samples were collected and analyzed by use of standard USGS equipment and procedures (Sullivan and Blanchard, 1994). Concentrations of suspended sediment and the percentage of suspended sediment in the fine fraction were determined by the USGS sediment laboratory in Iowa City, Iowa, by use of techniques described by Guy (1977). Sediment surface areas were determined by the USGS, Doraville, Ga., by use of the single point BET (Brunauer, Emmett, Teller) method with a mixture of 30 percent helium per 70 percent nitrogen gas (Horowitz and Elrick, 1987); reporting units are in square meters per gram. Nondestructive surface-area-measurement techniques were used instead of grain-size analysis because of the small sample size of suspended sediment. Surface area is inversely related to grain size (Horowitz, 1991). Concentrations of trace elements in suspended sediment were determined by the USGS Geologic Division, Branch of Geochemistry, Menlo Park, Calif., according to methods described by Fishman and Friedman (1989) and are listed in table B1. Total digestions were used. Minimum reporting levels are given in table B1.

Samples of streambed sediments collected by the IEPA were composite samples from the upper one-half inch of deposits, which consisted of formerly suspended materials (Illinois Environmental Protection Agency, 1987c). During the period of interest to this report, sieving practices changed. Approximately one-half of the samples are from unsieved samples of streambed sediments that were collected during 1978–82. The remainder are from samples collected during 1982–87 and sieved wet (less than 63  $\mu\text{m}$ ). Background information on the sample collection

and analysis is sketchy; however, partial digestions are known to have been used in the chemical analysis. Sampling was repeated at some sites; only the data from the most recent sampling are used in this report.

Streambed-sediment samples collected as part of the NAWQA program were composited from three to several subsamples from the oxic surface sediments (top 1 in.) at each site. High-order streams were sampled at 5-mi intervals in urban areas and at 10-mi intervals in agricultural areas. Methods of sampling and analysis were similar at sites on high- and low-order streams, except that sediments from high-order streams were sieved wet and sediments from low-order streams were sieved dry (Colman and Sanzolone, 1991).

A description of the methods used by the USGS to analyze for trace elements in streambed sediments and a listing of minimum reporting levels are given in table B1. Total digestions were used in the chemical analysis except for boron (Colman and Sanzolone, 1992). All reported concentrations are from the less-than-63- $\mu\text{m}$  fraction (silt- and clay-size particles). No data are available for the proportion of the whole sample that was less than 63  $\mu\text{m}$  in diameter.

Analysis of the variance between sieving methods used by the USGS at 22 sites indicated significant variations in median concentrations because of the sieving methods for most of the 48 elements surveyed (Colman and Sanzolone, 1992). For most elements, including the priority pollutants, concentrations from wet-sieved sediments were larger than from dry-sieved sediments. Only mercury concentrations were larger in dry-sieved sediments than in wet-sieved sediments (Colman and Sanzolone, 1992).

### **Biota**

Tissue samples for the analysis of trace elements were collected from 15 sites in 1989 and from 25 sites in 1990 according to field methods described in Crawford and Luoma (1993). Additional water samples were collected near the time of biological sampling at sites that were not part of the fixed-site sampling.

Mollusks were collected from four sites in 1989 and six sites in 1990 by hand gathering or by use of a clam rake. Each sample from a site was a composite of at least three individuals and, at all but two sites, was composed of individuals of a single species. Individuals were rinsed with deionized water and scrubbed with a soft nylon-bristle brush to remove

attached particles. Mollusks were then held in polyethylene aquariums containing deionized water at 10°C for a 48-hour depuration period to allow sediment and other material to pass through the gut. Water in the aquariums was replaced every 24 hours. After the depuration period, shell length was measured as greatest anterior-posterior dimension. The soft tissue was removed from the shell by use of stainless-steel scalpels that had been cleaned with nitric acid. Composite samples of soft tissues were placed in clean glass jars and frozen on dry ice for later analysis. Snails (*Physella integra*) and fingernail clams (*Musculium* sp.) were collected at only one site each and, unlike other mollusks sampled, were analyzed with the shells included. Concentrations in these two samples, therefore, represent elements adsorbed to the shell as well as bioaccumulated elements incorporated into soft tissues. Elemental concentrations in these two samples should be interpreted with caution and should not be compared to concentrations in other mollusks from the basin.

Fish samples for tissue analyses were collected by electrofishing. Backpack electrofishing units were used in wadable streams and boat-mounted units were used for nonwadable streams. In accordance with the sampling strategy for NAWQA (Crawford and Luoma, 1993), fish livers were extracted and composited for the analysis of trace elements. Each sample from a site consisted of a composite of 3 to 10 fish livers from a single species. Fish during the sampling were sacrificed by a sharp blow to the base of the skull. Fish were then blotted with a lint-free cloth to remove excess moisture, were weighed, and were measured for total length. The liver of each fish was removed by use of a stainless-steel scalpel, was placed in a clean glass jar with a Teflon-lined cap, and was frozen on dry ice for later analysis.

Only one sample of aquatic insects was collected; this was a sample of caddisflies (*Hydropsyche* sp.) from Salt Creek in 1989. Caddisflies were collected by use of kick nets and by handpicking of organic debris. The sample consisted of a composite of approximately 260 individual larval caddisflies.

Once collected, the sample was rinsed three times with deionized water in an effort to remove attached particles. The composite sample of whole individuals was then placed in a clean glass jar and frozen on dry ice.

Crayfish were sampled during 1989 but not during 1990. Collection methods included use of

1/8-in.-mesh seines. Composite samples of crayfish consisted of 4 to 30 whole individuals. Collections were made without regard to species. Subsequent identifications showed that the samples included three species of the genus *Orconectes*: *O. virilis*, *O. rusticus*, and *O. propinquus*. Each sample was rinsed three times with deionized water to remove attached particles. Composite samples of whole individuals were then placed in clean glass jars and frozen on dry ice. No depuration period was allowed for crayfish.

Rooted aquatic plants were collected by hand picking of leaves and stems from the apical 2 in. of submersed plants by use of unpowdered vinyl gloves. Enough plant material was collected to provide at least 25 g (wet weight) of material from a single species for each composite sample. The apical tissue was rinsed three times in deionized water, placed in a clean glass jar, and frozen on dry ice.

Laboratory methods for biota included homogenization followed by analysis of freeze-dried material. A nitric-perchloric acid decomposition method was used for all elements except mercury, for which nitric acid alone was used. Hydride generation atomic absorption spectrophotometry (AAS) was used for analysis of arsenic and selenium, and cold-vapor AAS was used for analysis of mercury. All other elements in biota were analyzed by means of inductively-coupled plasma emission spectroscopy (ICPES). Unless otherwise stated, element concentrations in biota are reported as micrograms per gram dry weight (DW). All laboratory analyses were done by the Environmental Trace Substances Laboratory, University of Missouri, Columbia, Mo. Quality-assurance methods for biota included blanks, duplicates, spikes, and reference standards (oyster tissue, bovine liver, and citrus leaves from the National Institute of Standards and Technology). Minimum reporting levels for elements in tissues of biota are listed in table B1.

## Statistical Methods

Numerous statistical techniques were used to analyze the data base that was compiled. This section provides a brief overview of these statistical procedures. Where possible, a reference is provided for a work that gives a more complete description of the statistical method and its application.

Water-quality data are typically highly skewed and not normally distributed. When a parametric statistical method is applied to this type of data, the

power of the method decreases, and the results may be in error (Helsel, 1987). Nonparametric statistics are more powerful tools for the analysis of highly skewed data and allow for successful analysis when normality cannot be assumed for all groups to be compared. Helsel (1987) examines these and other advantages of nonparametric statistics for the analysis of water-quality data. In light of the utility of nonparametric statistics for the analysis of water-quality data, nonparametric statistics were used primarily for the descriptive analyses of the data in this study.

Many sets of concentration data for dissolved or total recoverable elements in water are referred to as “censored” because some observations in the set are lower than limits deemed reliable enough to report as numerical values. These so-called less-than values are typically reported as “< *rl*,” where *rl* is the minimum reporting level. The presence of less-than values in data sets with multiple reporting levels is a problem with many of the trace elements, especially the environmentally important priority pollutants arsenic, beryllium, cadmium, chromium, copper, lead, mercury, and zinc. Reporting levels for these constituents varied over time because different laboratories did the analyses, laboratory equipment improved, or analytical techniques changed. The number of less-than values limits the usefulness of these data for statistical analysis and also for determining spatial distributions of trace elements across the basin. Because dissolved concentrations are usually smaller than total recoverable concentrations, fewer uncensored data are available for statistical analysis of the dissolved component. Unfortunately, the dissolved component is the most important phase for determining the bioavailability and toxicity of these elements to aquatic life. Statistical analyses of censored data required substitution of a numerical value for each less-than value. In general, zero was substituted for the less-than values; thus, all the less-than values were tied for the lowest rank in the rank-transformed data set. Where different substitutions were used for a statistical test, they are discussed with the description of that test.

The first level of analysis was a general description of the temporal and spatial distributions of concentrations for each target element. Percentiles were used to classify different parts of the distribution for some components. The percentiles that are used to group data in this report are the 10th, 25th, 50th, 75th, and 90th. The 50th percentile is the median,

or middle observation of the data when concentrations are ordered from smallest to largest. The 10th percentile is the concentration at which 10 percent of the measured concentrations are less than that value. Additional information on use of percentiles is presented by Iman and Conover (1983) and Kleiner and Graedel (1980). Statistics were computed for individual sites where at least 10 observations had been compiled for a given constituent. The 10th and 90th percentiles were not computed for sites where less than 30 observations had been compiled for a given constituent during water years 1978–86. Percentiles for censored data with multiple reporting levels were reported as less than the maximum reporting level for all percentiles smaller than this concentration and reported as numerical values for concentrations greater than this level.

Tukey schematic plots were used to show the distribution of all the data values in figures A1–A3. A Tukey schematic plot is a modified box plot. Tukey schematic plots are further described by Tukey (1977).

Tukey plots for data sets with multiple reporting levels were modified to display quartiles estimated by fitting the data to a log-normal distribution by use of a procedure described by Helsel (1990). A carat symbol on the box plot represents the maximum reporting level. Any part of the box below the maximum reporting level was drawn using estimated values based on Helsel (1990) procedures. If the maximum reporting level was greater than the upper adjacent value, no upper whisker was drawn. If the maximum reporting level was greater than the 25th percentile, no lower whisker was drawn. If the maximum reporting level was less than the lower adjacent value, the lower whisker was not extended below the maximum reporting level. Outside and detached values that were less than the maximum reporting level cannot be estimated and were not plotted.

Water-quality criteria provided a reference to describe concentrations that are considered to be elevated. These comparisons are not intended to identify violations of water-quality standards; the criteria used, which in some cases are provisional, nonenforceable guidelines, are not necessarily those adopted by Illinois, Indiana, and Wisconsin, nor are they always directly applicable to the conditions sampled. The descriptive part of the data analysis also included identifying the number of observations that exceeded water-quality criteria for a given

constituent. In this report, the Federal water-quality criteria administered by the USEPA (U.S. Environmental Protection Agency, 1986) and 85- and 95-percent Elevated Data Levels (EDL 85 and 95) from California's Toxic Substances Monitoring Program (TSMP) (Rasmussen, 1992) were used as the criteria for comparison unless otherwise noted. The reason these criteria were used is that the State criteria differ throughout the study area and have also been revised and updated over time. The use of the Federal criteria and TSMP EDL's provided a uniform set of criteria for comparison in the study area.

Concentrations of elements in sediment were log-transformed or standardized before graphical or statistical analyses. Statistical analyses of streambed-sediment data collected from 1978 through 1986 were done on the base 10 logarithm of the concentrations (log-transformed data) rather than the untransformed data. Taking the logarithm transformed the skewed distribution of values to a normal distribution, which then could be analyzed by use of common parametric statistical tests. Details on log transformation of data are given in Iman and Conover (1983).

The second level of analyses was examination of differences and similarities among groups of data. These included differences among sites or river basins, differences between periods, and correlations among elements. For all statistical tests in this report, a significance probability (p-level) was computed. This p-level indicates the probability of erroneously reporting a trend when data values are random, independent, and identically distributed. Results were considered significant when p-levels were less than 0.10.

The Wilcoxon signed-ranks procedure was used to test for differences between dissolved and total recoverable concentration of some constituents. The Wilcoxon test is a nonparametric test that is similar to a t-test, except that the test is done on the signed ranks of the differences between paired data points. A detailed description of the Wilcoxon test is given by Iman and Conover (1983).

The Kruskal-Wallis test is a nonparametric analysis of variance (ANOVA) on rank-transformed data. This test indicates whether the variance among samples in a group (such as at a site, in a river basin, or by use of a certain method) is large enough to mask differences among the medians of the groups. Details about the Kruskal-Wallis test are given in Iman and Conover (1983). The Kruskal-Wallis test indicates

whether at least one group is distinguishable from the others. The Tukey studentized range test (Neter and others, 1985) was used to identify which groups from the Kruskal-Wallis test were similar to each other.

Plots of the percentage of samples with concentrations greater than a given value (probability plots) were used to describe differences among samples collected at different times and to delineate background from elevated concentrations. Rickert and others (1977) proposed that probability plots of background concentrations in the Willamette River in Oregon, would follow a curve with few breaks. Breaks in curves of probability plots represent the delineation between background and elevated concentrations.

Correlation coefficients were used to identify elements that behaved similarly among sites, among the different components sampled, or over time. Linear correlation coefficients, signified by  $r$  (Iman and Conover, 1983), were used to quantify the strength of the linear relations among log-transformed element concentrations in streambed sediment. Rank correlation coefficients, signified by Spearman's rho ( $\rho$ ) (Johnson and Wichern, 1982; Iman and Conover, 1983), were used to identify and group trace elements that significantly correlated with each other in water, sediment, and biota. Spearman's rho quantifies the strength of the monotonic relations among elements without requiring the relation to be linear. Spearman's rho also enables comparisons from censored data because ranks, rather than actual values, are used. For data sets containing multiple reporting levels, correlations were calculated twice—first with less-than values set to zero and second with less-than values set to the reporting level—thus, some correlation coefficients may be represented by two values. If the coefficients from either of the calculations was not significant ( $p < 0.1$ ), neither coefficient was included in the tables or discussion. This procedure was especially important in correlating element concentrations in water because many of the elements were reported at multiple levels and correlation coefficients sometimes varied widely among the substituted values. Only correlations with p-levels less than 0.10 and coefficients ( $\rho$ ) greater than 0.5 were considered significant and are discussed. In addition, correlations among data sets in which greater than half of the observations that were below the reporting level were excluded. Correlations among sites were not

included in the tables and discussion if the data sets of interest were censored at more than 15 sites.

Factor analysis was used to summarize subsets of the water- and streambed-sediment-quality data by identifying groups of constituents that are highly correlated. Factor analysis is a technique that summarizes the variance-covariance or correlation structure of a data set by identifying major axes of variation within the data matrix (Davis, 1986). These axes, called principal components, are linear combinations of the original variables (Johnson and Wichern, 1982, p. 362). The first principal component expresses as much of the total system variability as can be explained by a single axis. Successive principal components each express part of the remaining variability and are uncorrelated to previously derived principal components. The degree of association between a variable and a principal component is expressed by a measure called the loading. Loadings reflect, "... the relative importance of a variable within a principal component, ..." (Davis, 1986, p. 537). If a group of variables all load heavily on a particular principal component, then the variables all behave similarly. For example, if a group of elements all load heavily on a particular component, then all of those elements are likely to be associated with a common source, such as a particular soil type. Detailed discussions of factor analysis are found in Johnson and Wichern (1982), Pielou (1984), and Davis (1986).

The third level of analysis was examination of the transport of dissolved and suspended material past water-quality-monitoring sites. The instantaneous amount of material transported past a site, the load, can be calculated by multiplying the constituent concentration by the discharge. A regression model can be developed between the instantaneous load and functions of discharge and time. This regression model was used to estimate daily loads from the daily discharge record. The best-fit regression model is in the form

$$\ln(CQk) = I + a(t) + b(\sin(2\pi t)) + c(\cos(2\pi t)) + d(\ln(Q)),$$

where

- $C$  is concentration, in milligrams per liter;
- $Q$  is discharge, in cubic feet per second;
- $k$  is units conversion factor, 0.002714;

$\ln$  is natural logarithm;

$\ln(CQk)$  is natural logarithm of the load, in tons per day;

$t$  is time, in decimal years, using January 1, 1978, as time = 0;

$\pi$  is 3.1416, a constant used here to convert decimal time to radians;

$\sin(2\pi t) + \cos(2\pi t)$  is a factor to account for seasonal variability;

$I$  is the y-axis intercept; and

$a, b, c, d$  are regression equation coefficients.

The best combination of independent variables, based on Mallows C statistic (Mallows, 1964), was chosen as the best load-estimation model. The best model was applied to the daily discharges for water years 1987 through 1990. The model results in the calculated log of the load; the log of the load was detransformed and multiplied by the Duan smearing estimate (Duan, 1983), a bias-correction factor. The daily loads were summed and averaged to produce a mean annual load for water years 1987 through 1990. For data sets containing multiple reporting levels, loads were calculated twice—first with less-than values set to zero and second with less-than values set to the reporting level—thus, some loads may be represented by two values.

The fourth level of analysis was an examination of seasonality, trends, and long-term changes in concentration over time. The seasonal Kendall test for trend and the seasonal Kendall slope estimator as described by Hirsch and others (1982) and Hirsch and Slack (1984) were used. With this test, the effect of seasonal variation is accounted for by comparing observations from the same season of the year. Twelve seasons per year were used for this investigation. Trend analyses were not done for sites where data sets consisted of less than 30 data values, less than 3 years of data, or a majority of less-than values. For data sets containing multiple reporting levels, trends were calculated twice—first with less-than values set to zero and second with less-than values set to the reporting level—thus, some trends may be represented by two values. The trend results were included in the tables and discussion only if the results of the two sets of calculations both indicated significant trends in the same direction.

Kendall's tau is an equivalent measure to the rank correlation coefficient (Spearman's rho).

Tau measures the strength of the monotonic relation between two values and the general increase or decrease in the data regardless of whether the increase or decrease is linear. The seasonal Kendall slope estimate estimates the yearly change in the concentration of the constituent. It is calculated by dividing the differences between data values in the same season by the time between the values and then taking the median of all these values.

These procedures determined the presence of a trend and its magnitude. The application of these procedures to water-quality data on a national level is described by Smith and others (1987).

## MAJOR AND TRACE ELEMENTS IN WATER, SEDIMENT, AND BIOTA

Element concentrations in water, sediment, and biota were compared among sites in the upper Illinois River Basin for a period before the NAWQA program (water and sediment only, from 1978 through 1986) and a period during the pilot NAWQA program (from 1987 through 1990). Dissolved and total recoverable concentrations in water and suspended sediment were analyzed for seasonal variations. Analysis for trends in dissolved and total recoverable concentrations in water were done for the period 1978 through 1990. Correlations of element concentrations with concentrations of other elements were examined within water, sediment, and biotic components. Finally, correlations among elements in water, sediment, and biota also were examined. Site numbers in parentheses after site names are referenced in table 6 and figure 5.

### Water

This description of trace elements in water is based on dissolved and total recoverable element concentrations in water samples collected from 1978 through 1986 at the 38 sites in the IEPA Ambient Water-Quality Monitoring Network and collected from 1987 through 1990 at a combination of IEPA and NAWQA fixed sites (fig. 5).

#### Results of Water-Data Collection, 1978–86

By Charles G. Crawford and Daniel J. Sullivan

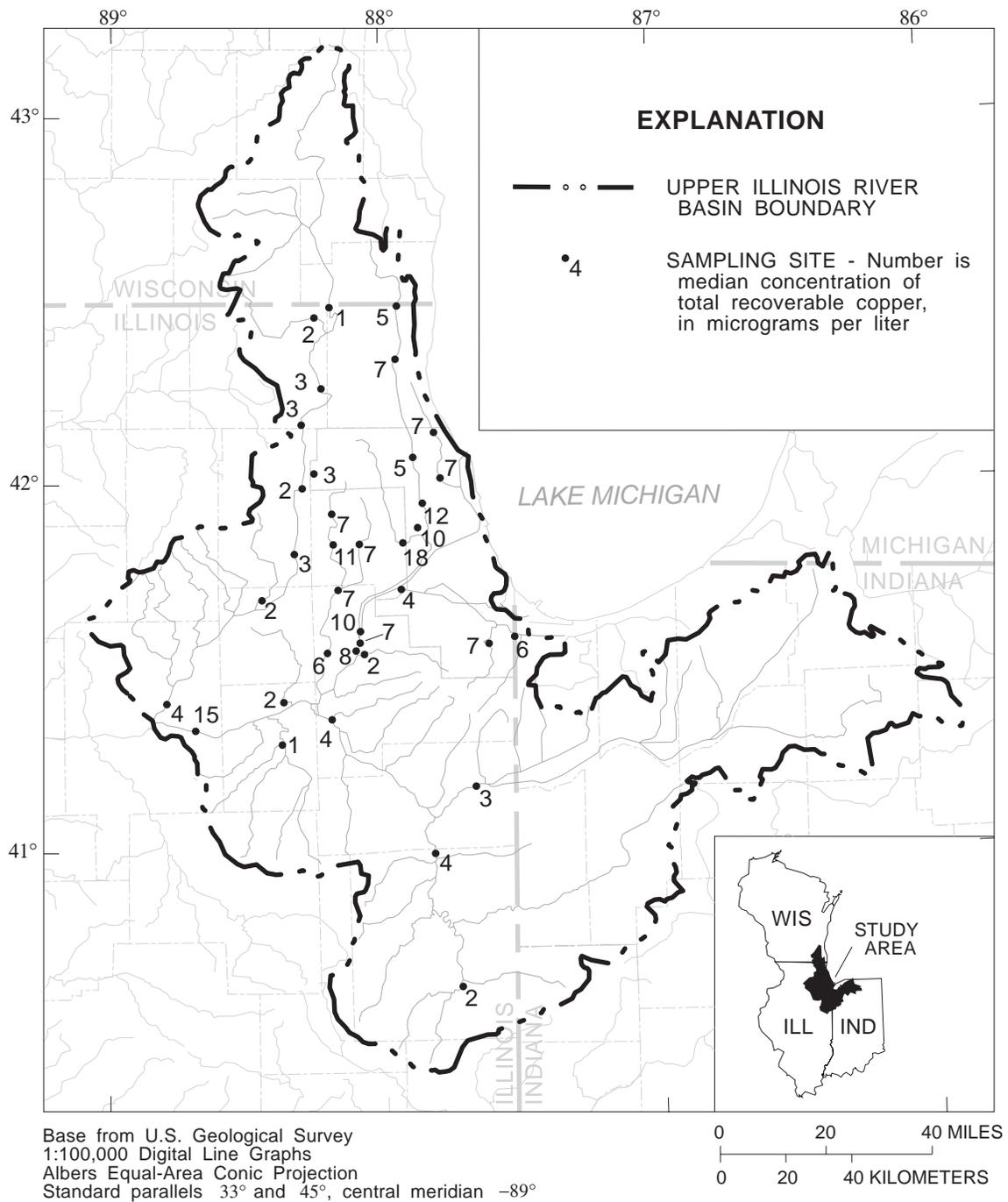
Historical data for dissolved and total recoverable element concentrations in water were limited to

the 38 sites sampled by IEPA as part of the Ambient Water-Quality Monitoring Network (fig. 5). Data were available for most of the 22 elements except antimony, molybdenum, and selenium. No data were available for dissolved arsenic and mercury. The number of observations and the period of record for each element is variable among elements; however, data were generally collected at most sites from 1978 through 1986 every 6 weeks.

Median concentrations of several of the major and trace elements were below the minimum reporting level. These elements were beryllium, cadmium, cobalt, lead, silver, and vanadium. In several individual samples, however, concentrations of cadmium, lead, and silver exceeded USEPA water-quality criteria.

Sites where total recoverable element concentrations exceeded USEPA freshwater chronic or acute criteria one or more times are listed in table 7. Sites where concentrations of several priority pollutants frequently exceeded USEPA water-quality criteria include the Des Plaines River near Gurnee (site 33), North Branch Chicago River at Niles (site 45), Addison Creek at Bellwood (site 39), Chicago Sanitary and Ship Canal at Lockport (site 56), West Branch Du Page River near Warrenville (site 64), and Illinois River at Marseilles (site 76). All of these sites except the Des Plaines River near Gurnee and the Illinois River at Marseilles are in highly populated areas that presently receive or historically received inputs from industrial and municipal sources. The Des Plaines River near Gurnee predominantly drains agricultural land. The Illinois River at Marseilles receives input from all sources in the basin except those in the Fox River. Concentrations of chromium, copper, lead, mercury, and zinc that exceeded USEPA freshwater chronic criteria were observed most frequently in the Des Plaines River Basin, an indication of the effects of urbanization in this basin. Concentrations of iron that exceeded USEPA freshwater chronic criteria for iron were evenly distributed across the upper Illinois River Basin.

Dissolved and total recoverable concentrations of most of the priority pollutants were largest in urban land-use areas. The spatial distribution of the median concentration of total recoverable copper (fig. 7) illustrates this pattern of urban effect. Median concentrations of total recoverable copper are largest at sites in the highly populated areas of the Des Plaines and Du Page River Basins and at sites downstream



**Figure 7.** Median concentrations of total recoverable copper in the upper Illinois River Basin, 1978–86.

from these areas. The sites where total recoverable copper concentrations are largest include Salt Creek at Western Springs (site 38), Des Plaines River at Lockport (site 42), and downstream at Illinois River at Marseilles (site 76). By contrast, median concentrations were 4.5 to 18 times smaller in the Fox, Kankakee, and Iroquois River Basins. The sites where total recoverable copper concentrations are largest and sites near them had the largest median concentrations of many of the elements, including dissolved and total recoverable boron, chromium, nickel, and strontium; total recoverable arsenic; and total recoverable zinc. Other urban sites with consistently larger median concentrations of many elements include the Des Plaines River near Schiller Park (site 35), Addison Creek at Bellwood (site 39), and the Calumet Sag Channel at Sag Bridge (site 54). The source of the elevated levels of these elements in the urban areas is likely a combination of industrial and municipal effluent, as well as runoff.

In contrast, median concentrations of some elements were larger in samples from the Fox, Kankakee, and Iroquois River Basins than in samples from the urbanized sites in the Des Plaines and Du Page River Basins. Median total recoverable concentrations of the soil-associated elements aluminum, iron, and manganese were largest in the Kankakee and Iroquois River Basins, where agriculture is the dominant land use. Large median concentrations of total recoverable aluminum (fig. 8), iron, and manganese in these agricultural basins are generally associated with agricultural practices, which cause increased erosion and increased solid-phase concentrations of soil-related elements. Dissolved concentrations of these elements, however, did not form the same patterns as the total recoverable concentrations. Median dissolved iron and manganese concentrations were larger in urban areas, whereas median dissolved aluminum concentrations were similar at sites across the basin. This overall pattern indicates that the cause of the larger concentrations in the soil-related elements in agricultural areas was the particulate, or solid-phase fraction. Overall, total concentrations of the soil-related elements were more evenly distributed across the entire upper Illinois River Basin than other elements.

Variability in concentrations over the sampling period from any one site is generally greatest in urban areas. Solute concentrations in nonurban areas are not as likely to show the variability observed in urban

streams. Nonurban areas are not as strongly affected by the spontaneity of storms and fluctuations in contributions of elements from point sources that may exist in urban drainages.

An analysis of the loads and yields further indicated the effect of urbanization and industrialization on the concentrations of major metals and trace elements in the upper Illinois River Basin. For most of the elements identified urban related, yields were considerably larger from urban areas than from agricultural areas. As an example, yields of total boron were 2 to 13 times greater from urban areas than from agricultural areas (fig. 9).

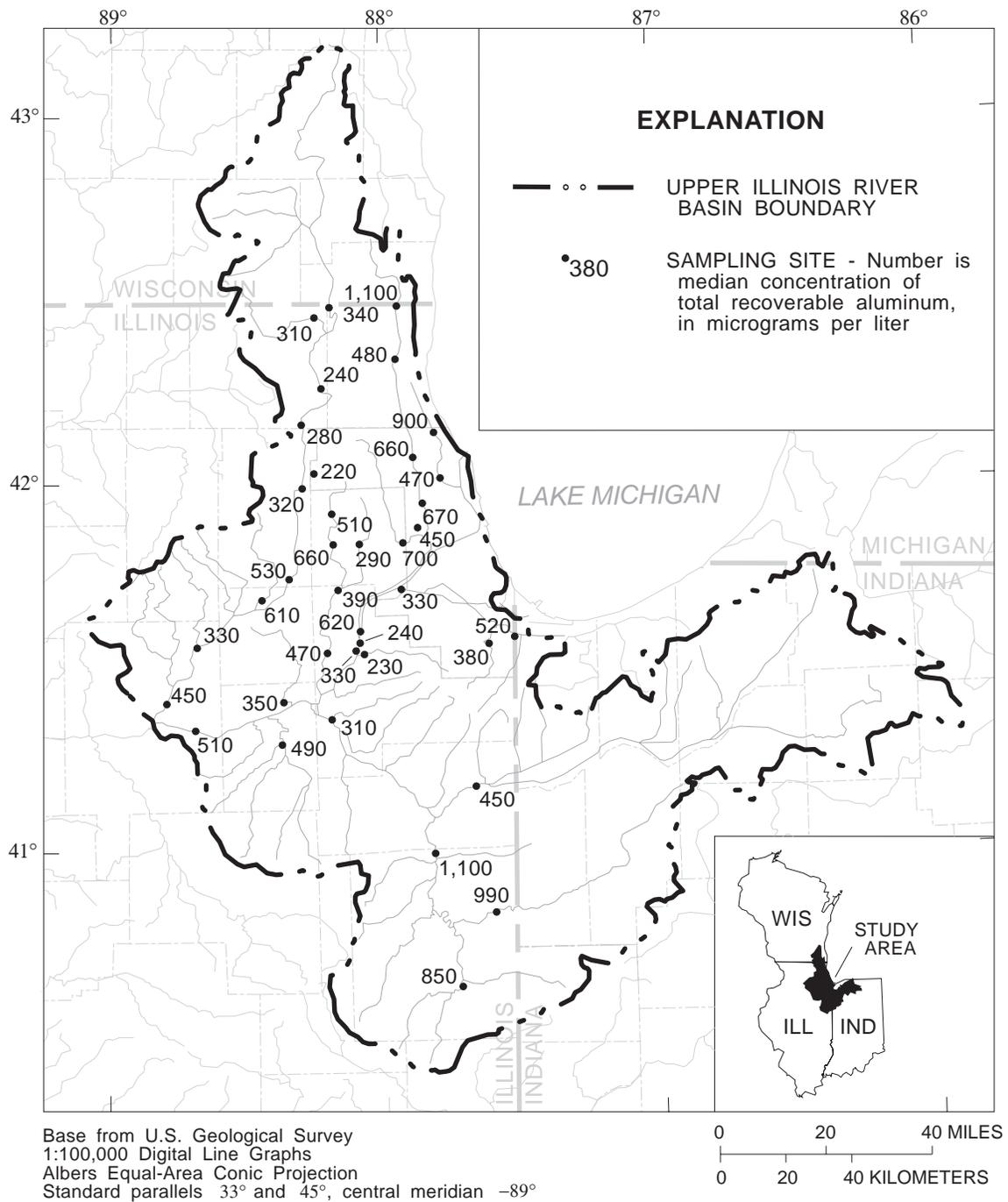
In conclusion, the largest concentrations and yields of most metals and trace elements were observed in urban areas. Total recoverable concentrations of soil-associated elements were slightly elevated in agricultural areas. The USEPA freshwater chronic and acute water-quality criteria were exceeded in a large number of samples collected from 1978 through 1986.

## Results of Water-Data Collection, 1987–90

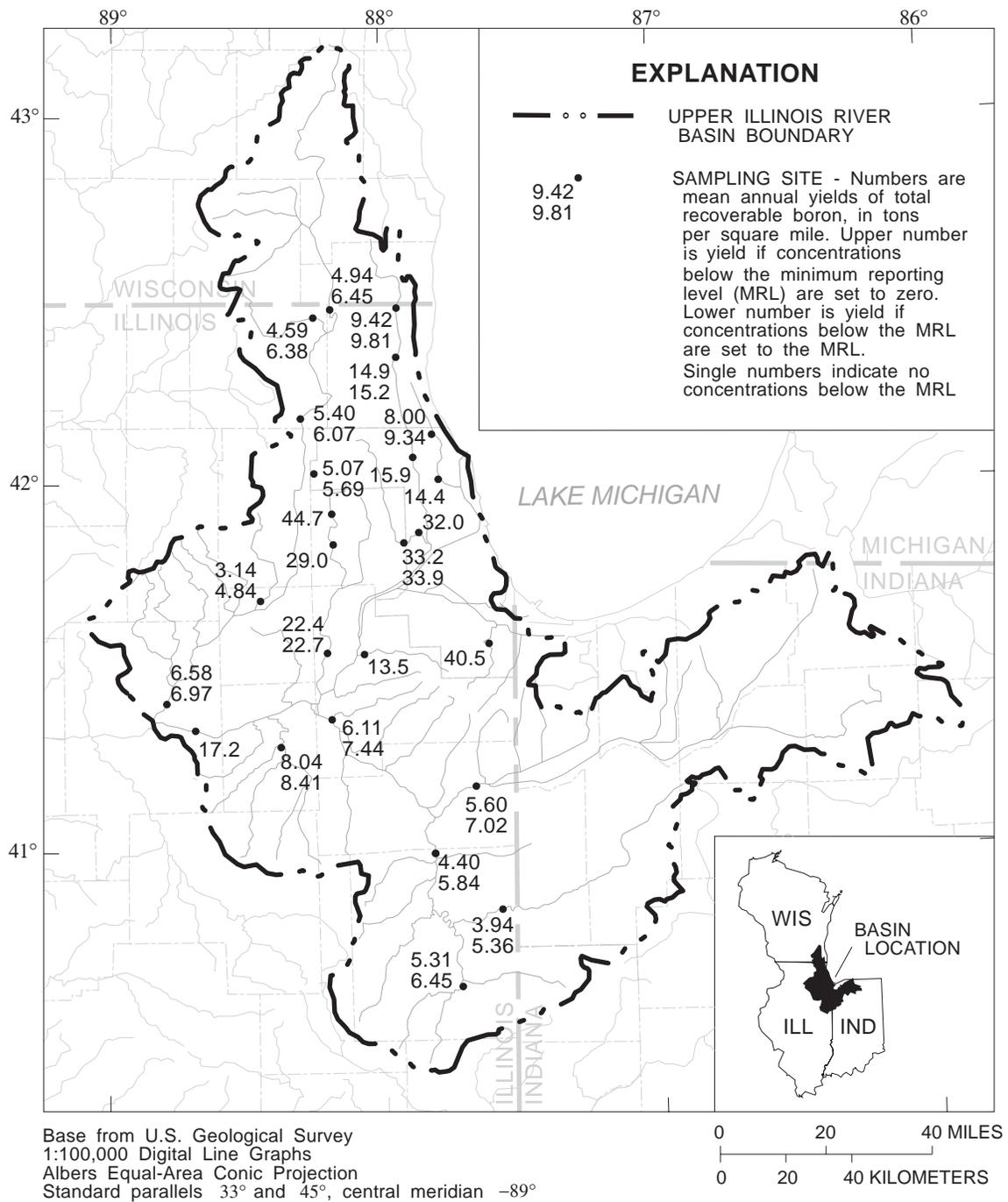
Data from analysis of trace elements in water (dissolved and total recoverable) from the eight NAWQA fixed stations are given in Sullivan and Blanchard (1994). Data from analysis of trace elements in water (dissolved and total recoverable) from the 8 NAWQA fixed stations and the 32 additional stations operated by the IEPA are given in USGS annual data reports (Fitzgerald and others, 1988; Coupe and others, 1989; Sullivan and others, 1990; Richards and others, 1991, 1992). Boxplots for dissolved and total recoverable concentrations in water from 1987 through 1990 are shown in figures A1 and A2, respectively.

As in the 1978–86 data, median concentrations of several elements were below or near the minimum reporting level (figs. A1 and A2), including dissolved aluminum, dissolved antimony, dissolved and total arsenic, dissolved cadmium, dissolved and total recoverable lead, dissolved and total selenium, dissolved and total recoverable vanadium, and dissolved and total recoverable zinc.

Results from Kruskal-Wallis analysis of variance tests indicate that concentrations of dissolved and total recoverable beryllium, dissolved chromium, dissolved and total recoverable cobalt, dissolved copper, dissolved iron, dissolved and total recoverable



**Figure 8.** Median concentrations of total recoverable aluminum in the upper Illinois River Basin, 1978–86.



**Figure 9.** Mean annual yields of total recoverable boron in the upper Illinois River Basin, 1978–86.

mercury, and dissolved and total recoverable silver were not significantly different ( $\alpha = 0.5$ ,  $p > 0.001$ ) among sites across the basin. The lack of differences of these element concentrations among sites may be due to the large number of less-than values for these elements.

Of the 13 elements for which acute and chronic water-quality criteria have been established for total recoverable concentrations (table 4), 8 elements were present at concentrations greater than acute, chronic, or both criteria: cadmium, chromium, copper, iron, lead, mercury, silver, and zinc. These elements were the same as those that exceeded the criteria from 1978 through 1986. The criteria were exceeded at approximately the same number of sites from 1978 through 1986 as from 1987 through 1990, and about the same proportion of concentrations exceeded acute and chronic criteria at individual sites. For example, at the Illinois River at Marseilles (site 76), 18 and 8 observations out of 80 samples collected by the IEPA from 1978 through 1986 exceeded the chronic and acute criteria for copper (table 7), and 11 and 4 observations out of 62 samples collected as part of the NAWQA program from 1987 through 1990 exceeded the chronic and acute criteria for copper.

All antimony, arsenic, beryllium, nickel, and selenium concentrations were below acute and chronic criteria at all sites from 1978 through 1990.

Dissolved and total recoverable concentrations of most major metals and trace elements, including many elements that are considered priority pollutants (table 4), were largest in urban land-use areas. In the upper Illinois River Basin, these elements include boron, cadmium, chromium, copper, lead, molybdenum, nickel, and zinc. These elements are referred to as "urban-related elements" in the following sections. Spatial patterns of total recoverable concentrations of antimony, arsenic, beryllium, mercury, selenium, and silver could not be related to land use because the large number of less-than values at agricultural and urban sites.

Concentrations of aluminum, iron, manganese, and vanadium in water did not coincide with any particular land use. These elements are typically considered soil-related elements and are common constituents in silt and clay. Thus, many agricultural streams that have an abundance of fine-grained sediment in their basins and are intensively farmed contain large total recoverable concentrations of these elements. Dissolved concentrations of these

elements in the same streams usually are below the minimum reporting level. At many urban sites, however, the large concentrations of dissolved aluminum, iron, and manganese indicate contributions of these elements from point sources such as metal-manufacturing industries. Therefore, large total recoverable concentrations of these elements may be due to either a large dissolved component from urban areas or a large particulate component from soils.

Large concentrations of barium and strontium in stream water from the Fox and Du Page Rivers appear to be linked with ground-water contributions and carbonate bedrock. In many public water-supply wells in Kane and Du Page Counties, ground water from the Cambrian and Ordovician aquifers contains dissolved barium concentrations that exceed 10 mg/L (Gilkeson and others, 1983). Water from many wells in eastern Wisconsin, especially Waukesha County, has greater than 1 mg/L strontium (Hem, 1985). Barium is not removed by conventional water- or wastewater-treatment methods; thus, concentrations of barium in the ground water may remain the same as the water is treated and used, unlike strontium, and discharged into the streams. Lime softening with soda-ash addition can remove approximately 90 percent of strontium (U.S. Environmental Protection Agency, 1991). Veins in carbonate rocks in this area may contain strontium-bearing minerals which may be mobilized under oxidized conditions when in contact with stream water (Brown and Maass, 1994). Even though concentrations of strontium are larger in the Fox and Du Page Rivers than in the rest of the streams in the upper Illinois River Basin, they are still within background concentrations found in rocks, soils, and surficial deposits (table 1).

Sites that receive large contributions of water from Lake Michigan (sites 54 and 55) contain some elements in concentrations that are more typical of water from a lacustrine environment than an urban riverine environment. For example, total recoverable barium concentrations are smaller at these sites (about 15 to 30  $\mu\text{g/L}$ ) than at other sites in the basin (about 25 to 100  $\mu\text{g/L}$ ). Lake Michigan water has concentrations of barium that range from 14 to 23  $\mu\text{g/L}$  near the water intakes for the city (City of Chicago and Illinois Environmental Protection Agency, 1989). In contrast, the median concentration for barium in public water supplies is 43  $\mu\text{g/L}$ , and from large rivers in the Nation is 45  $\mu\text{g/L}$  (Hem, 1985). Other concentrations that are much lower in Lake Michigan water than

stream water in the upper Illinois River Basin include aluminum, boron, iron, manganese, and strontium (City of Chicago and Illinois Environmental Protection Agency, 1989). Except for boron, these elements are related to sources such as soils and ground water.

Mean annual loads and yields (table A4) of the urban-related elements at urban sites typically were one order of magnitude larger than loads and yields of the same elements from agricultural areas. Mean annual loads and yields for water years 1987 through 1990 were calculated on the basis of total recoverable concentrations of elements at the 8 NAWQA fixed stations and at 18 additional IEPA stations for which streamflow data were available. For example, mean annual yields of lead and zinc from the Chicago Sanitary and Ship Canal at Romeoville (site 55) were about 0.065 ton/mi<sup>2</sup> and about 0.45 ton/mi<sup>2</sup>, respectively (table 8). In contrast, yields of lead and zinc from the Iroquois River near Chebanse (site 28), a more agricultural stream, were 0.005 ton/mi<sup>2</sup> and about 0.01 tons/mi<sup>2</sup>, respectively. At sites even more agricultural than the Iroquois River near Chebanse (such as Sugar Creek at Milford, site 22), too many values were below the minimum reporting levels for loads and yields of these urban-related elements to be adequately calculated.

Atmospheric loading has been shown to contribute significant amounts of some trace elements to Lake Michigan (Eisenreich, 1980). Atmospheric loadings estimated for southern Lake Michigan by Eisenreich (1980) were converted to yields and compared to yields from four urban streams in the Chicago area and one agricultural stream (table 8). Streams in the Chicago area were selected because Gatz and others (1988) showed that element concentrations in atmospheric deposition are larger southeast of Chicago and in northern Indiana and are smaller in the western suburbs of Chicago. This pattern in atmospheric deposition probably is because of the prevailing westerly winds that move the airborne elements eastward and out of the basin (Peters and Bonelli, 1982).

Some yields of urban- and industrial-related elements from atmospheric deposition were similar to yields from streams but others are not (table 8). Yields of lead in atmospheric deposition were very similar to those in streams in the Chicago area. A 56-percent reduction in the use of lead in gasoline from 1979 to 1983 resulted in decreases in atmospheric fluxes of lead (Eisenreich and others, 1986).

Yields of lead from streams and atmospheric deposition in the Chicago area were similar. This similarity indicates that much of the lead in streams is derived from atmospheric deposition in the Chicago area. Yields from the Iroquois River were an order of magnitude less than from streams and atmospheric deposition in the Chicago area. Much larger yields of copper and zinc were observed in streams in the Chicago area than in atmospheric deposition. This pattern indicates that the main source of copper and zinc is not from atmospheric deposition but from urban runoff, as found by Striegl and Cowan (1987), or from point sources. As can be seen in table 8, the yield of copper in water from the Iroquois River is similar to the yield of copper in atmospheric deposition. Because copper is not a common element in geologic deposits in the Iroquois River Basin and urban runoff and point sources are not common, this similarity indicates that most of the copper in agricultural streams is derived from atmospheric deposition.

Comparison of results from this study to results from other studies is of little help in determining whether concentrations in the upper Illinois River Basin are elevated or within background concentrations, because of differences in collection methods, sample processing and analyzing, and minimum reporting levels (Harmeson and Larson, 1969; Williams and others, 1974, p. 86; Feder, 1979; Kelly and Hite, 1981; Britton and others, 1983; City of Chicago and Illinois Environmental Protection Agency, 1985; Hem, 1985; Smith and others, 1987; Striegl and Cowan, 1987). In addition, many data for water are from the dissolved fraction and not highly reliable for the trace elements because of small concentrations. Thus, comparisons between studies can only be considered as highly general. Given those limitations, total recoverable concentrations of aluminum, arsenic, beryllium, cobalt, manganese, selenium, and vanadium all generally seem to be within background concentrations (table 1), although comparisons are inconclusive for beryllium, cobalt, and selenium because of too many less-than values. Some total recoverable concentrations of cadmium, chromium, copper, lead, mercury, nickel, silver, and zinc seem to be elevated in urban areas. An exact concentration that separates background from elevated concentrations in water cannot be identified; however, all elements whose concentrations exceed water-quality criteria (cadmium, chromium, copper, iron, lead, mercury, silver, and zinc) can be considered to

be elevated in the upper Illinois River Basin. Iron is the only one of these elements whose elevated concentrations in the upper Illinois River Basin does not seem to be related to urban sources.

### **Correlations Among Major and Trace Elements in Water, 1987–90**

Dissolved and total recoverable concentrations of the 22 elements of interest at 40 sites (8 NAWQA fixed sites and 32 IEPA Ambient Water-Quality Monitoring Network sites) were correlated and a suite of other chemical constituents including dissolved and total recoverable concentrations of major ions, chloride, dissolved solids, suspended solids, volatile suspended solids, and total organic carbon; and with measurements of discharge, specific conductance, pH, water temperature, dissolved oxygen, alkalinity, and hardness.

Correlation coefficients (Spearman's rho) were computed from ranked data sets in three different ways. First, the data from the 40 sites were combined to find correlations that best describe basinwide correlations on main stems in the upper Illinois River Basin. Next, data were limited to dissolved and total recoverable concentrations from the eight NAWQA fixed sites. Finally, correlations among constituents were examined separately at each of the eight NAWQA fixed sites to distinguish the variation in correlation patterns in water for each individual site. Results of the correlation analysis for the 40 sites combined, the 8 NAWQA fixed sites combined, and each individual NAWQA fixed site, are listed in table 9. Except for a few elements, the correlation results from the 40 sites and the 8 sites combined were similar.

Comparison of the correlation coefficients for the eight individual NAWQA fixed sites indicates that significant correlations among dissolved and total recoverable concentrations were not only element specific, but commonly site specific as well. These correlations reflect, in part, the site dependency of the partitioning of the element between the dissolved and particulate phases. If much of the element is in the dissolved phase, the dependence of the total recoverable concentration on the dissolved concentration increases, and, therefore, the correlation coefficient increases.

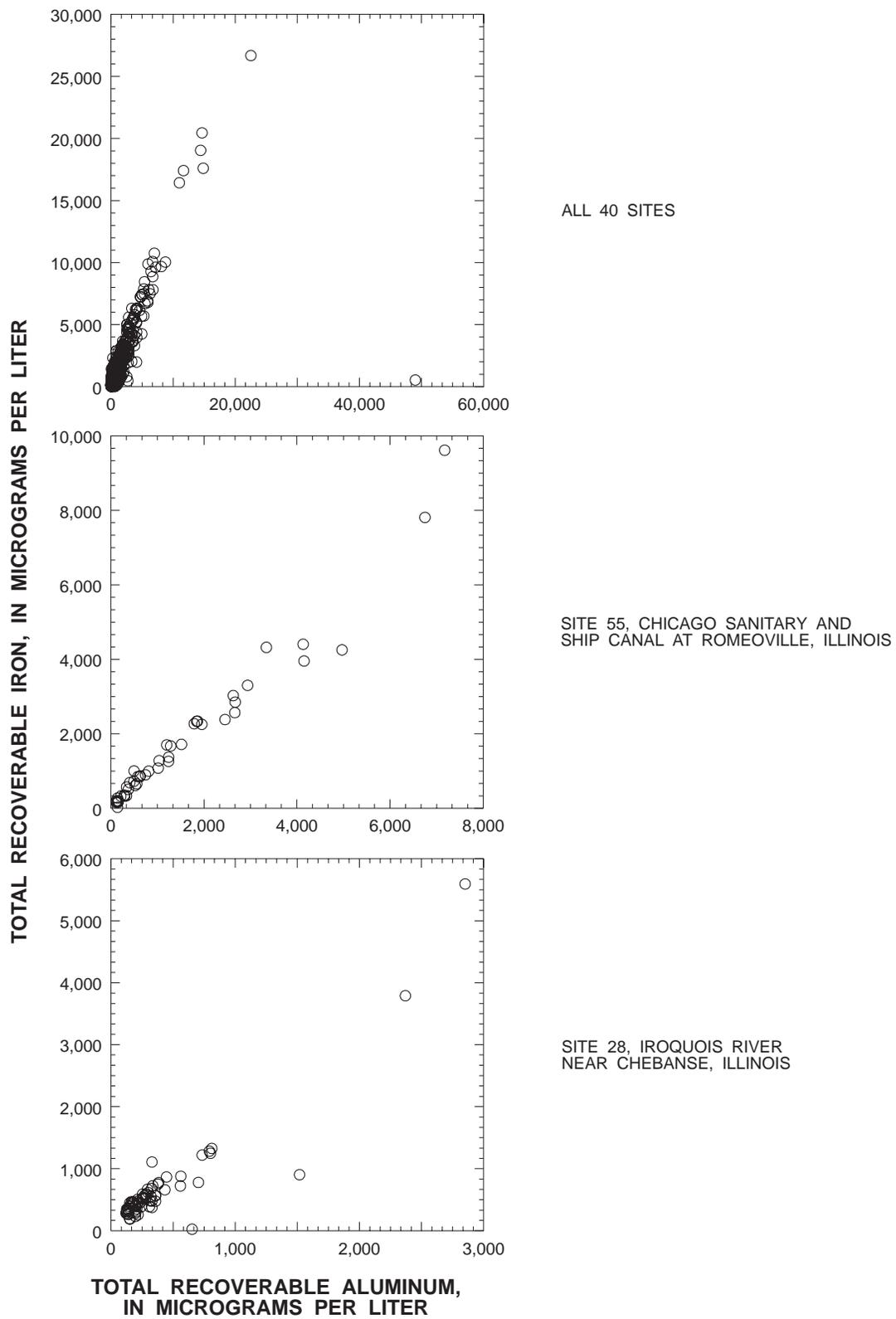
Large correlation coefficients for dissolved and total recoverable arsenic, barium, boron, and strontium

at the combined 40 sites and the combined 8 NAWQA fixed sites indicate that these elements were found mainly in the dissolved phase in water in the upper Illinois River Basin. Box plots of these elements (figs. A1 and A2) show the relation between dissolved and total recoverable concentrations. In particular, correlation coefficients for dissolved and total recoverable boron and strontium concentrations were greater than 0.94 at each of the eight NAWQA fixed sites; other studies have shown that, in river transport, ratios of dissolved to total strontium and boron are high (Meybeck and Helmer, 1989).

Correlation analyses indicated that relations between dissolved and total recoverable concentrations of some elements varied between sites, whereas no relations were observed for other sites. Dissolved and total recoverable concentrations of arsenic, barium, and nickel correlated at some of the eight NAWQA fixed sites ( $\rho > 0.5$ ) but not at all sites. This finding indicates that ratios of dissolved to total arsenic, barium, and nickel were site dependent; however, the correlations of dissolved to total recoverable concentrations were not dependent on land use because the coefficients were not consistent at sites with similar land use upstream. Dissolved and total recoverable phases did not correlate strongly at any of the sites for the elements aluminum, copper, iron, and lead; this finding indicates that these elements are mainly bound to the particulate phase or that the relation between the phases is variable. Dissolved and total recoverable manganese concentrations correlated strongly only at the Chicago Sanitary and Ship Canal (site 55). The variation in the pattern of box plots for all 40 sites for dissolved and total recoverable manganese (figs. A1 and A2) indicates the wide range in the proportions of manganese in the dissolved and particulate phases.

Total recoverable concentrations of aluminum and iron (fig. 10) were the only elements that were highly correlated at all 40 sites. Correlation coefficients between the two elements range from 0.8 at the Chicago Sanitary and Ship Canal (site 55) to 0.99 at the Iroquois River (site 28).

Total recoverable iron and manganese also correlated, although the correlation coefficients are somewhat smaller and cover a broader range—0.48 at the Des Plaines River at Riverside (site 40) to 0.90 at the Du Page River at Shorewood (site 69)—than those for iron and aluminum. The broader range in



**Figure 10.** Total recoverable aluminum and iron concentrations in the upper Illinois River Basin, 1987–90. (Site numbers refer to table 6.)

correlation coefficients across the eight NAWQA sites reflects the site dependence of dissolved manganese concentrations.

Total recoverable manganese concentrations also correlated to total recoverable aluminum concentrations in a similar way as they did to iron; the smallest correlation coefficients (0.48 and 0.24) at the Des Plaines River (site 40) and Chicago Sanitary and Ship Canal (site 55), respectively, and the largest (0.86) at the Du Page River (site 69).

Total recoverable iron, aluminum, and manganese all positively correlated with total recoverable arsenic and barium, suspended residue, and volatile suspended residue, and negatively correlated with hardness and dissolved calcium concentrations at four to six of the eight NAWQA fixed sites. Total recoverable arsenic and manganese correlated with each other at the Kankakee River (site 14), the Iroquois River (site 28), and the two sites on the Fox River (sites 89 and 99). Dissolved and total arsenic also strongly correlated with water temperature.

Dissolved and total recoverable boron and strontium also correlated with each other at four to five of the eight NAWQA fixed sites; all four concentrations positively correlated with dissolved and total recoverable sodium, and dissolved chloride. They inversely correlated with discharge. This pattern further indicates that the dissolved concentrations of boron and strontium are diluted during high streamflow and are concentrated during low streamflow.

None of the other elements consistently correlated with any other elements, chemical constituents, or physical parameters. Cadmium is commonly associated with lead and zinc (City of Chicago and Illinois Environmental Protection Agency, 1985); however, cadmium did not correlate with lead or zinc at any sites. Cadmium may be coprecipitated with manganese oxides or adsorbed onto mineral surfaces (Hem, 1985); however, cadmium did not correlate with manganese or iron at any sites.

In water, nickel tends to coprecipitate with iron oxides and especially with manganese oxides (Salomons and Förstner, 1984). Nickel did not correlate with iron or manganese at any sites in the upper Illinois River Basin; however, it did inversely correlate with alkalinity at the eight NAWQA fixed sites combined and at the Illinois River at Marseilles (site 76).

Striegl and Cowan (1987) observed strong correlations among copper, lead, and zinc, and

suspended-sediment concentrations from Lake Ellyn in Illinois. Similar correlations were not apparent in the NAWQA data; correlations among copper, lead, and zinc and total suspended solids were negligible (table 9). Instead, only total recoverable aluminum, iron, and manganese significantly correlated with total suspended solids.

Chromium, copper, lead, and nickel inversely correlated with alkalinity among the combined data and at some of the eight NAWQA fixed sites. Hence, increased alkalinity (or carbonate) is linked to reduced concentrations of these metals. Water-quality criteria for all these metals are dependent on hardness (thus indirectly on alkalinity) (table 4). The relatively large alkalinity in the upper Illinois River Basin helps stabilize pH; therefore, pH probably does not vary enough to affect the speciation of these metals. Even though changes in pH are known to affect the distribution of metals over the dissolved and particulate phases, the buffering capacity of the water is usually a more important control, especially in systems where fluctuations in pH are small (Salomons and Förstner, 1984). Thus, in the upper Illinois River Basin, alkalinity may be an important control on limiting the bioavailability of these metals.

### **Seasonal Variations and Long-Term Changes, 1978–90**

Data used for the analysis of seasonal variations in concentrations of elements in water include observations from the 40 IEPA and USGS water-sampling sites. Data from 1978 through 1990 from IEPA's 38 ambient water-quality monitoring sites also were examined to determine if extension of the period from 4 to 13 years changed the results of the analysis. The results from the comparison showed that the variations in median concentrations from month to month were the same, regardless of the period used; therefore, only the 1987 through 1990 data are discussed in this report. The seasonal variations discussed below are based on aggregated data for the 8 NAWQA fixed sites and the 32 IEPA monitoring sites.

Significant seasonal variations were observed in total recoverable concentrations of aluminum, arsenic, barium, boron, iron, manganese, and strontium in water (Kruskal-Wallis ANOVA,  $p \leq 0.10$ ). Seasonal variations may occur in other trace element concentrations; however, too many observations of most of these elements are below the minimum reporting levels for variations to be statistically

significant. Total recoverable aluminum, arsenic, iron, and manganese concentrations all varied similarly from month to month, with the largest concentrations occurring in the summer (fig. 11). These seasonal variations relate to seasonal variations in volatile and total suspended solids concentrations (fig. 11) and possibly reflect the amount of water available for dilution or the amount of suspended sediment in the water column. Dissolved manganese varied differently from month to month than total recoverable manganese. Largest dissolved manganese concentrations occurred in January through March, and smallest concentrations in July and September. Hydrogen-ion activity was smallest in February and March but largest in October and November; thus, some factor in addition to pH may have been affecting dissolved manganese concentrations.

Seasonal variations in dissolved and total recoverable strontium concentrations reflect variations in streamflow. Concentrations of dissolved and total recoverable strontium were largest in the summer and fall, and smallest in April, May, and December. These variations, which seem to be inversely related to streamflow, were largest in April, May, and December (fig. 12). Monthly boron concentrations also seem to be somewhat inversely related to streamflow, except in March and April (fig. 12). This is probably because of the effects of dilution of the elements at high flows. As mentioned previously, strontium in surface water is mainly from ground-water sources, and boron is probably from effluent from wastewater-treatment plants. When base flow contributes the most to overall streamflow, strontium and boron concentrations will be the largest.

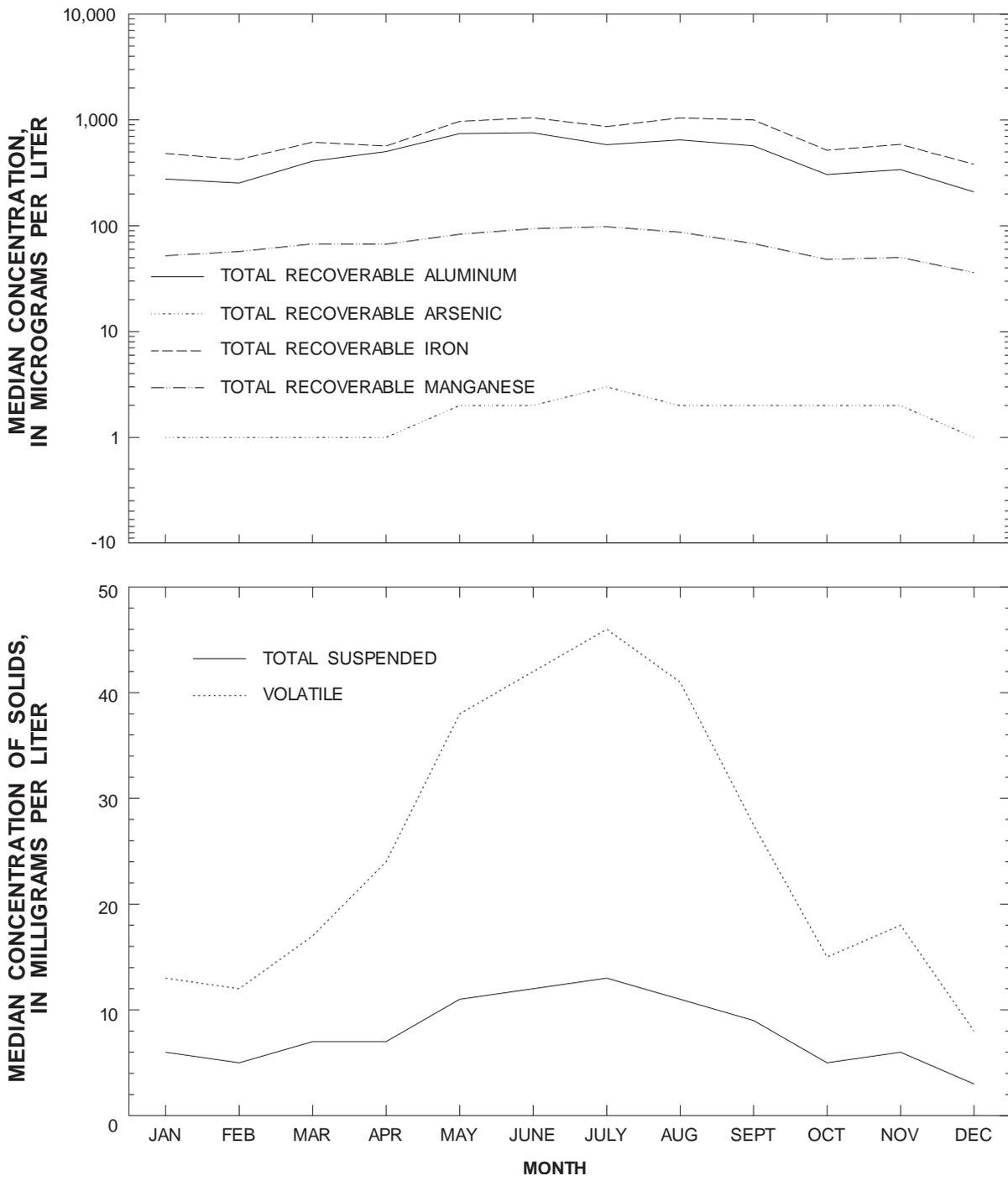
Seasonal patterns in element concentrations varied from site to site. Seasonal variations in elements in water at the 40 sites combined were compared to individual seasonal variations at each of the eight NAWQA fixed sites. The seasonal patterns of aluminum, cadmium, chromium, cobalt, copper, nickel, vanadium, and zinc in water were variable at the eight NAWQA fixed sites; thus, it seems that seasonal variations of these elements in water were not caused by basinwide factors but by site-specific factors that may include geochemical substrate and biological processes. This finding is supported by other studies that have shown different monthly variations of element concentrations in water from the middle Illinois River (Mathis and Cummings, 1970).

Trends in element concentrations in water from 1978 through 1990 were examined by use of seasonal Kendall analysis for 38 of the 40 sites sampled for water. The exact sampling periods differed among the sites but at least 9 years of data were available for most sites and as much as 13 years of data were available for some sites. The sampling period at the other two sites, the Des Plaines River (site 40) and the Chicago Sanitary and Ship Canal (site 55), was not long enough for trend analysis.

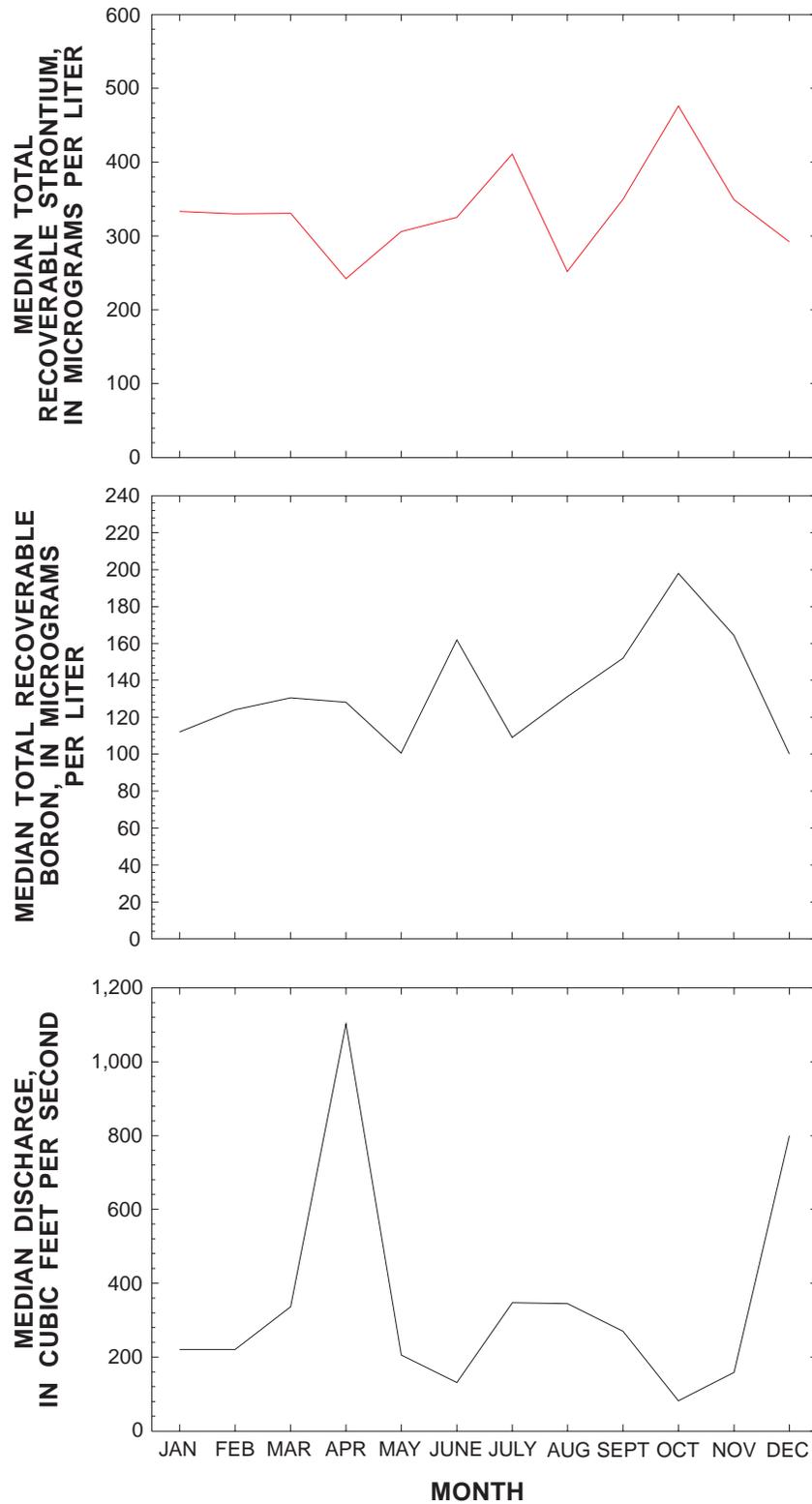
Results of the trend tests are given in table A5. Results are not included for sites where more than half of the observations were below the minimum reporting level. If less-than values were present, the trend tests were run twice—once with zero substituted for the less-than values and once with minimum reporting levels substituted for the less-than values. If the trend results differed between the two tests, the results were not included, and only trends with a significant probability level ( $p < 0.10$ ) are reported. Elements that were not analyzed for trends include the priority pollutants antimony, beryllium, mercury, silver, and zinc. Trend analysis of antimony concentrations were not possible because samples for antimony analysis were collected only during the NAWQA pilot study. More than half of the concentrations of beryllium, mercury, silver, and zinc were below the minimum reporting level at all sites, and many data sets for these elements contained multiple minimum reporting levels as well.

The number of sites where upward and downward trends were found for each element are listed in table 10. Concentrations of five elements had significant downward trends at a number of sites in the basin: dissolved and total recoverable barium (12 and 17 sites, respectively), total recoverable boron (13 sites), total recoverable iron (8 sites), dissolved and total recoverable manganese (13 and 14 sites, respectively), and dissolved and total recoverable strontium (7 and 6 sites, respectively). Dissolved and total strontium concentrations also had significant upward trends at many sites in the upper Illinois River Basin (9 and 15 sites, respectively). Plots of barium and boron at Salt Creek (site 38) and Thorn Creek (site 50) show the downward trends in these concentrations (fig. 13).

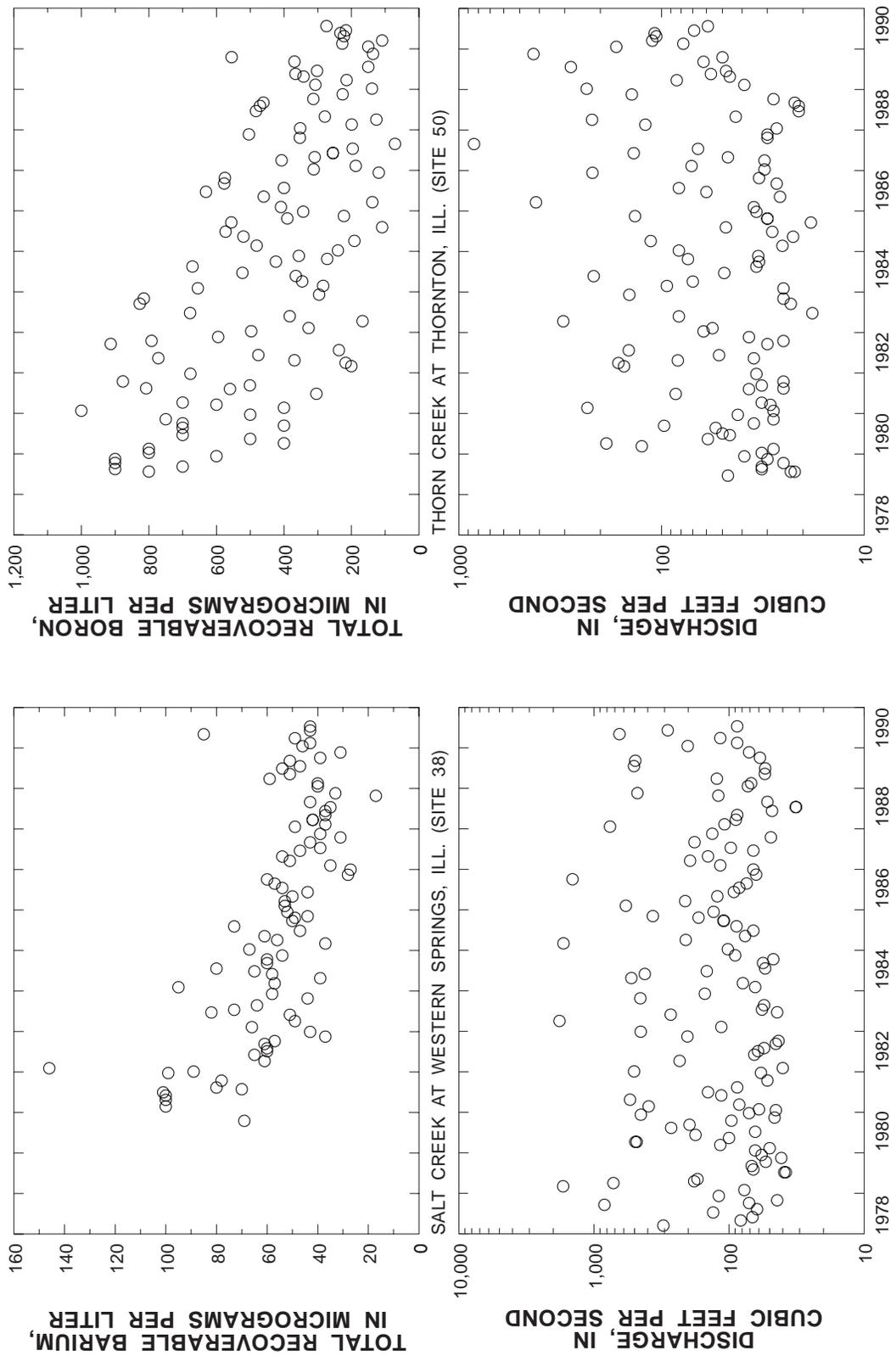
Sites where significant downward trends in barium were found were scattered across the Des Plaines, Du Page, and Fox River Basins; although these sites are mainly urban, a few



**Figure 11.** Seasonal variations in median monthly concentrations of aluminum, arsenic, iron, manganese, and volatile and total suspended solids in the upper Illinois River Basin, 1987-90.



**Figure 12.** Seasonal variations in median monthly concentrations of boron and strontium, and seasonal variation in median monthly discharge in the upper Illinois River Basin, 1987–90.



**Figure 13.** Concentrations of barium and boron at two urban stream sites in the upper Illinois River Basin, 1978–90. (Site numbers refer to table 6.)

agricultural sites are included. Downward trends in boron were found at urban sites in the Des Plaines and Du Page River Basins. Downward trends in iron concentrations were found at agricultural and urban sites in the upper and lower Des Plaines River and the upper and lower Fox River. Downward trends in manganese concentrations were found at urban and agricultural sites scattered across the northern part of the upper Illinois River Basin. Trends in total recoverable strontium concentrations were downward at urban sites in the lower Des Plaines River and tributaries to the Calumet Sag Channel and were upward at agricultural sites on the main stems of the Kankakee, Iroquois, and Fox River Basins.

Smith and others (1987) reported that trends in iron and manganese were strongly related to trends in streamflow from 1974 through 1981. In the upper Illinois River Basin, streamflow at the time of sample collection trended downward from 1978 through 1990 at only 6 of 38 sites: Sugar Creek at Milford (site 22), Des Plaines River at Russell (site 32), Illinois River at Marseilles (site 76), Fox River at Algonquin (site 89), Blackberry Creek near Yorkville (site 93), and the Fox River at Dayton (site 99). Sites where significant downward trends in streamflow were found were not the same sites where downward trends in barium, boron, iron, and manganese were found, except for the Illinois River at Marseilles (site 76). Thus, change in streamflow is not a likely explanation for the downward trends in these element concentrations from 1978 through 1990.

Most downward trends in dissolved lead concentrations in stream water across the conterminous United States from 1974 through 1981 have been attributed to the decrease in lead use (Smith and others, 1987). Gatz and others (1988) also reported a decrease in loading of atmospheric lead and cadmium over the Great Lakes during this period. Sites in or near the upper Illinois River Basin that were investigated by Smith and others (1987), however, generally did not show any trends in either dissolved or total recoverable lead concentration. Analysis of trends in dissolved and total recoverable lead in water in the upper Illinois River Basin was hindered by the large number of multiple minimum reporting levels. At only one site, the Des Plaines River at Lockport (site 42), were more than half of the observations of total recoverable lead above the minimum reporting level. Trend tests done with less-than values set to zero and to the minimum reporting level resulted in

different levels of significance, but neither set of tests indicated any change. One possible reason that no trends were observed for lead concentrations in water is that lead that has accumulated in the streambed sediment may be released to the water column, maintaining concentrations in water long after the initial source of the lead was removed.

## Sediment

This description of major and trace elements in sediments is based on streambed-sediment data collected by the IEPA from 1978 through 1986, suspended-sediment data collected by the USGS at the eight NAWQA fixed sites from 1987 through 1990, and streambed-sediment data collected by the USGS during NAWQA synoptic samplings in 1987 and 1990.

### Results of Streambed-Sediment Data Collection, 1978–87

By John A. Colman

Historical concentrations of streambed sediments are based on sieved and unsieved sediments collected by IEPA from 1978 through 1987. Percentiles for concentrations from the sieved and unsieved data sets are summarized in table 11. As mentioned previously, only 10 elements were measured in nearly every sample: arsenic, cadmium, chromium, copper, iron, lead, manganese, mercury, phosphorus, and zinc (table 11). Exceptions were arsenic and manganese in the unsieved data set, which were measured at only 54 to 56 sites as compared to 80 to 103 sites for the other eight elements. If two or more samples were collected at a site, only the data from the most recent sampling were used for statistical analysis.

Three characteristics of IEPA site distribution are evident from the location map (fig. 6): (1) the coverages by method are not uniformly distributed, (2) large parts of the study area (Indiana, Wisconsin, and the Iroquois River in Illinois) were not sampled by either method, and (3) site distribution is biased toward the high-order streams. The nonuniform coverage precludes statistical analysis of the lumped data set because the differences between sieved and unsieved samples could not be distinguished from the effects of spatial or temporal differences. The spatial and stream-order bias of the data restrict the

applicability of interpretation to the sampled areas rather than to the whole basin.

Spatial patterns were examined using the Kruskal-Wallis one-way ANOVA test on concentrations in each subbasin. All the major streams of the upper Illinois River Basin were treated as separate subbasins except for those with insufficient coverage (the Iroquois River Basin, for instance). Coverages needed to be similar for an effective analysis, so subbasins with a large amount of data (for example, the Fox River Basin) were split. In addition, data from subbasins with too little data were combined, notably Salt Creek and North Branch Chicago River for sieved samples. The Tukey studentized range test was used to identify subbasins where differences in concentrations were significant; the results are given in tables 12 and 13.

For the sieved-sample data, only arsenic did not differ significantly among subbasins. Concentration ranks for most other elements were elevated in high-order streams as compared to ranks in low-order streams. Of these elements, cadmium was elevated in the East and West Branches of the Du Page River and in the Des Plaines River. Elements not significantly elevated in main stems as compared to tributaries were arsenic, manganese, and iron. Phosphorus concentrations were large throughout the Du Page River; it was also elevated in Salt Creek and North Branch Chicago River Subbasins. Generally, concentrations of elements in sieved samples from tributaries of the lower Fox River, of the upper Fox River, and of the Des Plaines River did not differ. Exceptions were found for chromium, iron, and lead, which were larger in tributaries of the Des Plaines River.

Sieved samples from subbasins in the Chicago metropolitan area contained larger concentration ranks of chromium, copper, mercury, and zinc (table 12). Subbasins that drain mainly urban areas include the Little Calumet River, lower Du Page River, East and West Branches of the Du Page River, Des Plaines River, Salt Creek, and North Branch Chicago River. Larger concentration ranks of arsenic, iron, and manganese, however, do not appear to be related to urban sources because relatively large concentrations were present in both agricultural and urban subbasins.

For the unsieved-sample data, ANOVA indicated that all elements were significantly different in at least one subbasin (table 13). In no case, however, was there a difference between tributaries to the Fox River and tributaries to the Illinois River.

Although the sites in the subbasins were not always the same for sieved- and unsieved-sample data, concentrations in the high-order streams tended to be larger than concentrations in low-order streams for both data sets.

Spatial-distribution anomalies can be assessed by comparing concentration data with average or background concentrations for a particular geology (Rose and others, 1979). No compendium of average or background concentrations for trace elements in stream sediments in the United States is available for samples that have been collected and analyzed in the same manner as these data. However, consistent information is available for background concentrations in streambed sediments in Illinois (Kelly and Hite, 1984), as well as data collected nationwide for soil concentrations (Shacklette and Boerngen, 1984) (table 14). Data for streambed sediments at background sites in Illinois are available for unsieved sediments only, so that only unsieved-sample data can be compared directly with the background concentrations. Soil samples were collected at approximately 8-in. depth and at 50-mi intervals. Chemical analysis was done after complete digestion of the soil samples, in contrast to the analysis of streambed sediments by partial digestion.

The geometric means of the background concentrations in streambed sediments (Kelly and Hite, 1984) were slightly smaller than means for concentrations in the soil samples (Shacklette and Boerngen, 1984) (table 14), as would be expected considering the selection criterion for the background sites. Exceptions were iron, manganese, and phosphorus, which were substantially enriched in the streambed sediments from background streams. Sediment geochemistry likely contributed to the larger concentrations of these elements in background streams. Many concentrations of elements in streambed sediments in the upper Illinois River Basin (table 14) were elevated relative to background concentrations. Greater than 75 percent of the unsieved streambed-sediment samples were above the 98-percent confidence level for background concentrations of cadmium and lead. More than 50 percent of the unsieved streambed-sediment samples were above the 98-percent confidence level for background concentrations of chromium, copper, mercury, and zinc, whereas 25 percent were above the 98-percent confidence level for background concentrations of phosphorus. Arsenic, iron, and manganese seem to have been similar to background distributions.

Large concentration ranks of chromium, copper, mercury, and zinc from unsieved sediments also were found in urban subbasins (Calumet Sag Channel, Little Calumet River, and North Shore Channel); however, the correlation is not as clear. This may be caused by coarse-grained sediments diluting the patterns indicated in the concentration ranks of fine-grained sieved sediments.

Correlations were found between some elements in the basinwide data sets for sieved and for unsieved samples (tables 15 and 16, respectively). These correlations are indicated by large (near 1.0) correlation coefficients. The correlation coefficients were calculated from log-transformed data. For sieved-sample data, the largest correlations ( $\rho > 0.90$ ) were found among chromium, copper, and zinc. Correlations between this group and arsenic, iron, and manganese were low ( $\rho < 0.43$ ). Correlations among the unsieved-sample data were not as large as for the sieved-sample data; coefficients for chromium, copper, and zinc in the unsieved-sample data ranged from 0.80 to 0.85.

A useful method for grouping the correlations between elements is factor analysis. Factor analysis was applied to the log-transformed data. Sieved- and unsieved-sample data sets yielded two significant factors each (table 17). For sieved-sample data, the two-factor model accounted for 65 percent of the variance in the log-transformed data. The factor analysis results for sieved-sample data show that cadmium, chromium, copper, lead, mercury, phosphorus, and zinc are strongly associated (factor 1). The first factor accounts for approximately 54 percent of the variance of these elements. Manganese and arsenic also are strongly associated with the sieved-sample data set (factor 2).

The factor analysis for the data set of unsieved samples did not include arsenic, cadmium, iron, and manganese because of missing values in the data set for these elements. The two-factor model for the remaining six-element data set accounted for 90 percent of the total variance. The larger percentage of variance explained as compared to the unsieved-sample data is expected because of the reduced number of elements. Chromium, copper, lead, mercury, and zinc were associated in the unsieved-sample data set (factor loading greater than 77 percent). The second factor carries a large loading for phosphorus.

As discussed previously, unsieved sediments at a large percentage of upper Illinois River Basin sites were enriched in all elements except arsenic, iron, and manganese. Although the sources that may be contributing to enrichment are too numerous to be individually assessed in this report, some generalizations can be made. Current mining activity, other than rock and gravel quarrying, is not present in the upper Illinois River Basin. Point sources of trace metals in the Chicago metropolitan area contain combined concentrations from wastewater-treatment-plant outfalls and storm-sewer overflows because many industries in the area discharge to sewage-treatment plants. Thus, the point-source effects of mine tailings, chlor-alkali plants, paper mills, and so forth, which are responsible for the largest anthropogenic metal enrichments of sediments worldwide (Förstner and Wittman, 1979), cannot be distinguished individually in the upper Illinois River Basin. The large industrial base in the basin does contribute trace metals. This contribution, however, may be input more from diffuse sources such as atmospheric deposition or combined sources from municipal wastewater-treatment plants and sewer overflows.

The "averaged" input from municipal and nonpoint sources may serve to explain the results of the factor analysis. The factors are results of both anthropogenic mobilization of elements in the basin as well as geochemical occurrence and deposition processes; that is, geochemical processes serve to concentrate insoluble elements in the sediments, but sources of elements are also necessary for elevated sediment concentrations to be observed. The implication of the large loading of several elements on one factor is that either the sources of the various elements are related or that a single large nonpoint source, such as atmospheric deposition or urban runoff, contributes many elements over a wide area.

### **Results of Suspended- and Streambed-Sediment Data Collection, 1987–90**

Observation of spatial distributions of the trace elements in stream sediment was possible because most observations were above the minimum reporting level, in contrast to the many trace element concentrations in water that were below the minimum reporting level. In addition, stream-sediment samples are less likely to be contaminated during sampling and analysis than water samples because concentrations usually are much larger in stream sediments (table 18). For

example, total recoverable chromium concentrations in water in the upper Illinois River Basin were commonly in the range of less than 5 to 420  $\mu\text{g/L}$ , whereas concentrations of chromium in suspended sediment ranged from about 16 to 980  $\mu\text{g/g}$  and in streambed sediment ranged from 17 to 640  $\mu\text{g/g}$  (table 18). Out of all the suspended-sediment data collected as part of the NAWQA program at the eight fixed sites, only concentrations of beryllium were consistently below the minimum reporting level. Almost all other elements in suspended sediment were found at concentrations above the minimum reporting levels (fig. A3). Concentrations of cadmium, molybdenum, and silver were below the minimum reporting level in streambed sediments from sites outside of the Chicago area (Colman and Sanzolone, 1991).

For most elements, suspended-sediment data from the eight NAWQA fixed sites did not provide an adequate representation of the range of concentrations observed in streambed sediments in the upper Illinois River Basin (table 18). Concentrations of only beryllium, cadmium, and silver in suspended sediments collected during 1987 through 1990 are within a similar range for concentrations in streambed sediments collected during the 1987 NAWQA synoptic sampling.

Most of the priority pollutants were found in larger concentrations in streambed sediments from urban sites. Streambed sediments from the urban sites typically had concentrations that can be considered elevated compared to the range found in background concentrations in nonindustrial, low-order streams in the Illinois River Basin (Mathis and Cummings, 1970) (table 1). Largest concentrations of antimony, boron, cadmium, chromium, copper, lead, mercury, nickel, silver, and zinc were found in suspended and streambed sediments from the Chicago area. The signature of this suite of elements continued downstream in Illinois River sediments, although concentrations were diluted by sediment originating from the Fox and Kankakee River Basins (Colman and Sanzolone, 1992). Cadmium concentrations in fine-grained streambed sediments in the North Branch Chicago River, Calumet Sag Channel, Chicago Sanitary and Ship Canal, lower Des Plaines River, and the Illinois River exceeded 4  $\mu\text{g/g}$  and in some cases were as large as 46  $\mu\text{g/g}$  (Colman and Sanzolone, 1991). This range in concentration is two orders of magnitude larger than that reported for unsieved sediment from nonindustrial

streams (Mathis and Cummings, 1970) (table 1). Some of the largest concentrations of copper, lead, and zinc found in the upper Illinois River Basin are similar to concentrations of these elements in fine-grained sediments in Lake Ellyn, a small lake in a Chicago suburb (Striegl and Cowan, 1987). Large lead and zinc concentrations in Lake Ellyn were linked to urban runoff because road dirt also contained large concentrations of lead and zinc (Striegl and Cowan, 1987). Antimony and silver in sediments were associated with urban sources; however, in water, no spatial patterns could be distinguished because of the large number of observations below the minimum reporting level.

Countywide aggregates of discharges of 17 elements discussed in an IEPA report on toxic chemicals (Illinois Environmental Protection Agency, 1991) (table 3) were compared to mean streambed-sediment concentrations for high- and low-order streams in each county. Industries in Cook County release the largest amounts of aluminum, antimony, arsenic, cadmium, chromium, copper, lead, manganese, molybdenum, silver, and zinc compared to other counties in the Illinois part of the upper Illinois River Basin. The largest amounts of cobalt and nickel are released in Will County (Illinois Environmental Protection Agency, 1991). The largest concentrations of many of these urban-associated elements in sediments were observed in the industrial areas of Cook, Will, and Du Page Counties. Large concentrations of aluminum, barium, beryllium, cobalt, molybdenum, and vanadium in streambed sediments, however, were scattered across the upper Illinois River Basin at some agricultural and some urban sites. All were within the range found for background concentrations in rocks, soils, surficial deposits, and streambed sediments (table 1).

Although larger concentrations of many elements can be attributed specifically to urban or agricultural inputs, larger concentrations of some elements cannot be attributed to one source. Larger concentrations of arsenic in the Kankakee River suspended and streambed sediments, for example, are not directly related to inputs from agricultural practices, because large concentrations were not found in the Iroquois River Basin, which is more intensely farmed. Arsenic in streambed sediment was commonly found in concentrations from 20 to 140  $\mu\text{g/g}$  in the Kankakee River (Colman and Sanzolone, 1991). Concentrations in suspended sediment from the Kankakee

River at Momence (site 14) ranged from about 20 to 50  $\mu\text{g/g}$  (fig. A3). These concentrations are larger than background concentrations, which are typically less than 15  $\mu\text{g/g}$ . Only 1 to 4 percent of streambed sediments were clay sized in the Kankakee River (Gross and Berg, 1981), and sediments from the Kankakee River also contain larger iron and manganese concentrations than other streams in the upper Illinois River Basin. This pattern indicates that the small amount of fine-fraction sediments in the Kankakee River probably contain a greater proportion of iron and manganese coatings than is typical of other streams in the basin. Arsenic has been shown to have a large affinity for iron and manganese coatings (Horowitz, 1991). In addition, unsieved sediments from the Kankakee River were not enriched in arsenic, iron, or manganese, and neither were water samples collected during the NAWQA sampling.

Another possible source for arsenic in the Kankakee River Basin is shallow ground water. Shallow ground water in the Kankakee River Basin typically contains large arsenic concentrations (John Winters, Indiana Department of Environmental Management, oral commun., 1992) and is commonly used for irrigation in the basin. The coarse-grained soils in the Kankakee River Basin typically require more irrigation than the fine-grained soils in the Iroquois River Basin.

Concentrations of barium and strontium in water were larger from sites on the Fox River than other sites in the upper Illinois River Basin, and, in a previous section of the report, were attributed to ground-water contributions; however, only concentrations of strontium were larger in the Fox River stream sediments. Carbonate rocks contain considerably less barium than strontium (Hem, 1985), and strontium might possibly be leached from the carbonate particles in the Fox River and be transported in the water column. Barium, on the other hand, would be derived only from wastewater effluent originating from the Ordovician-Cambrian sandstone aquifer, where it is present in the dissolved phase (Gilkeson and others, 1983), and would not be associated with the carbonate-rich streambed sediments.

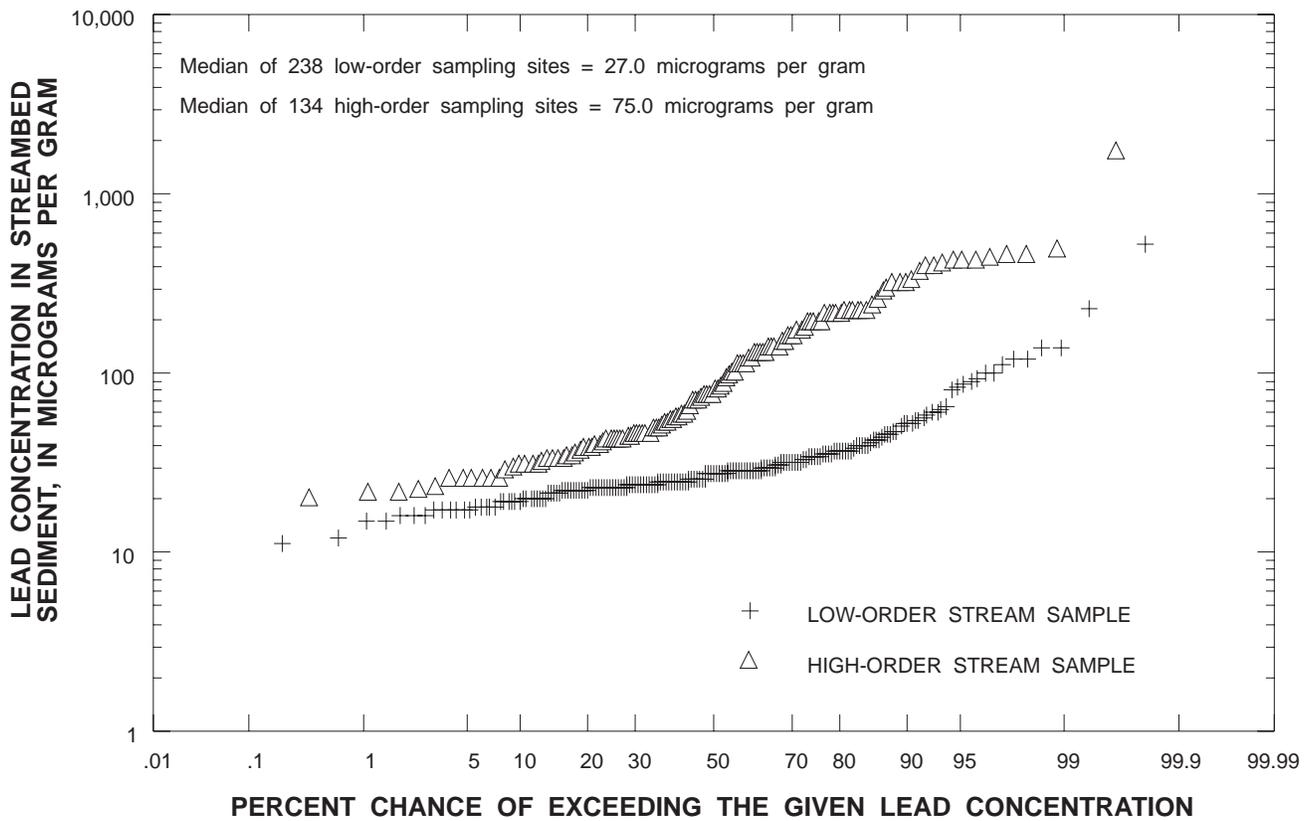
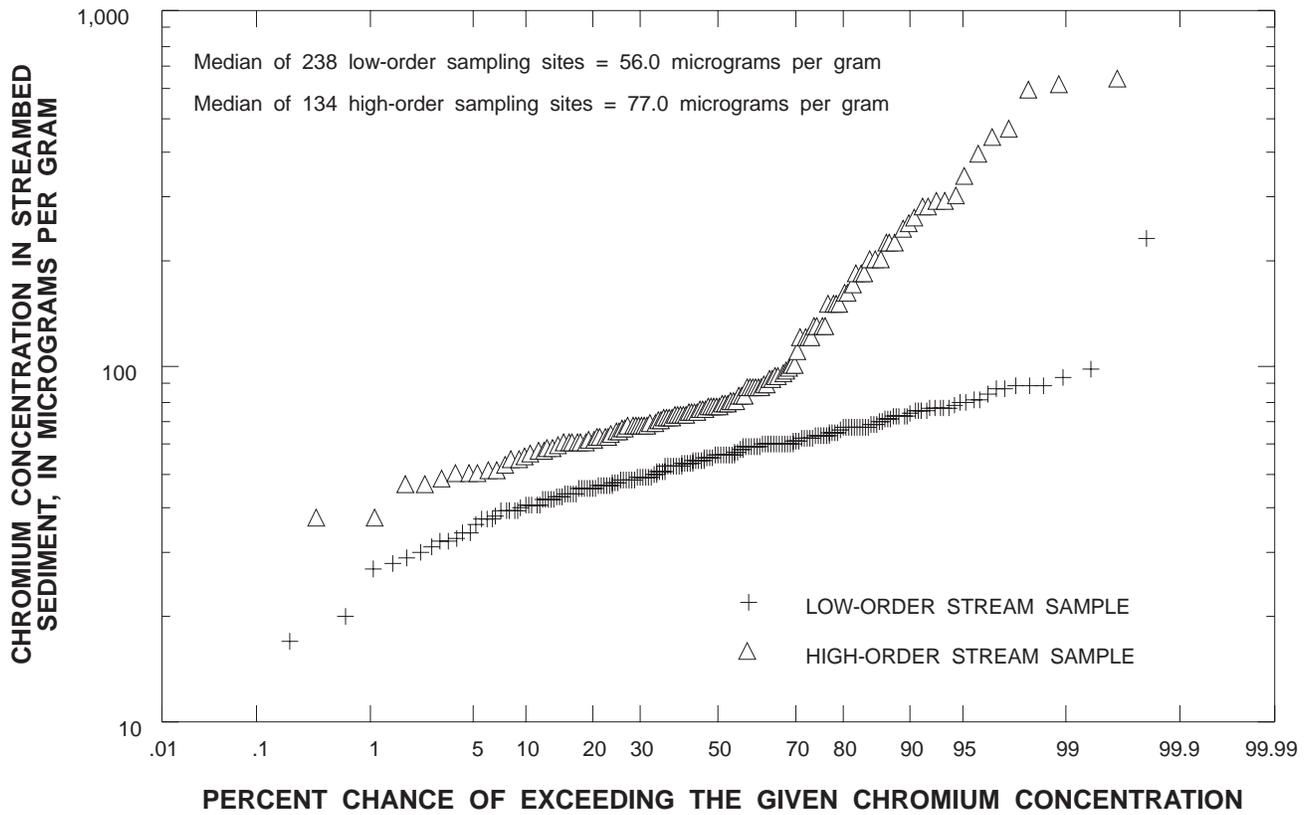
Other studies have identified element concentrations that are elevated or within normal background levels for example, Kelly and Hite (1984). As with the water data, methods of collection, preparation, and analysis may be different among studies. Sieving techniques are variable, with some investigators using

whole sediments and some sieving wet or dry sediments with different sized screens. Digestion techniques also can differ. Thus, any conclusions drawn from comparison of different data sets are limited by these factors. Background concentrations (those not related to human influences) also may cover a wide range, depending on the geologic setting in the study area (table 1).

Rickert and others (1977) proposed that probability plots of background concentrations in the Willamette River in Oregon, would follow a curve with few breaks. Breaks in curves of probability plots represent the delineation between background and elevated concentrations. Probability plots of chromium and lead (fig. 14) are similar to those found in Rickert and others (1977). Data for streambed sediment in these plots were divided into two groups, high-order streams and low-order streams. These plots show that high-order streams typically were more enriched with chromium and lead than low-order streams. The same relation between high- and low-order streams is found for the other priority pollutants that are not shown in figure 14. The curve for chromium at low-order stream sites does not appear to break, whereas the curve for high-order streams appears to break at about 90  $\mu\text{g/g}$ . (In the Willamette River, the break in the chromium curve was at about 60  $\mu\text{g/g}$  (Rickert and others, 1977).) Except for one data point, all the low-order stream data are below this concentration. This distribution of data indicates that background concentration for streams in the upper Illinois River Basin is less than 90  $\mu\text{g/g}$  and that chromium is at background concentrations in the streambed sediment of most low-order streams.

Concentrations above 90  $\mu\text{g/g}$  in streambed sediments were mainly clustered in the Chicago area (Colman and Sanzalone, 1992). Median concentrations above 90  $\mu\text{g/g}$  in suspended sediments were found at the Des Plaines River at Riverside (site 40), the Chicago Sanitary and Ship Canal at Romeoville (site 55), and the Illinois River at Marseilles (site 76). At the other five NAWQA fixed sites, few observations of chromium in suspended sediments were above 90  $\mu\text{g/g}$  (fig. A3).

Probability plots for lead in streambed sediments in high- and low-order streams break at about 40  $\mu\text{g/g}$  (fig. 14), although the breaks are not as well defined as for probability plots of the chromium data. (In the Willamette River, the break in the lead curve also was at about 40  $\mu\text{g/g}$  (Rickert and others, 1977),



**Figure 14.** Probability distributions of chromium, lead, aluminum, and manganese in fine-grained streambed sediments in the upper Illinois River Basin.

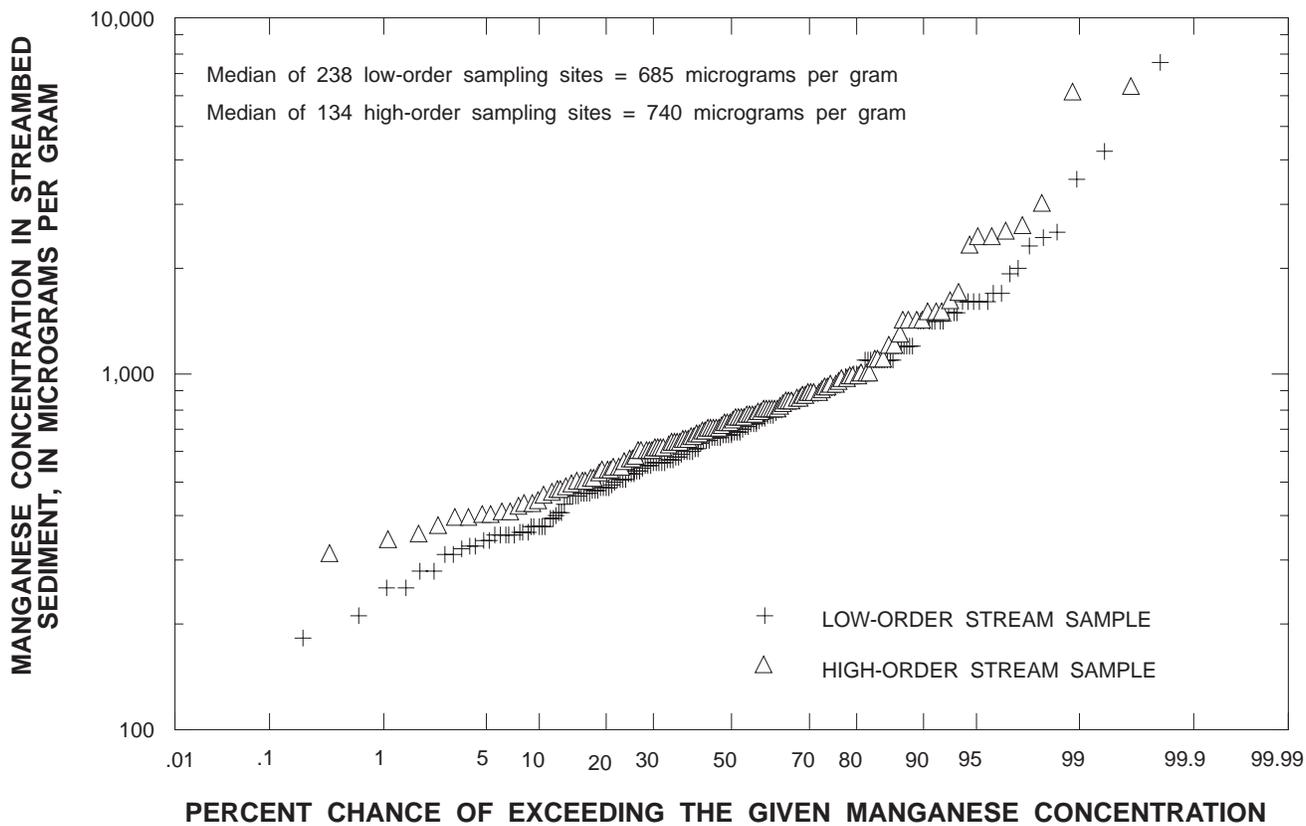
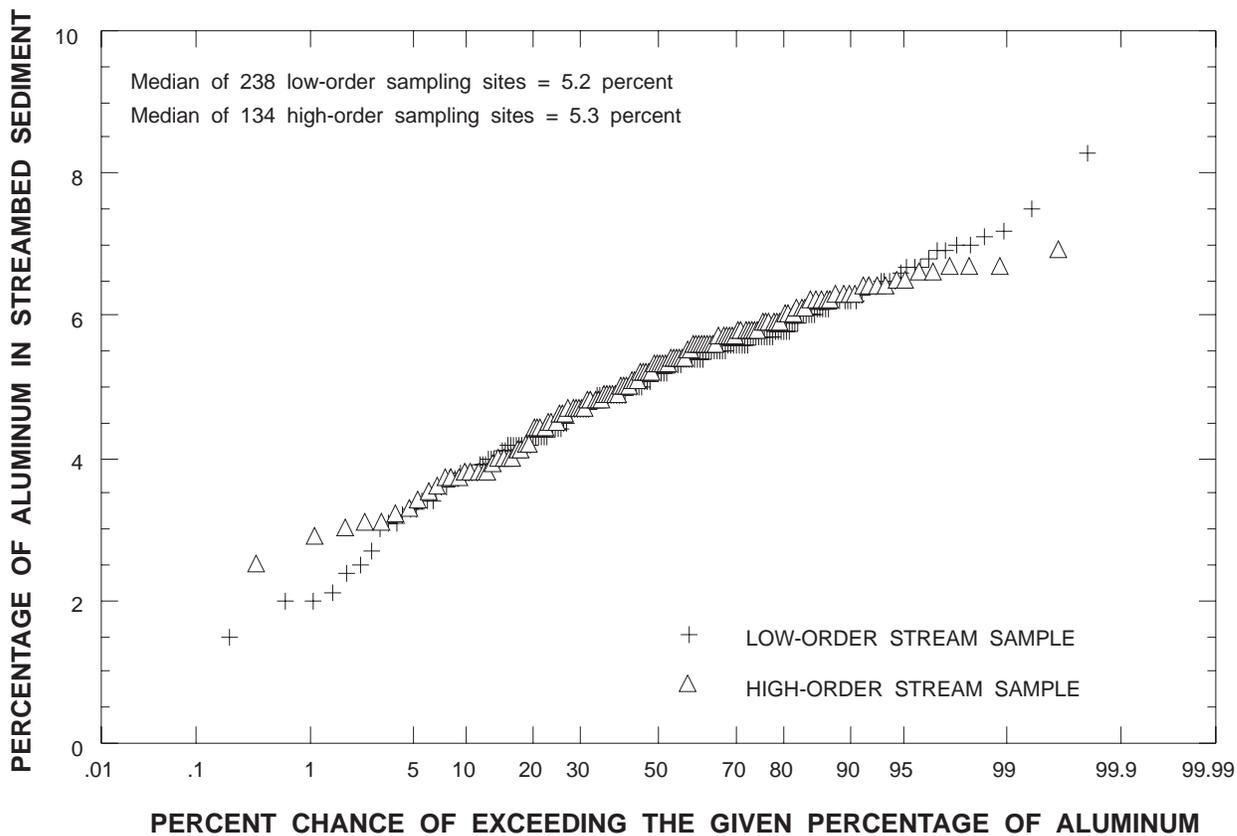


Figure 14. Continued.

although the samples in that study were sieved to the less-than-20- $\mu\text{m}$  fraction.) Concentrations of lead in streambed sediments above these breakpoints were also clustered in the Chicago area and near some medium-sized urban areas outside of Chicago (Colman and Sanzalone, 1992). In suspended sediments from the eight NAWQA fixed sites, median lead concentrations exceeded 40  $\mu\text{g/g}$  at all sites except the Iroquois River (site 28) (fig. A3).

In contrast, the curves from probability plots of aluminum and manganese show that concentrations in high-order streams were very similar to concentrations in low-order streams (fig. 14). The absence of a break in the curve for aluminum indicates that all concentrations of aluminum in streambed sediment in the upper Illinois River Basin were equal to or less than background concentrations. The curve for manganese seems to break slightly around 1,500  $\mu\text{g/g}$ . Concentrations above 1,500  $\mu\text{g/g}$  were found in streambed sediments from the high-order streams of the Kankakee River and occasionally from low-order streams scattered through the Chicago metropolitan area. Median concentration of manganese in suspended sediment from the Kankakee River was about 4,500  $\mu\text{g/g}$  (fig. A3). Median concentrations in suspended sediment from the Des Plaines and Illinois Rivers were between 1,500 and 2,000  $\mu\text{g/g}$  (fig. A3).

Breaks in the curves on the probability plots were compared to a classification scheme designed by Kelly and Hite (1984) that identifies levels of contamination of selected elements in Illinois stream sediments (table 19). Concentrations of elements cannot be compared directly because Kelly and Hite's scheme was based on unsieved sediments that were partially digested, in contrast to the NAWQA samples that were sieved and totally digested. Nevertheless, the breaks in the curves most commonly are near the "elevated" to "highly elevated" concentrations reported by Kelly and Hite (1984), except for chromium. Concentrations from the fine-grained sediment were expected to be larger than those concentrations identified as "slightly elevated" in table 19 because the elements are known to be more concentrated in the fine-grained sediments. The break in the probability curve for chromium (90  $\mu\text{g/g}$ ) corresponded to a concentration greater than "extreme" in Kelly and Hite's (1984) classification. It is not known why the break in the probability curve for chromium is at a more extreme classification than the breaks for the other elements. Chromium concentrations have been

shown to have larger correlation coefficients with grain size than some of the other elements listed in table 19 (Horowitz, 1991); however, the correlation coefficients probably are not appreciably different to explain such a large difference in classification.

Probability plots are helpful in establishing general guidelines for distinguishing background from elevated concentrations of elements in streambed sediments. Elevated concentrations defined in this manner have no significance in terms of ecosystem health or water-quality criteria; they simply are anomalously large compared to the rest of the samples. On the basis of probability plots, concentrations in fine-grained streambed sediments larger than the following concentrations can be considered elevated in the upper Illinois River Basin: arsenic, 10  $\mu\text{g/g}$ ; cadmium, 2  $\mu\text{g/g}$ ; chromium, 90  $\mu\text{g/g}$ ; copper, 80  $\mu\text{g/g}$ ; lead, 40  $\mu\text{g/g}$ ; nickel, 50  $\mu\text{g/g}$ ; and zinc, 200  $\mu\text{g/g}$  (table 19). These concentrations are similar but somewhat larger than those for Great Lakes harbor sediments classified "heavily polluted," and they fall between the "lowest effect level" and "severe effect level" of Ontario sediment-quality guidelines (table 5).

#### **Correlations Among Major and Trace Elements in Sediment, 1987–90**

Correlation coefficients were computed for ranked element data from suspended-sediment samples collected at the eight NAWQA fixed sites from 1987 through 1990 (table 20) and for streambed-sediment samples collected in 1987 (Colman and Sanzalone, 1991) (table 21). Correlation analysis also was done on other physical and geochemical characteristics that have been shown to control element concentrations in sediment. For suspended sediment, the characteristics included discharge, sediment surface area, proportion of the sample less than 0.062 mm, suspended-sediment concentration, and total organic carbon concentration. Total organic carbon data also were analyzed for streambed sediments collected in 1987.

Correlations among the priority pollutants were strong in sieved streambed sediments from high-order streams sampled by NAWQA in 1987 (Colman and Sanzalone, 1991); in a previous section of this report, correlations were shown to be strong among priority pollutants in sieved streambed sediments collected by IEPA from 1982 through 1987 (table 15).

Correlations among priority pollutants in suspended sediment were similar to correlations among priority pollutants in streambed sediments. These

correlations by means of two examples, one for copper and zinc, and one for chromium and nickel are shown in figure 15. Correlation coefficients from suspended-sediment data were greater than 0.65 for all correlations among antimony, cadmium, chromium, copper, lead, nickel, silver, and zinc. Cahill and Steele (1986) observed similar correlations among priority pollutants in backwater sediments from the Illinois River.

Many studies have shown that concentrations of chromium, copper, lead, nickel, and zinc in streambed sediments are affected by or correlated with clay-mineral content, particle size, and the amounts of organic material, total extractable iron, iron hydroxides, total extractable manganese, and manganese hydroxides (Leed and Belanger, 1981; Förstner and Salomons, 1983; Alberts and others, 1984; Johnson, 1986; Horowitz and Elrick, 1987; Holden, 1989; Horowitz and others, 1989). In studies in or near the upper Illinois River Basin, significant correlations were found between these metals and clay content and organic content in the upper Mississippi River sediments (Bailey and Rada, 1984; Buhl and McConville, 1984), upper Peoria Lake sediments (Collinson and Shimp, 1972), and backwater sediments along the Illinois River (Cahill and Steele, 1986). In this study, concentrations of chromium, copper, lead, nickel and zinc in suspended sediment from the eight NAWQA fixed sites did not correlate with surface area, amount of sample less than 0.062 mm, total organic carbon content, or iron and manganese concentrations. As an example, figure 16 illustrates the lack of correlations between copper concentrations and surface area and between nickel concentrations and surface area in suspended sediments. Considerable scatter in concentrations is evident in the range of 5 to 20 square meters per gram.

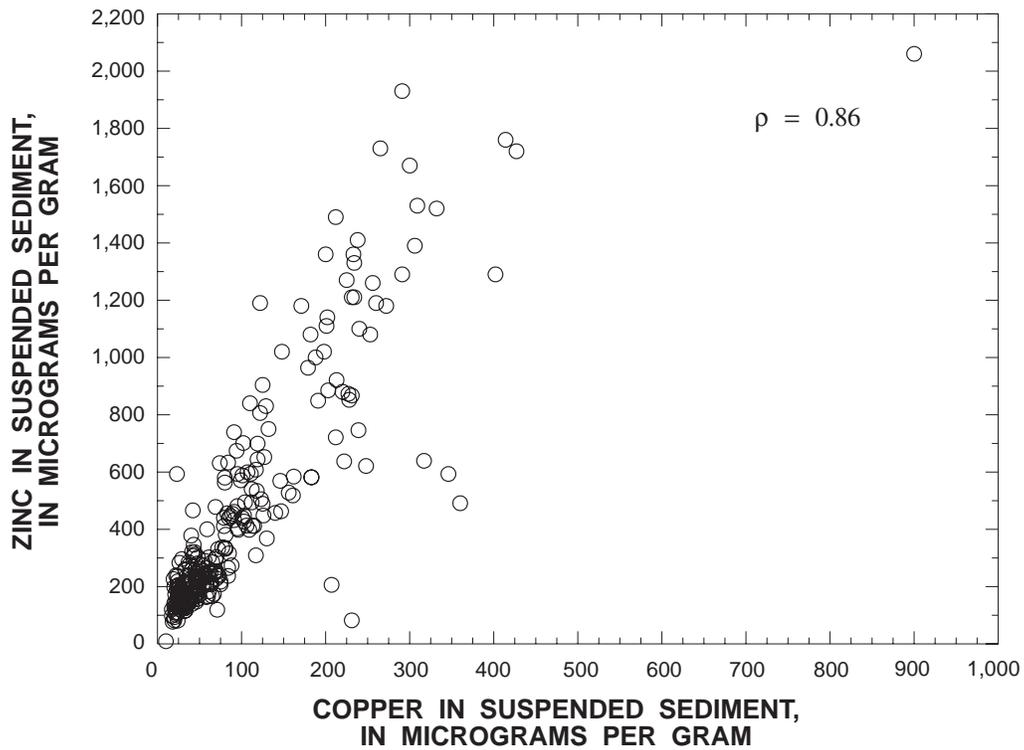
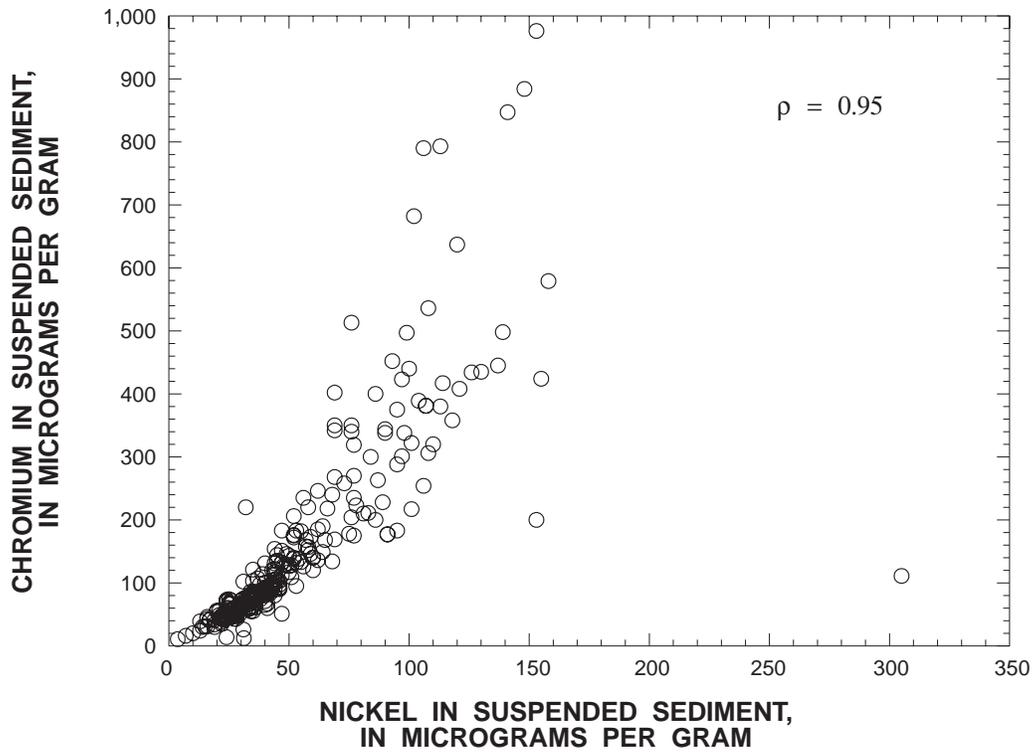
Correlations from individual NAWQA fixed sites (table 20) were examined to determine whether the lack of correlation observed between the urban-associated metals and other elements and properties was related to the mixing of data from individual sites with varying correlations. The difference in correlations between surface area and copper and nickel differed from site to site is shown in figure 17. Although copper did not correlate with surface area at the Iroquois River (site 28), copper and surface area negatively correlated ( $\rho = -0.58$ ) at the Illinois River (site 76) (fig. 17). Nickel in suspended sediment from the Iroquois River (site 28) and the Illinois River

(site 76) did not correlate with surface area (fig. 17); however, correlations were found for the Kankakee River (site 14) and the Fox River (site 99) (table 20).

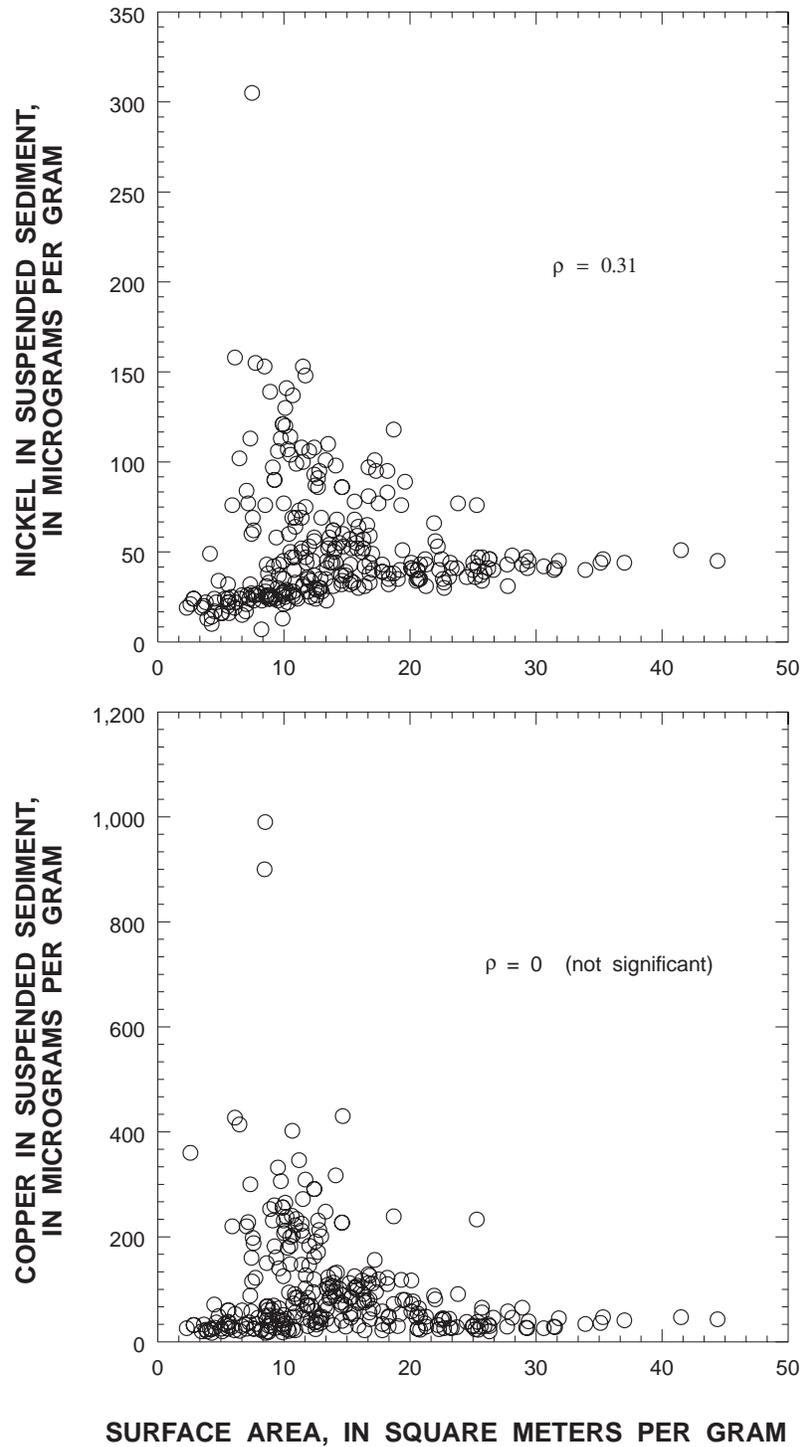
Chromium, copper, lead, nickel, and zinc concentrations in suspended sediment did not correlate with streamflow in the upper Illinois River Basin in data from all eight NAWQA sites combined. However, lead and nickel in suspended sediments positively correlated with streamflow at the Fox River at Dayton (site 99) ( $\rho = 0.57$  and  $0.56$ , respectively), whereas lead and nickel negatively correlated with streamflow at the Illinois River at Marseilles (site 76) ( $\rho = -0.62$  and  $-0.64$ , respectively). These substantial differences indicate that the correlation between metal concentrations and streamflow is complex and not predictable from site to site in the upper Illinois River Basin.

Two priority pollutants, arsenic and beryllium, did not correlate with the other priority pollutants in suspended sediment or in streambed sediment. As mentioned earlier, large concentrations of arsenic and beryllium in streambed sediments were not limited to urban areas. In suspended sediments, beryllium strongly correlated with aluminum, iron, potassium, vanadium, and surface area, and inversely correlated with calcium. Thus, beryllium concentrations in suspended sediment seem to be strongly related to clay minerals. Arsenic in suspended sediment from the eight NAWQA fixed sites combined, correlated with iron ( $\rho = 0.67$ ) but did not correlate with the other clay-mineral-related elements. Correlations from the individual sites show that arsenic correlated with iron at only four of the NAWQA fixed sites (table 20).

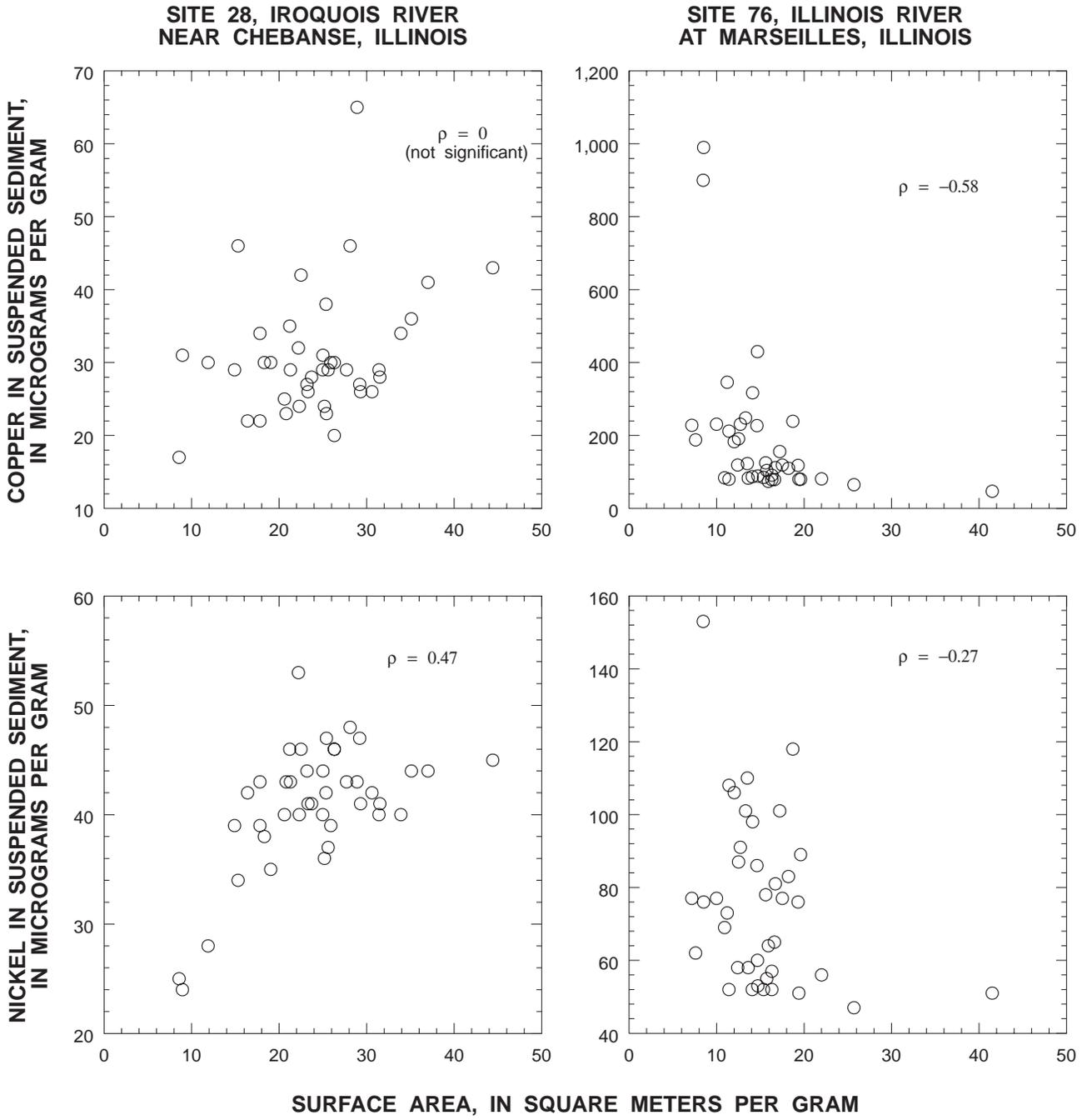
Correlations between arsenic and iron and manganese concentrations in suspended sediments were generally similar (but weak) in magnitude. This result contrasts with the Förstner and Salomons (1983) finding that arsenic is commonly associated more with iron coatings than with manganese coatings or organic material. At the Kankakee River at Momence (site 14), for example, correlation coefficients were large between arsenic and iron and arsenic and manganese ( $\rho = 0.80$  and  $0.79$ , respectively). At the Iroquois River near Chebanse (site 28), in contrast, arsenic correlated weakly with iron ( $\rho = 0.32$ ) and did not correlate with manganese. At the Chicago Sanitary and Ship Canal (site 55), neither iron nor manganese correlated with arsenic. Arsenic in streambed sediment correlated weakly with iron ( $\rho = 0.41$ ). Correlations between arsenic and iron in



**Figure 15.** Correlations among selected priority pollutants in suspended sediments from the upper Illinois River Basin ( $\rho$  = Spearman's ranked correlation coefficient).



**Figure 16.** Correlations between surface area and copper and nickel concentrations in suspended sediments from the upper Illinois River Basin ( $\rho$  = Spearman's ranked correlation coefficient).



**Figure 17.** Correlations between surface area and copper and nickel concentrations in suspended sediments at two sites in the upper Illinois River Basin ( $\rho$  = Spearman's ranked correlation coefficient). (Site numbers refer to table 6.)

historical streambed-sediment data (table 15) were even weaker ( $\rho = 0.30$ ).

In suspended sediments (table 20) and in streambed sediments (table 21), correlations were strong among aluminum, potassium, and vanadium ( $\rho > 0.84$ ). These three elements in suspended sediment also correlated with sediment surface area and inversely correlated with calcium concentrations. Correlations with surface area seem to form a logarithmic curve (fig. 18). Cahill and Steele (1986) found that aluminum, potassium, and vanadium in streambed sediments are related to clay minerals in the clay-sized fraction of the sample. The inverse correlation of aluminum, potassium, vanadium, and surface area to calcium in the sediment in the upper Illinois River Basin indicates that calcium may be derived from larger grained particles of calcite. Calcite typically has a smaller surface area than most clay minerals (Horowitz, 1991). Therefore, smaller surface areas may indicate a greater amount of calcite in the suspended sediments, whereas larger surface areas may indicate a greater amount of clay minerals in the sediment. Most suspended sediments sampled contained a larger proportion of clay- and silt-sized particles (greater than 80 percent) (Sullivan and Blanchard, 1994).

Iron correlated with aluminum at all but one NAWQA fixed site and also with vanadium ( $\rho = 0.70$ ) and surface area ( $\rho = 0.72$ ). The relation between iron and aluminum in suspended sediment from an agricultural and urban site is shown in figure 19. Horowitz (1991) reported that, in general, iron is not considered a common component of clay minerals; instead, it is associated with iron oxide coatings on the surfaces of particulates. It is possible that the aluminum- and vanadium-containing clay minerals provide a large surface area that can be coated with iron oxides.

### **Seasonal Variations and Long-Term Changes, 1978–90**

Seasonal variations in median element concentrations in suspended sediment were significant at each of the eight NAWQA fixed sites (Kruskal-Wallis ANOVA,  $p \leq 0.10$ ). Seasonal variations in median concentrations in suspended sediments, however, did not relate to seasonal variations in median total recoverable concentrations from the same eight sites, nor did they relate to discharge, volatile and total suspended-solids concentrations, or suspended-

sediment concentrations. Concentrations of many elements in suspended sediment, including aluminum, antimony, beryllium, cobalt, iron, manganese, nickel, and vanadium, were largest in February. However, monthly variations were not similar among any element concentrations for the rest of the months. As mentioned previously, pH was lowest in February; thus, pH may have been a factor in controlling the concentrations of elements associated with the suspended sediment. When pH is low, these elements seem to accumulate in larger concentrations in the suspended sediment than when pH is high.

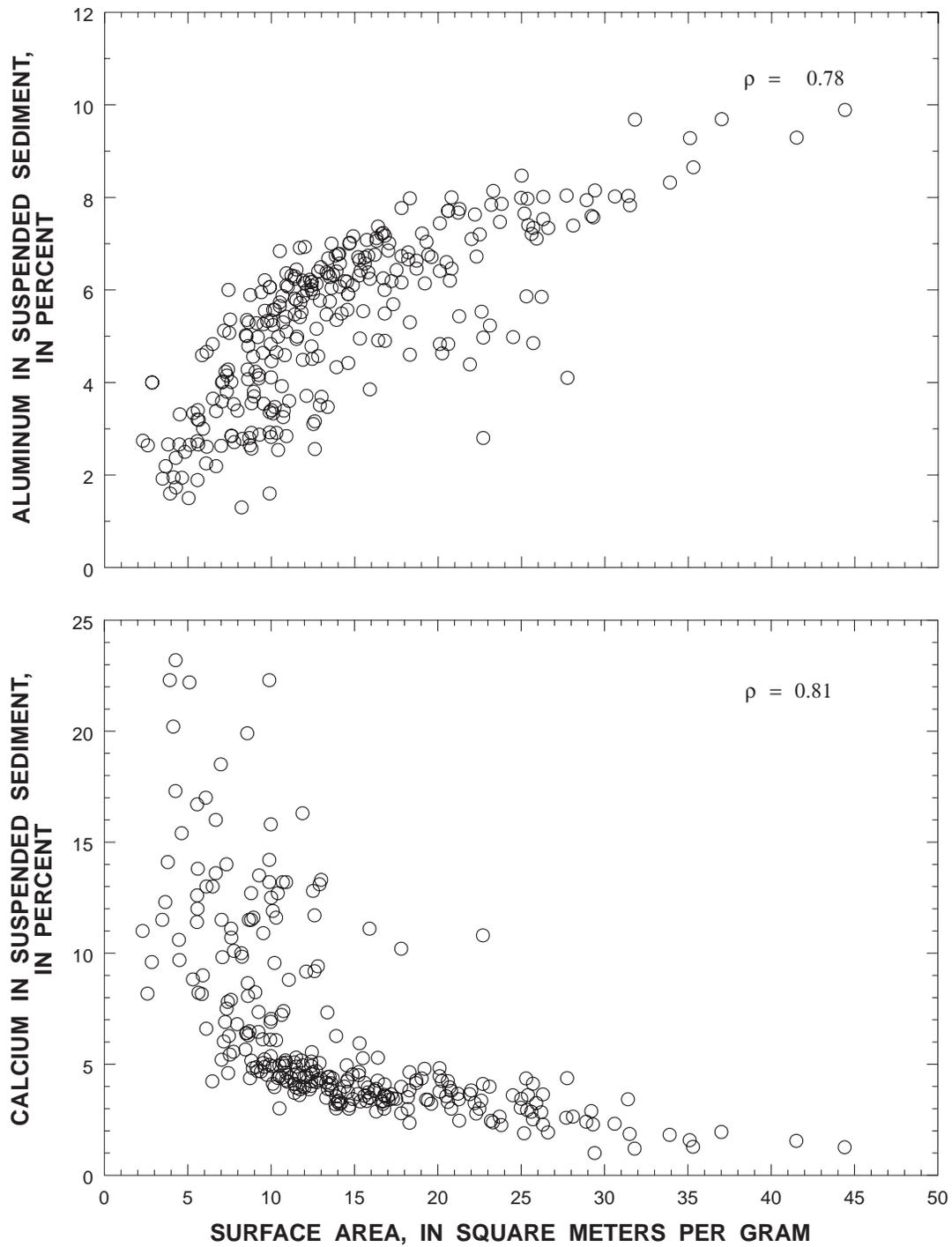
No trend analyses were done on elements in suspended sediment or streambed sediment because the sampling periods were too short. In general, concentrations were similar between streambed sediments collected by USGS in 1987 and sieved streambed sediments collected by IEPA from 1982 through 1987. Elements associated with urban sources from the IEPA data also were associated with urban sources in the 1987 USGS data. Two exceptions were chromium and manganese, which were larger in samples collected during the 1987 NAWQA synoptic sampling than identified in IEPA data collected from 1982 through 1987. Different analytical techniques (partial digestions for the IEPA data and total digestions for the NAWQA data) may account for these differences.

## **Biota**

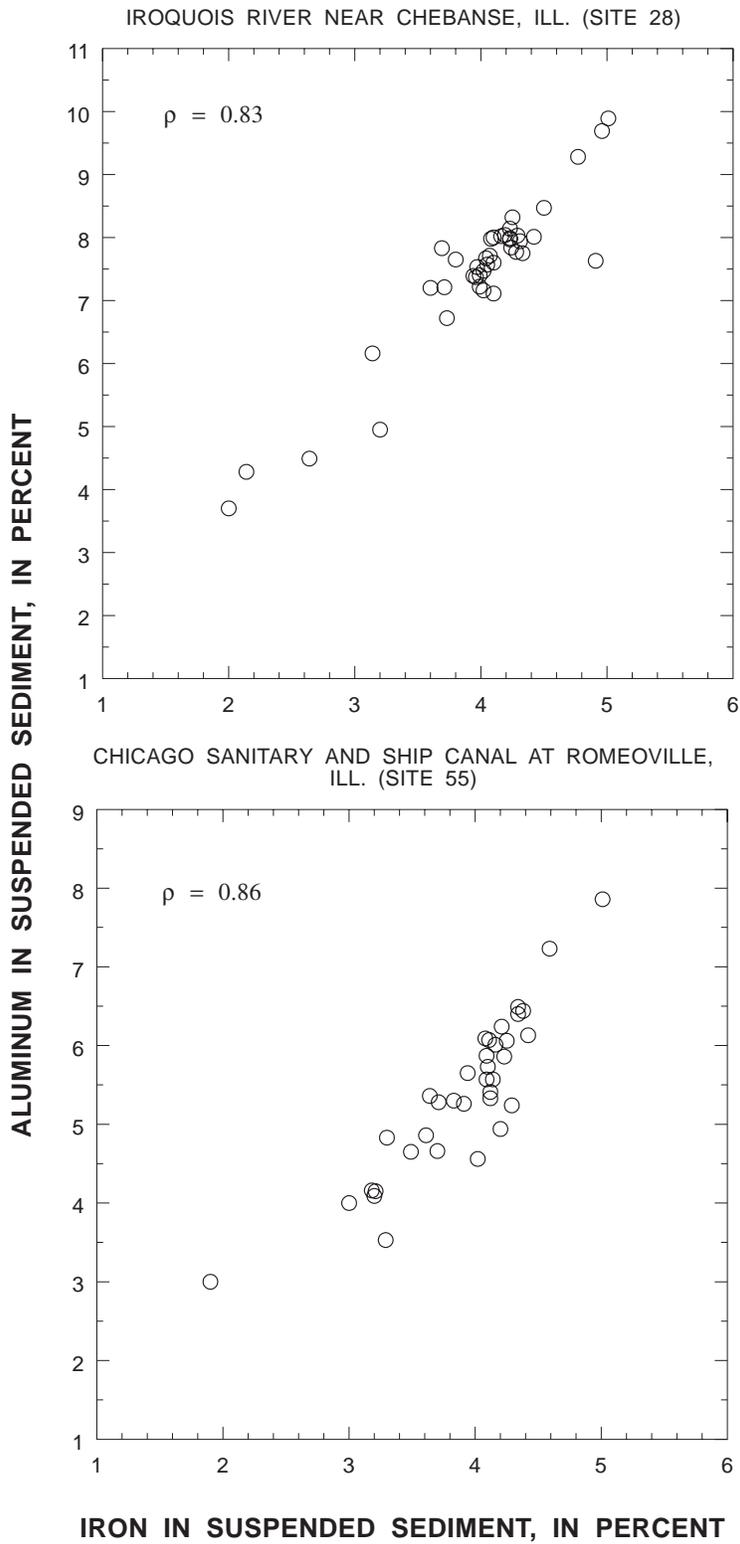
### **Results of Biotic Data Collection, 1989 and 1990**

Major element and trace element concentrations in biota from the upper Illinois River Basin were interpreted on the basis of samples collected from 15 sites in 1989 and 25 sites in 1990 (table A1). Comparisons of element concentrations in biota among sites could not be statistically examined because of an insufficient number of samples at any one site and for any one species of biota. However, histograms of selected elements in fish livers, mollusks, caddisflies, crayfish, and plants (figs. 20–23, respectively) indicate the wide variability and possible enrichment of some elements in biota in the upper Illinois River Basin.

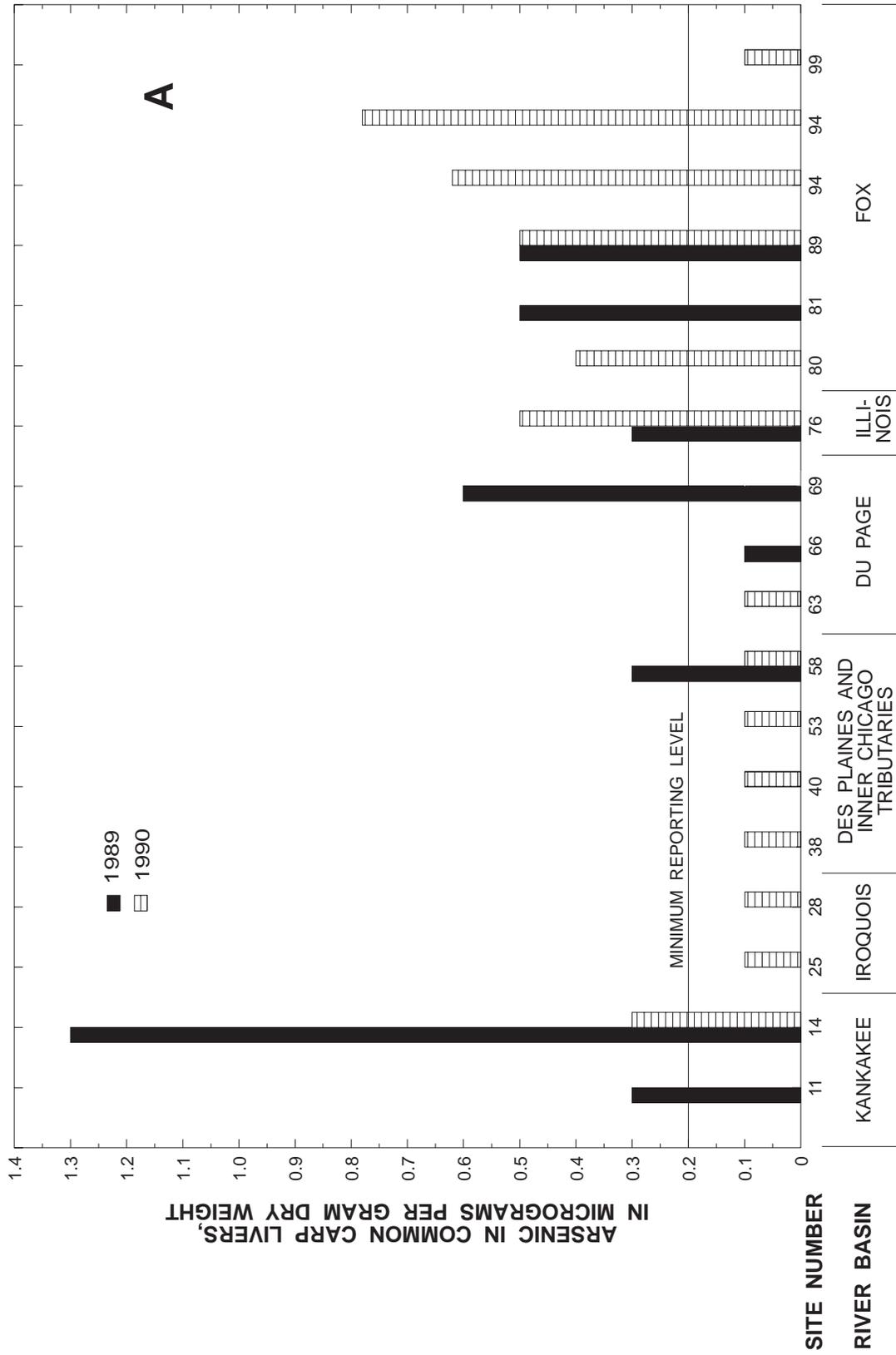
Comparable data from the literature were limited for evaluation of element concentrations in biota from the basin. Although some element concentrations in soft tissues of mollusks could be converted to wet weight (by use of the percent



**Figure 18.** Effects of sediment surface areas on concentrations of aluminum and calcium in suspended sediments from the upper Illinois River Basin ( $\rho$  = Spearman's ranked correlation coefficient).



**Figure 19.** Relations of aluminum and iron in suspended sediments at two sites in the upper Illinois River Basin, 1987–90 ( $\rho$  = Spearman's ranked correlation coefficient). (Site numbers refer to table 6.)



**Figure 20.** Element concentrations in common carp and white sucker livers from the upper Illinois River Basin, 1989–90. (Concentrations below the minimum reporting level were set to 0.1 microgram per gram.) (Site numbers refer to table 6.)

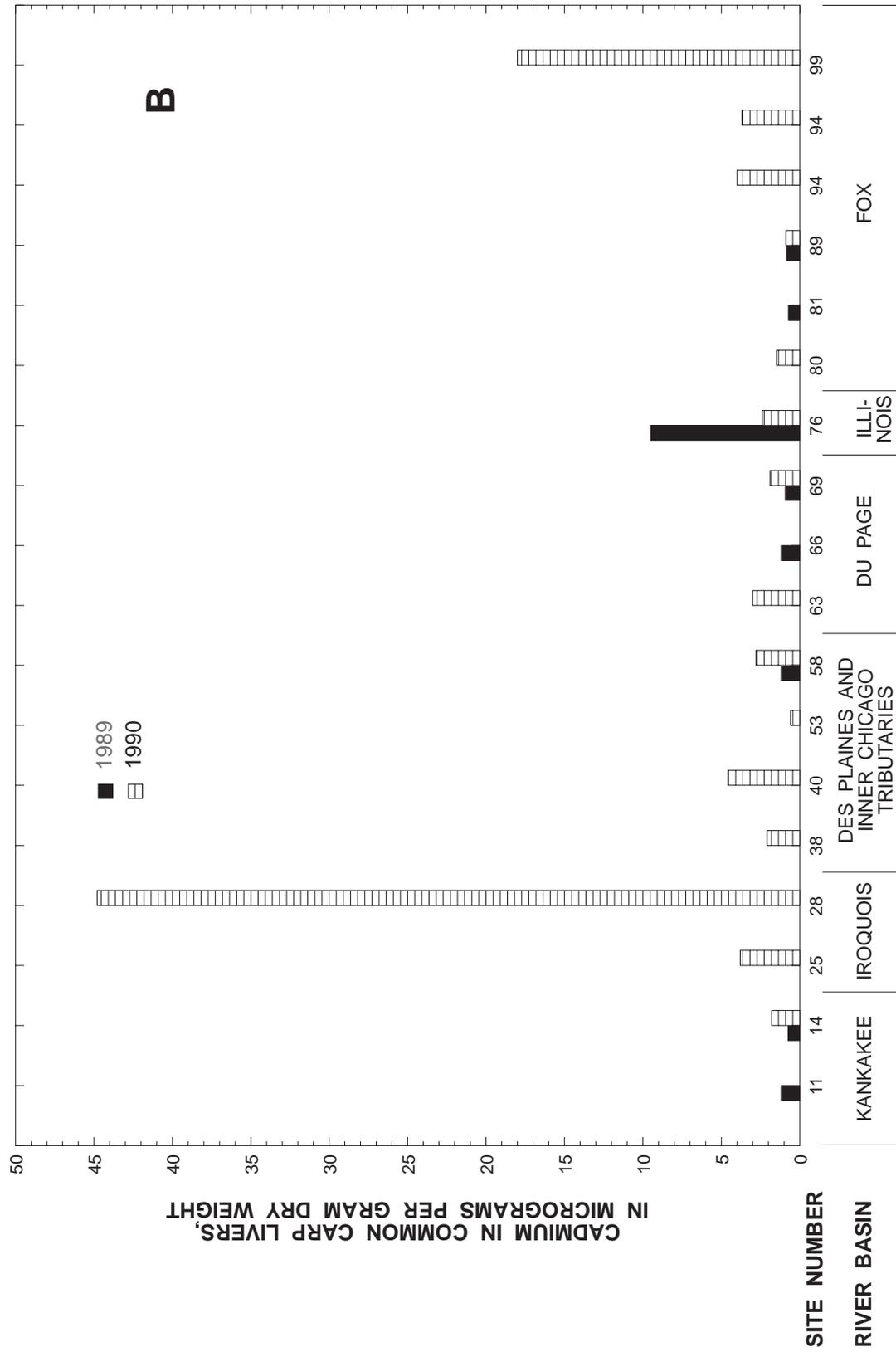


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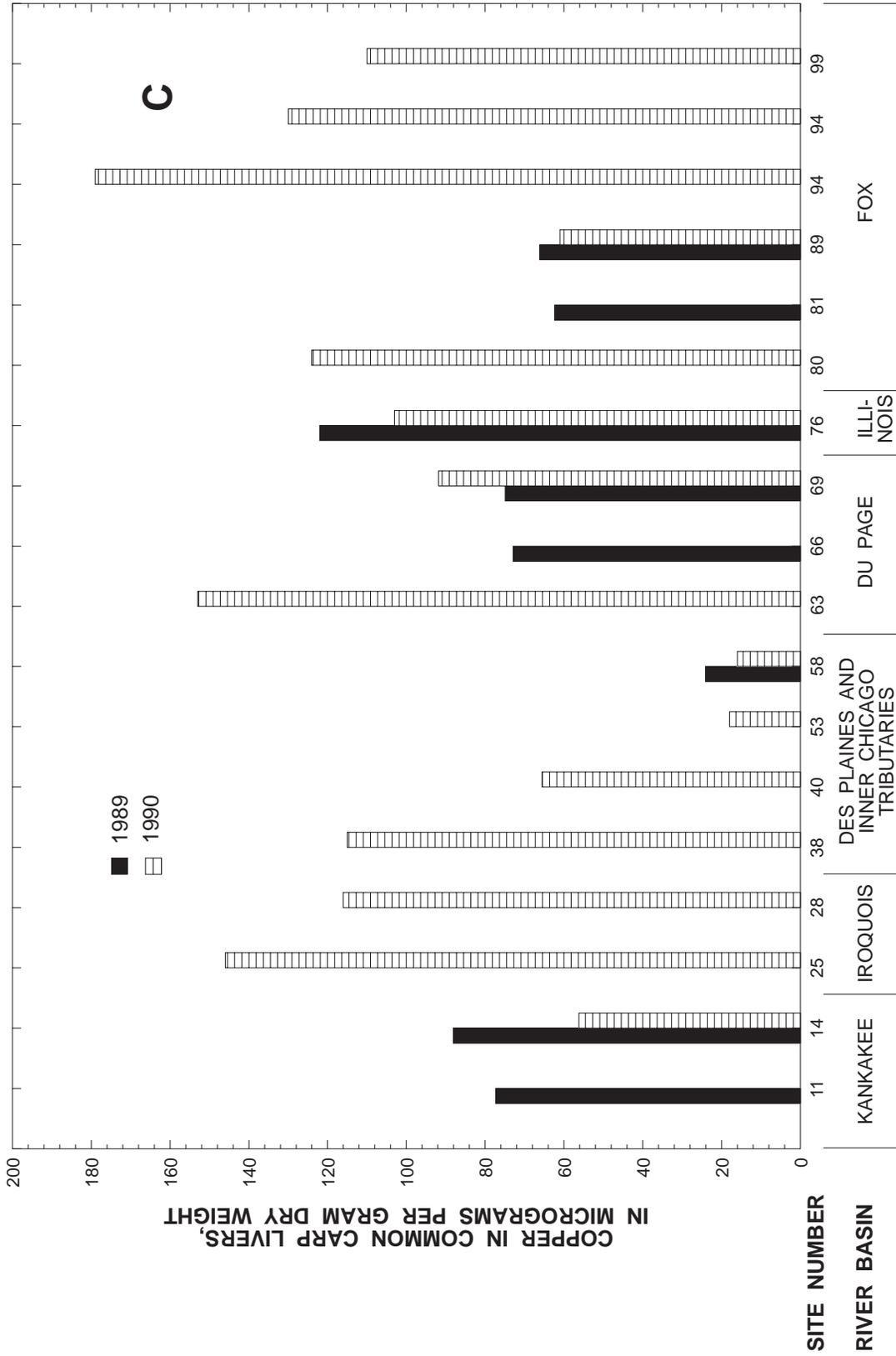


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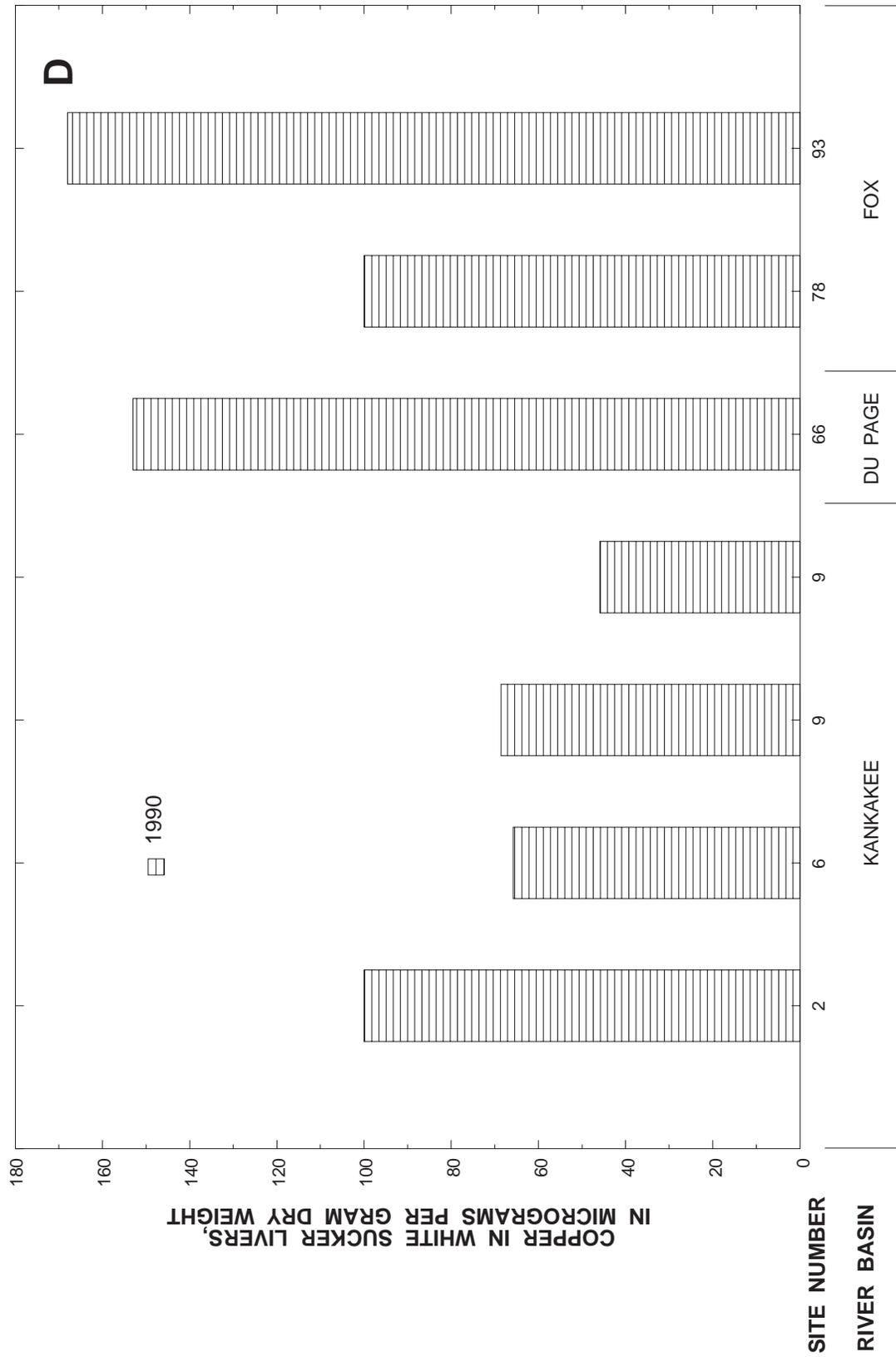


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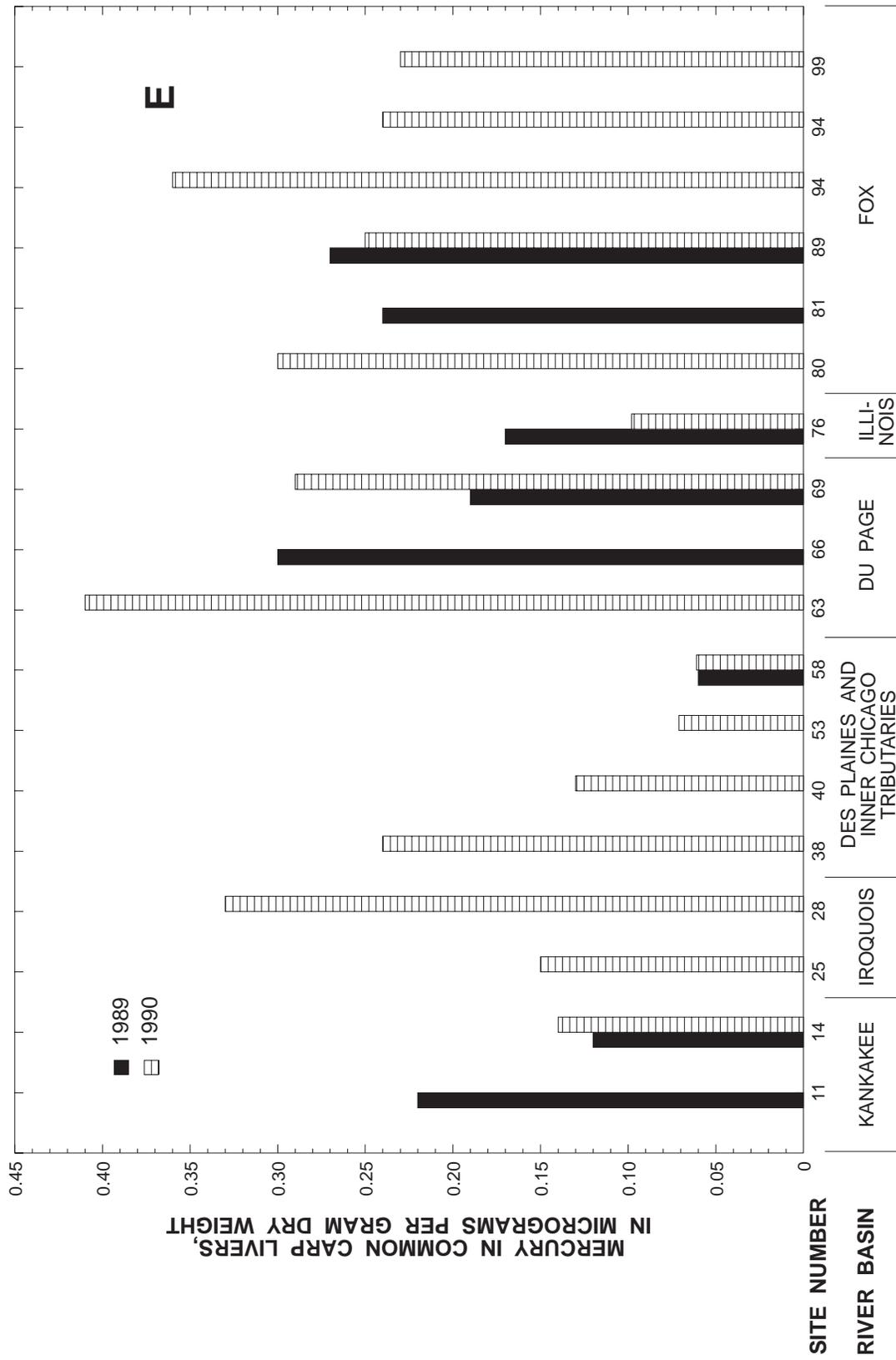


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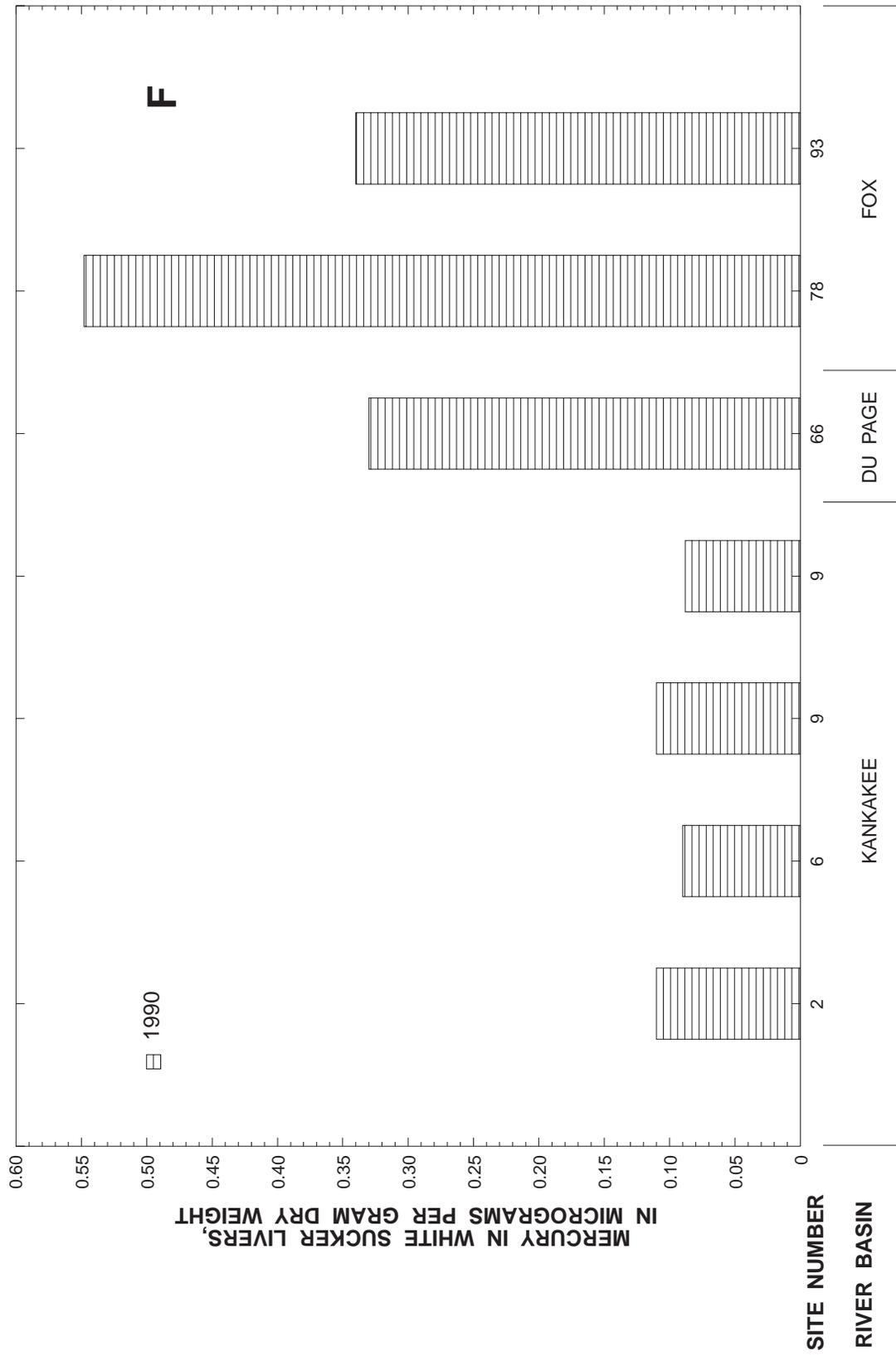


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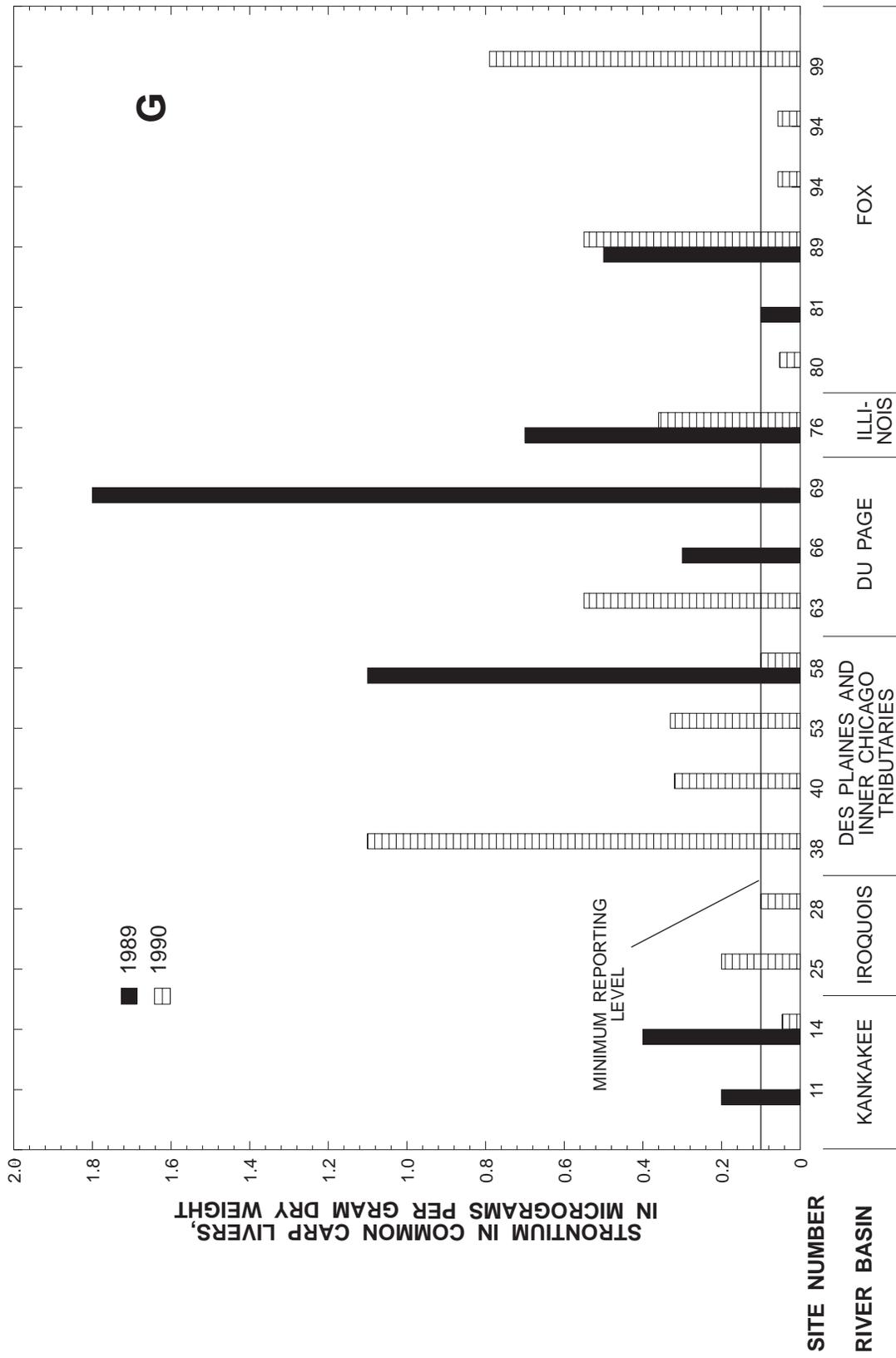


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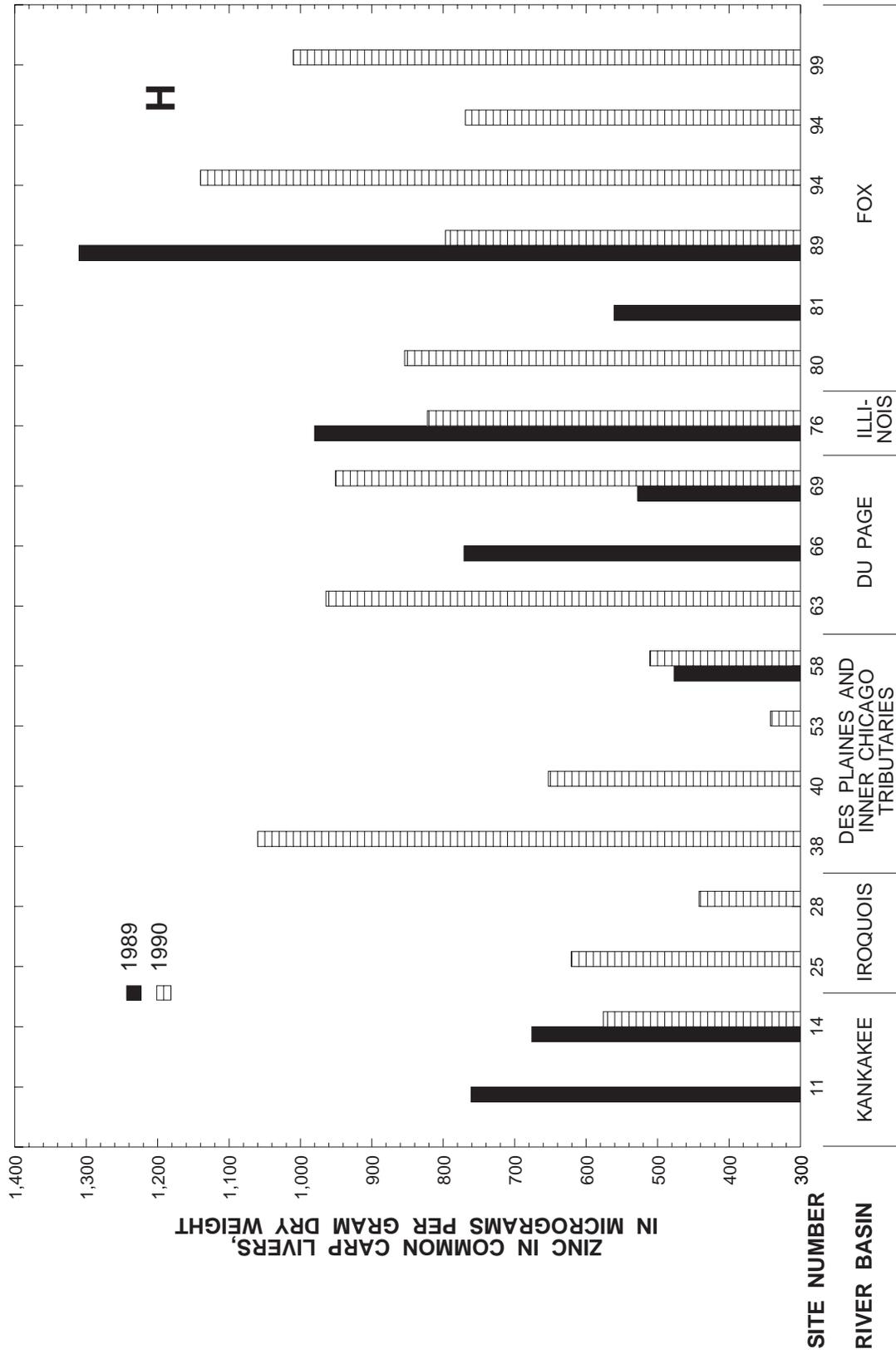


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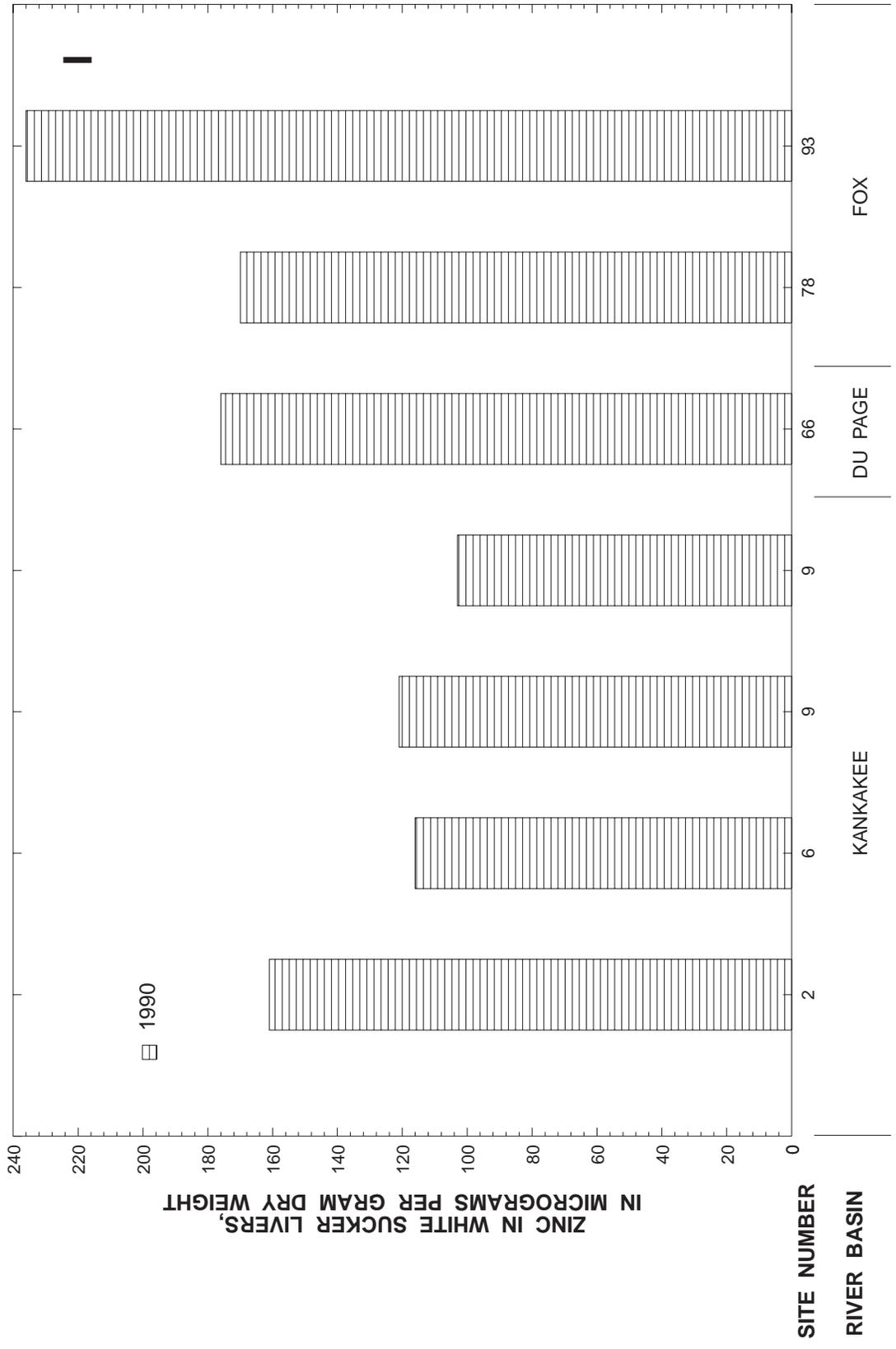


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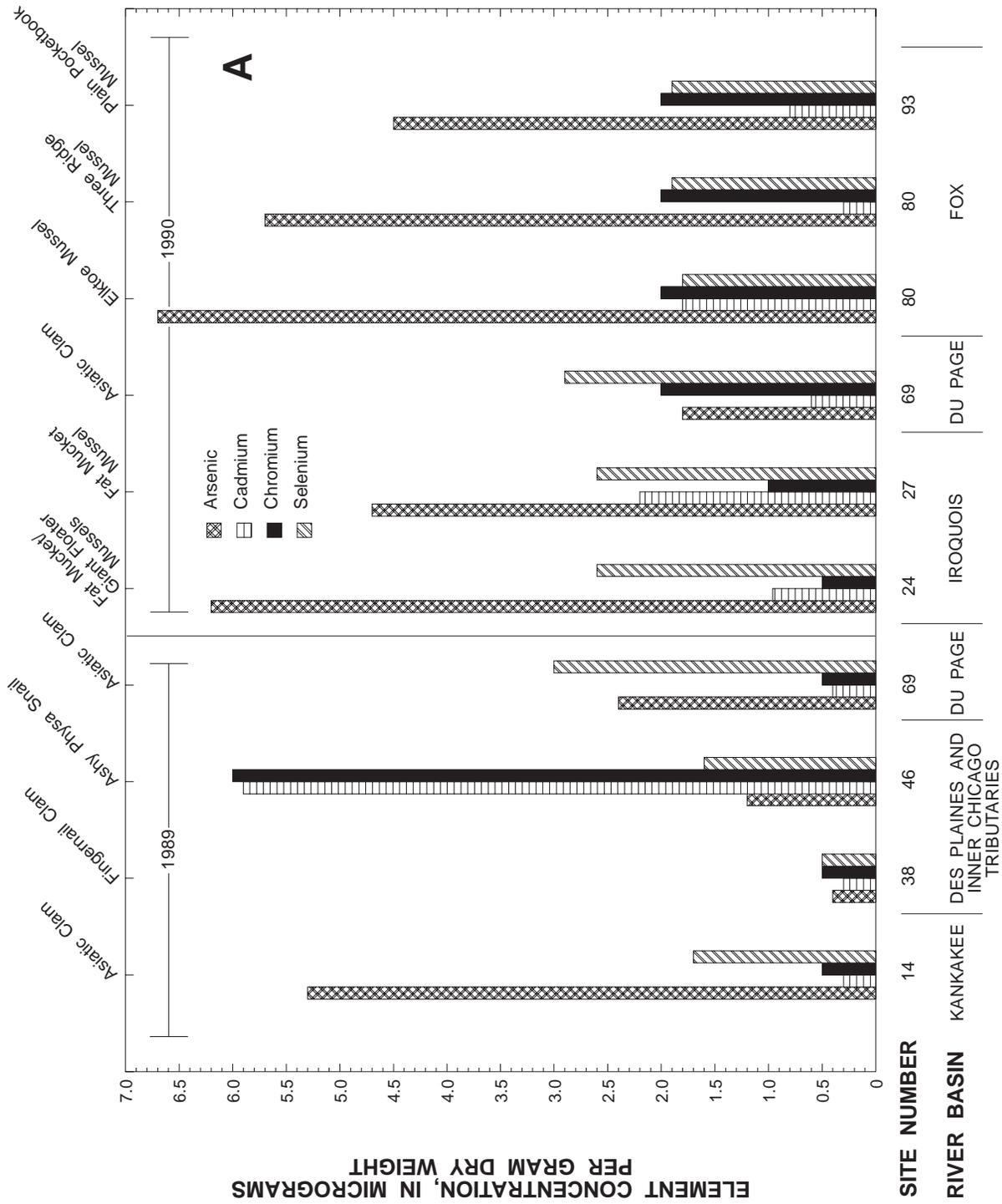


Figure 21. Element concentrations in mollusks from the upper Illinois River Basin, 1989–90. (Site numbers refer to table 6.)

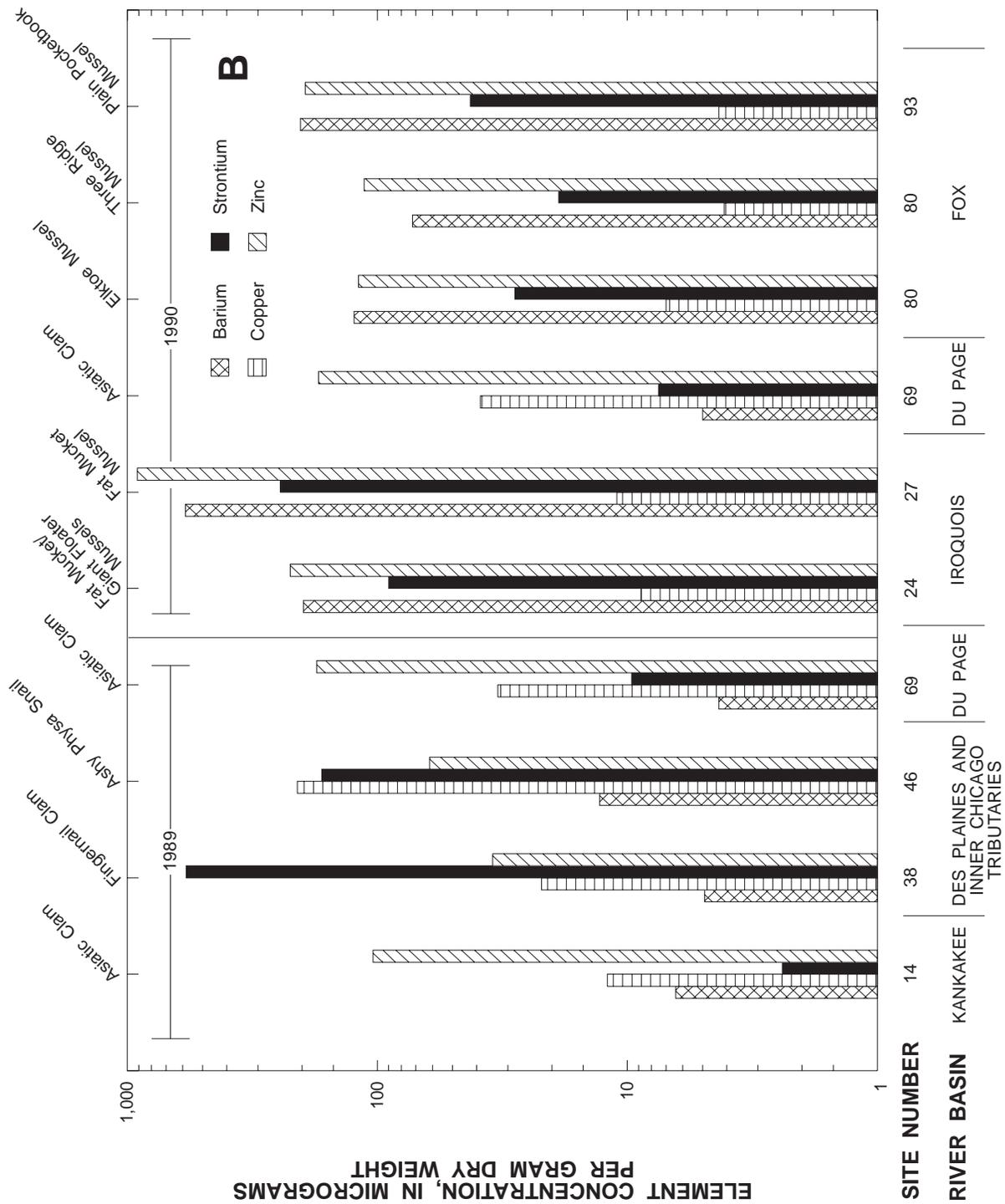


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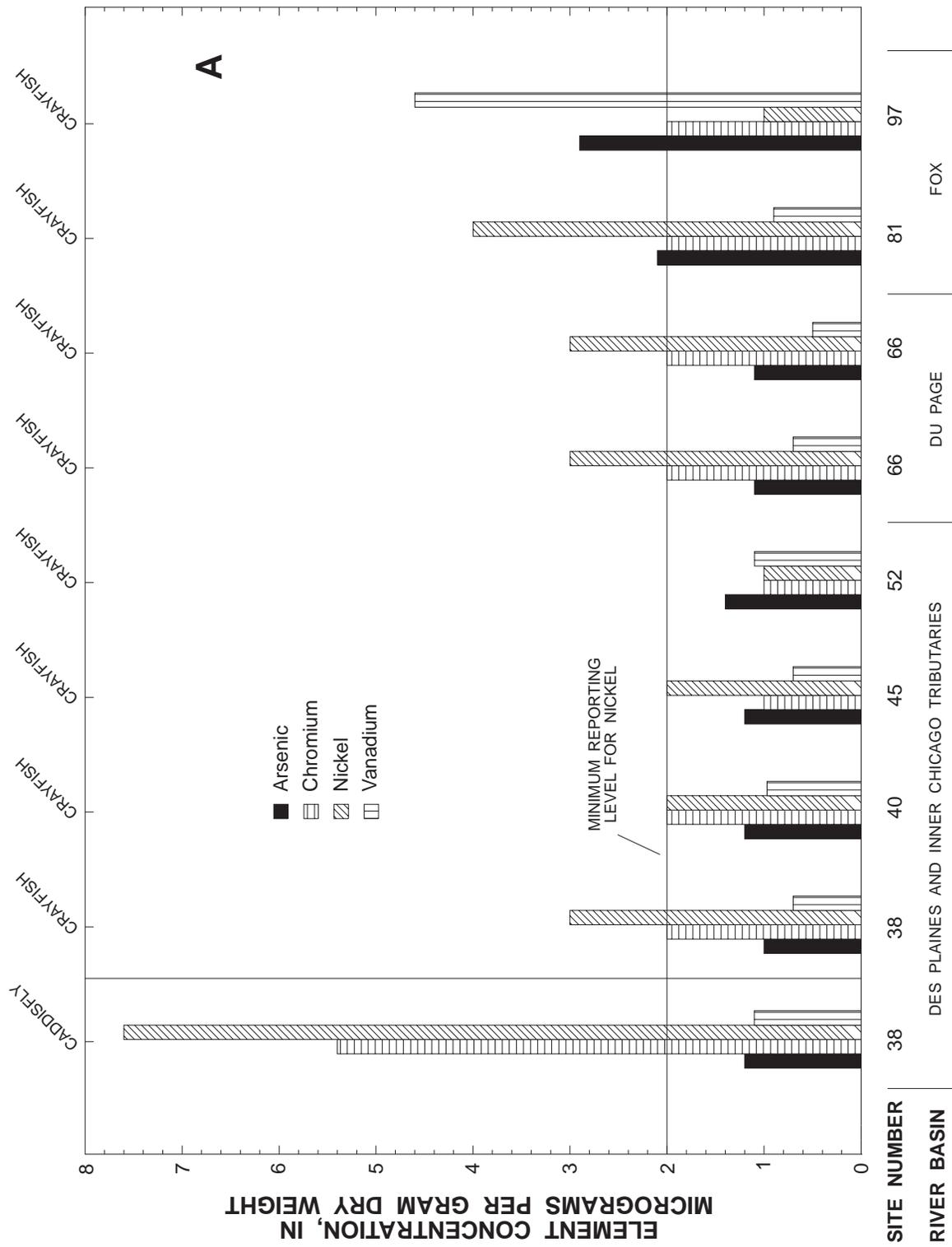


Figure 22. Element concentrations in caddisflies and crayfish from the upper Illinois River Basin, 1989. (Concentrations below the minimum reporting level of nickel were set to 1 microgram per gram.) (Site numbers refer to table 6.)

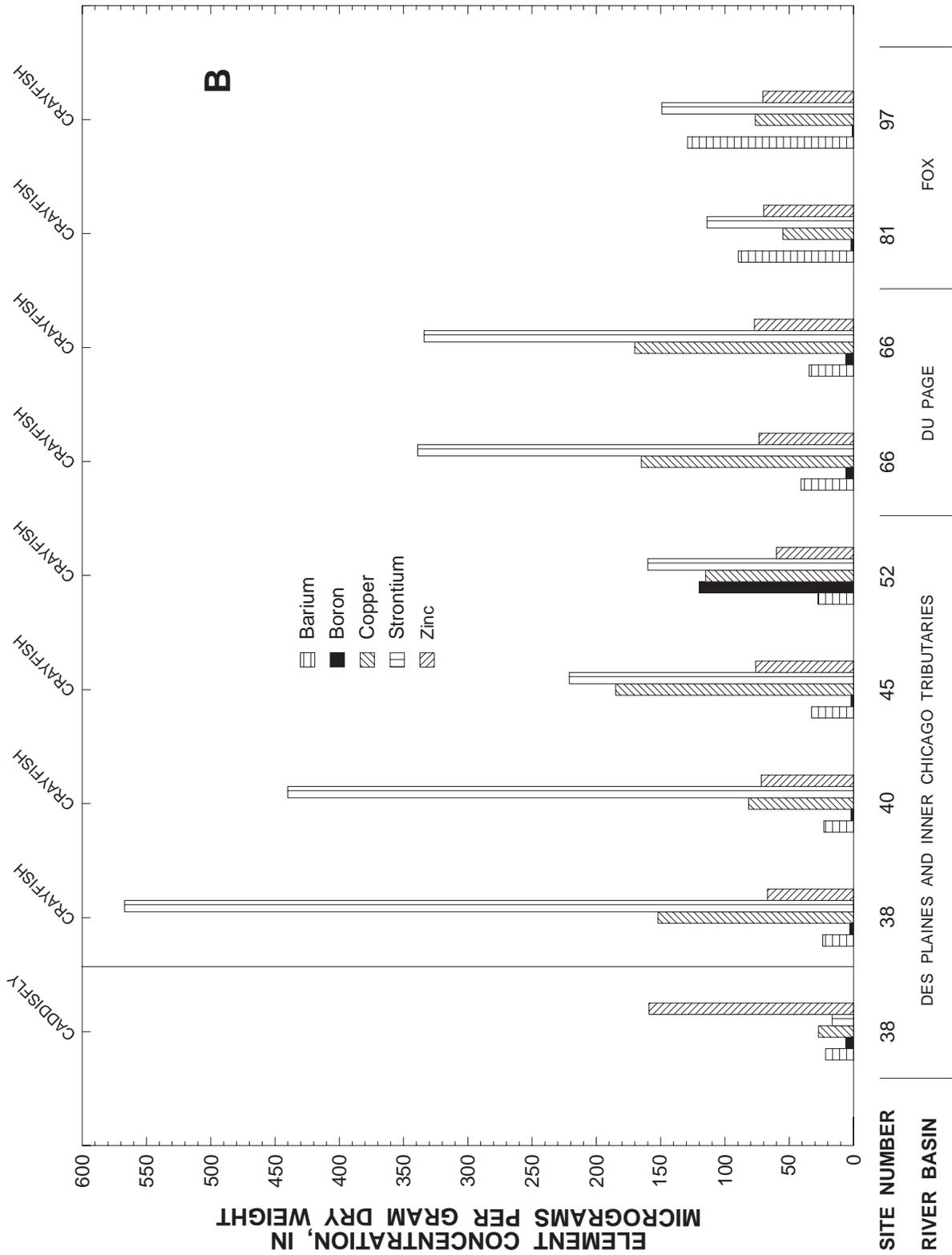


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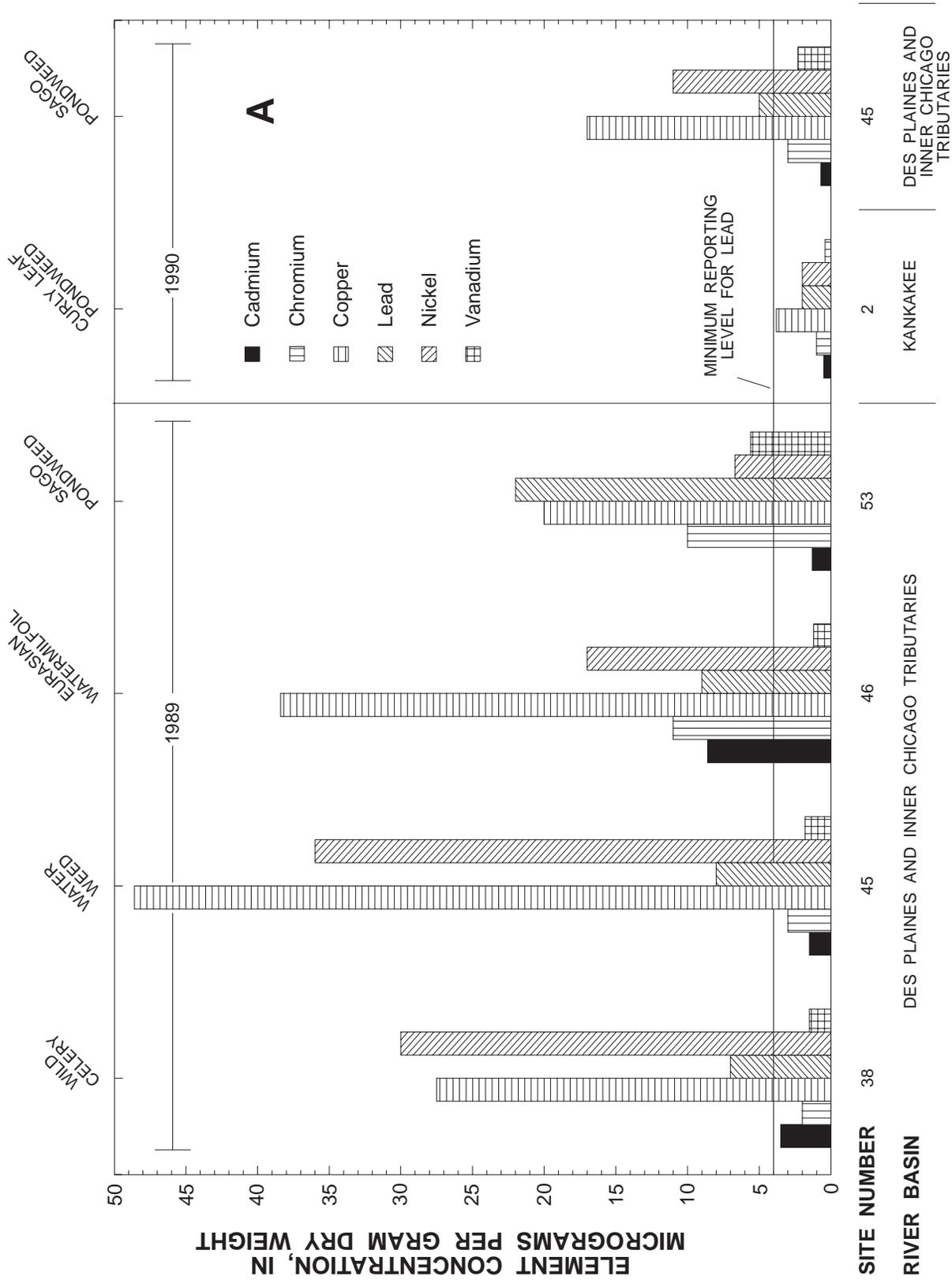


Figure 23. Element concentrations in plants from the upper Illinois River Basin, 1989–90. (Concentrations of lead below the minimum reporting level were set to 2 micrograms per gram.) (Site numbers refer to table 6.)

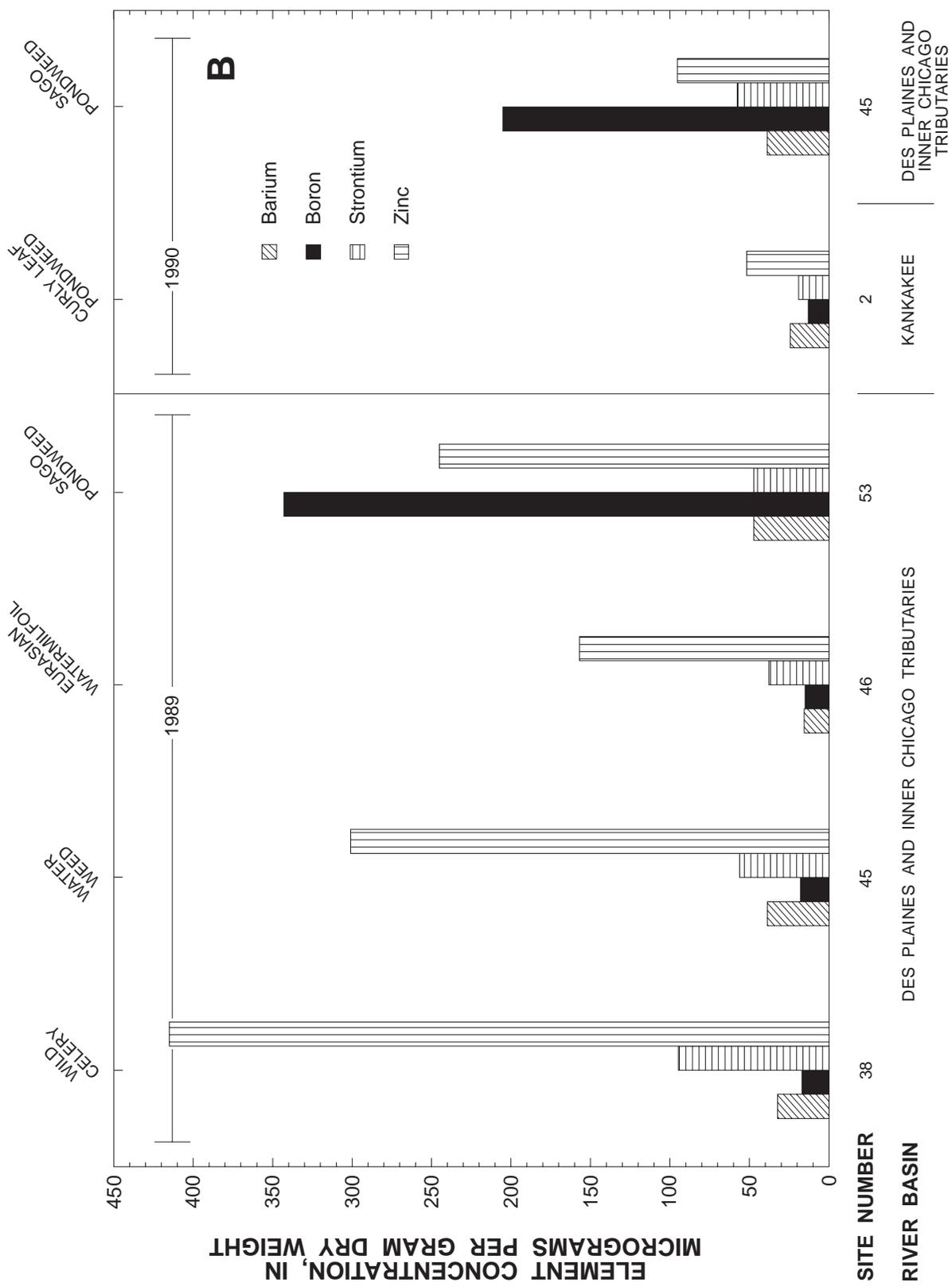


Figure 23. Continued.

moisture values obtained for each composite sample) and compared to the Median International Standard (MIS) for marine shellfish (Nauen, 1983), element concentrations in fish livers from this study are not directly comparable to concentrations in whole fish collected by the National Contaminant Biomonitoring Program (NCBP) of the U.S. Fish and Wildlife Service (Schmitt and Brumbaugh, 1990). (As of 1991, the NCBP is now known as the Biomonitoring of Environmental Status and Trends (BEST) program.) With the exception of aluminum and mercury, concentrations of elements in whole fish are generally lower than in fish livers (Bollingberg and Johansen, 1979; Boyer, 1984; Saltes and Bailey, 1984; Brumbaugh and Kane, 1985; Cuvin-Aralar and Furness, 1990; Harrison and Klaverkamp, 1990). Wiener and others (1984) found significant correlations between whole common carp and common carp liver for concentrations of cadmium, mercury, and lead in the upper Mississippi River; sites where large concentrations were found in whole fish also were sites where large concentrations were found in livers. Unfortunately, no NCBP/BEST sites are located in the upper Illinois River Basin so that such a comparison could be made for the basin. Concentrations of some elements in fish livers were converted to wet weight (by use of the percent moisture values obtained for each composite sample) and compared to the EDL 85 and 95 for livers of freshwater fish in California's TSMP (Rasmussen, 1992). The EDL 85 and 95 values were based on TSMP data for fish collected from various inland waters in California from 1978 through 1990. These values were generated to allow determination of elevated contaminant levels in California and do not represent national guidelines or toxic-effect levels. At present, neither national guidelines nor sufficient comparable data from the literature are available to determine the toxic effects of element concentrations in biota from the upper Illinois River Basin.

The variety of species collected at sites in 1989 and 1990 also made comparisons for element concentrations in biota among subbasins difficult. Even comparisons for the largest data set, common carp, were limited with only one or less representative site in three of the six subbasins within each year (fig. 20). Still, tentative conclusions may be possible. For example, arsenic concentrations in common carp livers were generally larger from the Kankakee and Fox River Basins than from the other basins (fig. 20), manganese concentrations were generally larger in the

Kankakee River Basin, and vanadium concentrations were generally larger in the Fox River Basin than in the other basins (table A1).

Concentrations of the major elements aluminum, boron, iron, and manganese were variable among biota. With the exception of iron, concentrations of these elements were smallest in fish livers. Concentrations of aluminum were near or below the minimum reporting level in most samples of fish livers; exceptions included a concentration of 13.0  $\mu\text{g/g}$  in common carp livers from the Kankakee River at Momence (site 14) in 1989 and a concentration of 54  $\mu\text{g/g}$  aluminum in common carp livers from the Fox River at Dayton (site 99) in 1990 (table A1). Boron concentrations in sago pondweed (*Potamogeton pectinatus*) (fig. 23b) and crayfish (fig. 22b) from two sites on the Little Calumet River (sites 53 and 52, respectively) indicate enrichment in this urban/industrial stream. Crayfish from the Little Calumet River (site 52) contained 120  $\mu\text{g/g}$  boron; this concentration was at least 20 times those found in crayfish from other sites in the basin (fig. 22b). Although no water or sediment data are available for this site in 1989, large total recoverable and dissolved boron concentrations were found during the summer of 1990. The largest concentrations of aluminum and iron in biota (2,140  $\mu\text{g/g}$  and 2,370  $\mu\text{g/g}$ ) were observed in caddisflies from Salt Creek (site 38) in 1989 (table A1). Concentrations of manganese in crayfish collected in 1989 from Indian Creek (site 97) and the North Branch Chicago River (site 45) were approximately five times those in crayfish at the Des Plaines River (site 40) (table A1), possibly indicating manganese enrichment at these two sites.

Concentrations of lead, molybdenum, and silver were below minimum reporting levels in most samples of biota, and beryllium was below the minimum reporting level in all samples (table A1). Although concentrations of boron, chromium, nickel, and lead were measurable in most samples of aquatic plants (fig. 23), concentrations of these elements were below minimum reporting levels in fish livers at all sites (table A1). The scarcity or absence of those elements at detectable concentrations in the sampled organisms indicates that concentrations of these elements were generally small in biota from the basin; however, it may mean either that some tissues were insensitive measures of contamination of these elements or that more sensitive methods of analysis need to be used, especially for lead (minimum reporting level between

4 and 6 µg/g). For example, the largest lead concentration in streambed sediment sampled in 1990 was 260 µg/g from the Des Plaines River above Brandon Road Dam at Joliet (site 58) (table A3). Colman and Sanzalone (1991) reported a concentration of 440 µg/g in a sample of streambed sediments collected from this site in 1987, and this concentration ranked eighth out of 135 high-order sites. Only fish livers, however, were sampled at this site, and lead concentrations in these tissues were below the minimum reporting level of 4 µg/g. Use of good indicator organisms or tissues and sensitive analytical methods capable of achieving environmentally relevant minimum reporting levels is critical for interpretation of small concentrations of trace elements.

Several trace elements seem to be enriched in biota from sites in the upper Illinois River Basin when compared to other sampled sites or literature values. Unlike water and sediment data, however, spatial patterns of some urban- or soil-associated elements were not readily apparent in the biotic data; thus, concentrations of these elements are discussed separately for each element.

Arsenic concentrations in biota from the basin were largest at sites in areas of agricultural land use. Most arsenic concentrations in fish livers from the basin were near or below the minimum reporting level except for a composite sample of common carp livers from the Kankakee River at Momence (site 14) in 1989 (fig. 20a). The concentration of 1.3 µg/g in livers from this agricultural site exceeded the TSMP EDL 85. This concentration was also larger than that found for livers of common carp by Wiener and others (1984) for the upper Mississippi in 1979. The arsenic concentration in Asiatic clams (*Corbicula fluminea*) (fig. 21a) from the Kankakee River at Momence (site 14) was also relatively large compared to concentrations in this species from the Du Page River at Shorewood (site 69), an urban site. The largest arsenic concentrations in biota were found in elktoe clams (*Alasmidonta marginata*) from Honey Creek (site 80), another agricultural site and a Fox River tributary, in 1990. The two highest arsenic concentrations in crayfish were found at the only two agricultural sites sampled for crayfish (fig. 22a). Concentrations of 2.1 and 2.9 µg/g were found in crayfish from Honey Creek (site 81) and Indian Creek (site 97), respectively, both are agricultural sites and Fox River tributaries. Indian Creek (site 97) had been selected as a reference site for the Central Corn Belt Plains

(CCBP) ecoregion. At six other sites that represented urban land uses in the CCBP ecoregion, arsenic concentrations in crayfish were 1.4 µg/g or less. These results indicate that biota from three agricultural sites, Kankakee River (site 14), Honey Creek (site 81), and Indian Creek (site 97) are enriched in arsenic.

Barium concentrations in biota from the upper Illinois River Basin indicate enrichment at urban as well as agricultural sites (table A1). In 1989, the largest barium concentrations observed in biota were 89.6 and 129 µg/g in crayfish from Honey Creek (site 81), an agricultural site, and Indian Creek (site 97), a reference site, respectively. These values were more than twice those found in crayfish from other sample sites. The largest concentrations of barium in aquatic plants were found in sago pondweed from two urban/industrial sites, 38.9 and 47.3 µg/g from the Little Calumet River at Calumet Park (site 53) and the North Branch Chicago River at Niles (site 45), respectively. Tazik (1988) reported 29.2 µg/g barium in shoots of this species collected from the Des Plaines River below Brandon Road Dam in 1987. This indicates that concentrations of barium in biota are elevated at Honey Creek (site 81) and the North Branch Chicago River (site 45).

Cadmium concentrations in biota, although variable among sites and biota collected, indicate enrichment at six sites representing agricultural and urban land uses, as well as at one reference site. Cadmium concentrations in mollusks were less than 1.0 µg/g at 7 of 10 sites (fig. 21a), and concentrations at all sample sites were smaller than those reported for fat mucket (*Lampsilis siliquoidea*) and five other species of clams collected from the Fox River in Illinois and Wisconsin in 1973 (Anderson, 1977). Eurasian water milfoil (*Myriophyllum spicatum*) from the North Shore Channel (site 46) contained 8.6 µg/g cadmium (fig. 23a), and the cadmium concentration in whole snails from this site was 5.9 µg/g (table A1). This concentration in milfoil is similar to that reported for milfoil species from a contaminated lake in Canada (Franzin and McFarlane, 1980), and it is much larger than that reported for milfoil species from the Des Plaines River in 1987 (Tazik, 1988) and the upper Mississippi River in 1977 (Buhl and McConville, 1984). Although concentrations were near or below the minimum reporting levels in crayfish and in white sucker (*Catostomus commersoni*) livers (table A1), concentrations in common carp livers from 12 sites exceeded the TSMP EDL 85. Concentrations

of cadmium in carp livers from Iroquois River (site 28), Fox River (site 99), Big Rock Creek (site 94), Illinois River (site 76), and Des Plaines River (site 40) were elevated with respect to concentrations at other sites in the basin (fig. 20b), and these concentrations exceeded the TSMP EDL 95. These sites represent both agricultural and urban land uses. The concentrations of cadmium in carp livers of 44.8 µg/g at the Iroquois River near Chebanse (site 28), 18.0 µg/g at the Fox River at Dayton (site 99), and 9.5 µg/g at the Illinois River at Marseilles (site 76) greatly exceeded concentrations reported by Wiener and others (1984) for carp livers collected from the upper Mississippi River in 1977; however, cadmium concentrations in streambed sediments were near minimum reporting levels in 1989 and 1990 at Iroquois River near Chebanse (site 28) and Fox River at Dayton (site 99) (table A3). Most concentrations in carp livers from the upper Illinois River Basin were larger than those reported by Wiener and others (1984) for livers of common carp from the upper Mississippi River.

Chromium concentrations were found at larger concentrations in aquatic plants (fig. 23) than in other biota sampled in the basin, and concentrations in clams (fig. 21a), crayfish (fig. 22a), and fish livers (table A1) were near or less than the minimum reporting level of 1 µg/g at all sites. Concentrations in plants ranged from 1 µg/g in curly leaf pondweed (*Potamogeton crispus*) at the reference site Mill Creek (site 2) to 10 µg/g in sago pondweed from the Little Calumet River (site 53) and 11 µg/g in Eurasian water milfoil from the North Shore Channel (site 46). The concentration in sago pondweed is similar not only to the largest concentration reported by Tazik (1988) for shoots of this species from the Des Plaines River in 1987 but also to means reported for shoots of broadleaf pondweed (*Potamogeton americanus*) from the upper Mississippi River in 1977 (Buhl and McConville, 1984). Chromium in Eurasian water milfoil from the North Shore Channel (site 46) exceeds the range of 2.3 to 8.9 µg/g reported by Tazik (1988) for shoots of milfoil species. These results indicate that aquatic plants at these two urban/industrial sites, the Little Calumet River (site 53) and North Shore Channel (site 46), are enriched in chromium.

Copper concentrations differed greatly among biota sampled in the basin, and tissue samples from many of the urban and agricultural sites seem to contain elevated concentrations. The highest concen-

tration of copper in soft tissues of clams was at the Du Page River at Shorewood (site 69) (fig. 21b). Samples of Asiatic clams from this site contained 32.9 µg/g copper in 1989 and 38.6 µg/g in 1990. These concentrations were in the range of 23 to 45 µg/g copper reported by Leland and Scudder (1990) for composite samples of Asiatic clams from the San Joaquin River in California but were higher than concentrations reported by Anderson (1977) for six other species of clams from the Fox River in 1973. The largest copper concentrations in crayfish and aquatic plants were found at the North Branch Chicago River at Niles (site 45) in 1989 (figs. 22b and 23a). Replicate samples of crayfish from the East Branch Du Page River at Naperville (site 66) also contained large amounts of copper when compared to other sites in the basin (fig. 22b). Whole snails from the North Shore Channel (site 46) contained the largest copper concentration observed in all biota, 209 µg/g, and may indicate enrichment at this site. Most concentrations of copper in common carp livers (fig. 20c) and white sucker livers (fig. 20d) exceeded the TSMP EDL 85, and concentrations at six sites exceeded the TSMP EDL 95. Copper concentrations in carp livers were elevated at 15 of 17 sites with respect to concentrations at the Little Calumet River at Calumet Park (site 53) and the Des Plaines River above Brandon Road Dam at Joliet (site 58) (fig. 20c). The largest concentration was observed at Big Rock Creek (site 94), a Fox River tributary and a reference site for the CCBP ecoregion. When compared to samples from two Kankakee River tributaries, copper concentrations in white suckers were elevated at Mill Creek (site 2), the Mukwonago River (site 78), the East Branch Du Page River (site 66), and Blackberry Creek (site 93) (fig. 20d). As was observed for common carp, these sites include not only reference streams but also streams draining urban and agricultural land.

Lead concentrations in most biota were below the minimum reporting levels of 4 to 6 µg/g; however, a concentration of 9.0 µg/g lead was found in whole snails (table A1) and Eurasian water milfoil (fig. 23a) from the North Shore Channel (site 46). The largest lead concentration in aquatic plants from the basin (22 µg/g) was found in sago pondweed from the Little Calumet River (site 53). This lead concentration is similar to that reported by Franzin and McFarlane (1980) for plants of the same genus from a contaminated lake in Canada. Lead concen-

trations in all species of pondweed (including sago pondweed) were below a minimum reporting level of 1.2 µg/g in Tazik's study (1988). Concentrations of lead in caddisflies (9.0 µg/g) (table A1) and wild celery (*Vallisneria* sp.) (fig. 23a) (7.0 µg/g) from Salt Creek (site 38) indicate that these biota are also enriched relative to biota from other sites in the basin. These data seem to indicate lead enrichment at the North Shore Channel (site 46), Little Calumet River (site 53), and Salt Creek (site 38), all of which represent urban land uses.

Mercury was found at small concentrations in most biota from the basin with the exception of fish livers. A mercury concentration of 0.55 µg/g in white sucker livers from the Mukwonago River (site 78) was large when compared to approximately background concentrations of 0.1 µg/g in white sucker livers from Kankakee River tributaries (fig. 20f). Livers of common carp from the West Branch Du Page River (site 63) contained 0.41 µg/g mercury, and Fox River tributaries as a group yielded carp livers containing relatively large mercury concentrations (fig. 20e). The Illinois Fish Contaminant Monitoring Program of the IEPA found generally small concentrations of mercury in fish from the upper Illinois River Basin during 1974–82 (Illinois Environmental Protection Agency, unpublished data, 1987b); however, samples of single largemouth bass fillets collected from the Fox River near the Illinois-Wisconsin State line and near Wedron, Ill., in 1974 contained relatively large concentrations of mercury compared to samples from other sites. These concentrations, however, did not exceed established U.S. Food and Drug Administration (USFDA) action levels for edible portions of fish (U.S. Food and Drug Administration, 1984). In the upper Mississippi River study by Wiener and others (1984), mercury concentrations in common carp livers were less than 0.4 µg/g at 12 of 15 sites. Samples of carp livers from three other sites had concentrations as large as 7.91 µg/g mercury. Using U.S. Fish and Wildlife Service's NCBP data, Wiener and others (1984) concluded that the concentrations in carp livers from the upper Mississippi River were large compared to concentrations in carp from other streams in the Nation. Relative to other sites in the upper Illinois River Basin, mercury concentrations in livers of common carp and white sucker indicate enrichment in the West and East Branches of the Du Page River (site 63 and 66), Iroquois River (site 28), and in three

tributaries of the Fox River: the Mukwonago River (site 78), Blackberry Creek (site 93), and Big Rock Creek (site 94) (figs. 20e and f). These sites represent a mixture of urban/residential and agricultural land uses; Big Rock and Blackberry Creeks were both rated "highly valued aquatic resources" by the IEPA on the basis of a 1982 survey of fish and invertebrate communities together with water quality and habitat sampling (Illinois Environmental Protection Agency, 1987a).

Nickel concentrations in biota were largest in aquatic plants (fig. 23a), whereas concentrations in crayfish (fig. 22a) and fish (table A1) were near or below the minimum reporting level of 2 µg/g. A concentration of 36 µg/g nickel in waterweed from the North Branch Chicago River at Niles (site 45) was the largest observed in biota from the basin. The largest nickel concentration in mollusks was 28.0 µg/g, observed in whole snails from the North Shore Channel (site 46) (table A1). This nickel concentration was the largest in all invertebrates sampled, and it was three times larger than the next smallest observation in other invertebrates. Comparison data for these species is not available; however, such large concentrations may indicate nickel enrichment at these two urban sites. Nickel concentrations in Asiatic clams from the Du Page River at Shorewood (site 69) increased from 2.0 to 5.0 µg/g from 1989 to 1990. Both concentrations are larger than those reported by Leland and Scudder (1990) for Asiatic clams from the San Joaquin River in California and may indicate nickel enrichment in this urban stream.

Selenium concentrations in biota were similar in occurrence to mercury concentrations (generally small, except in fish livers). Concentrations in the upper Illinois River Basin (table A1) were below the TSMP EDL 95 for freshwater fish from primarily selenium contaminated waters in California; however, selenium concentrations greater than 6 µg/g were found at eight sites sampled for carp in the upper Illinois River Basin and are elevated with respect to a mean selenium concentration of 3.6 µg/g for carp livers from the upper Mississippi River in 1979 (Wiener and others, 1984). The eight sites where selenium concentrations were elevated were Kankakee River (site 14), Des Plaines River and above Brandon Road Dam (sites 40 and 58), West Branch Du Page River (site 63), East Branch Du Page River (site 66), Illinois River (site 76), Honey Creek (site 80), and Big Rock Creek (site 94). These sites represent urban and agricultural land uses.

Strontium concentrations differed by two orders of magnitude among the different groups of biota. The three largest concentrations found for mollusks, crayfish, and plants were from Salt Creek (site 38) (figs. 21b, 22b, and 23b). Fingernail clams and crayfish from this urban/industrial site contained 582 and 562  $\mu\text{g/g}$  strontium, respectively, and a concentration of 94.7  $\mu\text{g/g}$  was found in wild celery. Livers of common carp from this site also contained a large amount of strontium compared to carp livers from other sites in the basin (fig. 20g). Therefore, data for a variety of biota from Salt Creek (site 38) indicate strontium enrichment in this urban stream.

Zinc concentrations seem to be elevated at most sites sampled for fish livers in the upper Illinois River Basin. All concentrations of zinc in common carp livers were larger than 200  $\mu\text{g/g}$  and greatly exceeded the TSMP EDL 95 (fig. 20h). The largest concentrations in carp were at Salt Creek at Western Springs (site 38), Fox River at Algonquin (site 89), Fox River at Dayton (site 99), and one of two composite samples from Big Rock Creek (site 94). White suckers were enriched in zinc at four of seven sites sampled and exceeded the TSMP EDL 95 at East Branch Du Page River (site 66) and Blackberry Creek (site 93) (fig. 20i). Although no fish livers were collected from the reference site Langan Creek (site 27), zinc concentrations in fat mucket clams from this Iroquois River tributary were at least four times larger than concentrations in other invertebrates and were much larger than concentrations reported for this species by Anderson (1977) for the Fox River in 1973 (fig. 21b and 22b). In addition, this concentration of zinc in fat mucket clams from Langan Creek (site 27) greatly exceeded the MIS for marine shellfish. These results indicate that zinc concentrations at the reference site, Langan Creek (site 27), are elevated also.

Biota from some urban sites in the basin were enriched with respect to several elements. Relative to other invertebrates sampled, large concentrations of cadmium (5.9  $\mu\text{g/g}$ ), chromium (6.0  $\mu\text{g/g}$ ), copper (209  $\mu\text{g/g}$ ), nickel (28  $\mu\text{g/g}$ ), and lead (9  $\mu\text{g/g}$ ) were found in whole snails from the North Shore Channel (site 46) in 1989 (fig. 21 and table A1), and large concentrations of chromium (11  $\mu\text{g/g}$ ), copper (38.4  $\mu\text{g/g}$ ), and lead (22  $\mu\text{g/g}$ ) were also found in Eurasian water milfoil from this industrial stream (fig. 23a). Another industrial stream, the North Branch Chicago River at Niles (site 45), seems to be enriched in copper and

nickel in biota. Copper concentrations in water at this site have exceeded the USEPA chronic water-quality criterion. Relative to values in the literature, concentrations of chromium (10  $\mu\text{g/g}$ ), lead (22  $\mu\text{g/g}$ ), and vanadium (5.6  $\mu\text{g/g}$ ) were also large in sago pondweed from the Little Calumet River at Calumet Park (site 53), a highly industrial site. Biota from Salt Creek (site 38), a residential stream, contained large concentrations of lead, manganese, nickel, and strontium when compared to biota from other sampled sites. Total recoverable concentrations in water from this site have exceeded the USEPA chronic criterion for lead.

Variations were observed between the 1989 and 1990 synoptic surveys for some element concentrations in biota. Although 12 sites were sampled both years, only 5 sites were sampled for the same species of biota in both years; this incomplete correspondence between the two surveys precluded statistical analysis of the data. However, some element concentrations among this data set are worth noting. Asiatic clams sampled from the Du Page River at Shorewood (site 69) had fairly similar concentrations of most elements, with the exception of nickel, as described earlier. In 1989, the concentration of arsenic in carp livers from the Kankakee River at Momence (site 14) was 1.3  $\mu\text{g/g}$ ; however, the concentration in 1990 was only 0.3  $\mu\text{g/g}$ . Concentrations of aluminum and copper in carp livers from the Kankakee River (site 14) and the Des Plaines River above Brandon Road Dam (site 58) were smaller in 1990 than in 1989; cadmium and selenium concentrations were larger in 1990. Similarly, aluminum and copper concentrations were smaller in 1990 at the Illinois River at Marseilles (site 76), and cadmium and selenium concentrations were larger in 1990 at the Du Page River at Shorewood (site 69). Additional sampling would be needed to establish trends, such as whether cadmium and selenium concentrations in carp livers are increasing at these three sites.

In most cases where several species were collected from a site at one time, large concentrations of elements observed in one taxon were observed in the other species as well. Some exceptions were found. For example, concentrations of barium, cadmium, and nickel differed greatly between two species of mollusks at Honey Creek (site 80) in 1990 (fig. 21b). Elktoe clams contained 124  $\mu\text{g/g}$  barium, whereas three ridge mussels (*Amblema plicata*) from this site contained only 72.2  $\mu\text{g/g}$  barium. These two

species of mollusks from Honey Creek (site 80) differed considerably in their accumulation of cadmium also. Elktoe clams collected from Honey Creek (site 80) in 1990 contained 7.0  $\mu\text{g/g}$  nickel, whereas concentrations in three ridge clams from this site were below the minimum reporting level. Although the largest concentrations of barium in aquatic plants were observed in sago pondweed from the North Branch Chicago River at Niles (site 45) (fig. 23b), composite samples of crayfish collected at the same time from this site were not enriched in barium (fig. 22b). Chromium concentrations in four species of biota from Salt Creek (site 38) during 1989 ranged from less than the minimum reporting level of 1.0  $\mu\text{g/g}$  (fingernail clams) to 5.4  $\mu\text{g/g}$  (caddisflies). These results demonstrate the potentially large differences in element concentrations among species collected from a site and emphasize the importance of collecting more than one species at a site whenever possible.

#### **Correlations Among Major and Trace Elements in Biota, 1989 and 1990**

Spearman's rank correlation coefficients were calculated for concentrations of elements in tissues of common carp, white sucker, and crayfish collected from the upper Illinois River Basin during 1989 and 1990 (table 22). Relations among a number of elements in these tissues were not possible because at least half of the concentrations were below minimum reporting levels. Correlations for concentrations between boron, barium, beryllium, chromium, lead, molybdenum, nickel, and silver in common carp livers could not be examined for this reason. More elements in white sucker livers could not be examined by correlation, than in common carp livers. In addition, correlations could not be examined for mollusks or aquatic plants because of insufficient single-species data. Nevertheless, correlations were found among some element concentrations in fish and also in crayfish tissues. This finding indicates similar spatial patterns in bioaccumulation for these elements.

In common carp livers, positive correlations were found among concentrations of copper, mercury, and zinc ( $\rho > 0.53$ ); concentrations of cadmium, copper, and selenium also positively correlated with each other. Strontium negatively correlated with selenium ( $\rho = -0.47$  to  $-0.51$ ).

Although correlations among element concentrations in white sucker livers could be

computed for only copper, iron, mercury, manganese, selenium, and zinc, some similarities were found between common carp and white sucker for correlations among elements in liver tissue. As was found for common carp, concentrations of copper, mercury, and zinc in white sucker livers all positively correlated with each other ( $\rho \geq 0.83$ ), and positive correlations were found between concentrations of copper and selenium ( $\rho = 0.66$ ). This similarity indicates a common source and mode of accumulation for these elements in livers of common carp and white sucker.

More correlations were observed among elements in crayfish tissues than were observed for fish. Some similarities were found between the two groups of biota. As was seen for common carp, a moderate positive correlation was found between concentrations of aluminum and strontium ( $\rho = 0.74$ ). This positive relation of aluminum and strontium in both organisms was puzzling because, although aluminum was generally in the particulate phase, strontium was mostly in the dissolved phase in water samples from the basin. Concentrations of aluminum, chromium, iron, and vanadium positively correlated with each other in analyses of whole crayfish ( $\rho = 0.63$  to  $0.90$ ). Aluminum, chromium, and vanadium were mostly in the particulate phase in water samples from the basin in 1989. In contrast, aluminum negatively correlated with manganese ( $\rho = -0.74$ ). Elevated manganese concentrations in some organisms can interfere with iron absorption in the gut (Donaldson, 1980), so a negative correlation between these two elements in tissues was not unexpected. Significant negative correlations were observed between strontium and arsenic concentrations ( $\rho = -0.87$ ) and strontium and barium concentrations ( $\rho = -0.71$ ) in crayfish. Barium was mostly in the dissolved phase in water, as was strontium, and the two were strongly correlated with each other in that component. A positive correlation was found for tissue concentrations of selenium with concentrations of barium ( $\rho = 0.65$ ).

Similar modes of uptake and accumulation, as well as physiological interactions, may help explain some of the correlations found in element concentrations of biota. Copper and zinc concentrations were positively correlated in common carp ( $\rho = 0.54$ ), white suckers ( $\rho = 0.99$ ), and crayfish ( $\rho = 0.62$ ). As mentioned earlier, both of these elements are nutritionally required, and they are essential for the proper

functioning of several enzymes. They are physiologically regulated in vertebrates, and much of the copper and zinc in these organisms is found in the liver (Sternlieb, 1988).

### Correlations of Element Concentrations Among Water, Sediment, and Biota

Ranked element concentrations were correlated among water, sediment, and biota. First, dissolved and total recoverable concentrations in water were compared to element concentrations in suspended sediment collected at the eight NAWQA fixed sites from 1987 through 1990. Next, concentrations in water were compared to element concentrations in streambed sediment collected at the same site or the nearest site upstream. Finally, concentrations in biota were compared to dissolved and total recoverable element concentrations in water, element concentrations in suspended sediment, and element concentrations in streambed sediment.

Even though general spatial patterns among water and suspended sediment were similar for the urban-associated elements antimony, boron, cadmium, chromium, copper, lead, molybdenum, nickel, and phosphorus (Appendix A), correlation coefficients among these elements in water and sediment were generally negligible (table 23). Only antimony, cadmium, nickel, and phosphorus in suspended sediment correlated ( $\rho = 0.52$  to  $0.60$ ) with either dissolved or total recoverable concentrations of the same element. The correlations are so few probably because of the large number of observations of dissolved and total recoverable concentrations below the minimum reporting level for many of the urban-associated elements.

Chromium, cobalt, and nickel concentrations in suspended sediment negatively correlated with both alkalinity and with pH in water ( $\rho = -0.57$  to  $-0.76$ ). Aluminum, arsenic, and beryllium in suspended sediment negatively correlated with alkalinity ( $\rho = -0.50$  to  $-0.53$ ), and antimony and molybdenum in suspended sediment negatively correlated with pH ( $\rho = -0.57$ ). The correlations indicate that the concentrations of these elements in the suspended sediments may be linked to the buffering capacity of the water. However, it is not known how much of the correlation was due to association and how much of the concentrations in the suspended sediment were actually caused by smaller buffering capacity.

Antimony, chromium, lead, nickel, silver, and zinc in suspended sediment positively correlated ( $\rho > 0.5$ ) with total recoverable and dissolved phosphorus. This set of correlations indicates that large concentrations of some of the priority pollutants in suspended sediments are associated with large concentrations of phosphorus in water.

Correlations among elements in water and streambed sediment were calculated by means of three methods to clarify the relation of concentrations in water and the sediment. Streambed sediments were collected at 29 of the 40 sites where water samples were collected (table 6). Streambed-sediment concentrations were correlated with median concentrations in water, 90th percentiles in water, and concurrent concentrations from water samples that were collected closest to the date when the streambed-sediment samples were collected. Correlation coefficients from median concentrations in water indicate how the most typical concentrations in water from 1987 through 1990 compared with concentrations in streambed sediment in 1987 (table 24). Correlation coefficients from the 90th percentiles of the water data indicate whether larger concentrations in water better reflect concentrations in the streambed sediment than median concentrations do (table 25). Lastly, correlation between concentrations from concurrent water samples and streambed sediment samples indicate whether relations among the water and sediment components are strongest if the time of sample collection is similar (table 26). Median and concurrent concentrations for many of the priority pollutants were below the minimum reporting level; if concentrations at more than 15 of the sites were below the minimum reporting level, the element was not included in the tables.

For some elements, correlation coefficients were similar regardless of the water data used. Correlation coefficients between streambed sediment and total recoverable and dissolved concentrations of boron, phosphorus, and strontium in water ranged from 0.58 to 0.68 regardless of whether the medians, 90th percentiles, or concurrent samples were used.

For other elements, correlation coefficients depended strongly on the water data set used. For example, correlation coefficients among streambed sediment and total recoverable concentrations of copper, iron, lead, and nickel ranged from 0.51 to 0.60 when the 90th-percentile water data were used; however, correlation coefficients among these elements in streambed sediment and total recoverable

concentrations were less or were not significant ( $\rho < 0.5$  or  $\rho > 0.10$ ) when the median and concurrent samples were used. Thus, large concentrations in water seem to correlate best with concentrations in streambed sediments for these elements. It must be noted, however, that correlations among median and concurrent concentrations in water and concentrations in streambed sediment were hindered by the many concentrations in water below the minimum reporting level.

Within-element correlations were not similar between streambed sediment and water and suspended sediment and water. Only nickel concentrations in streambed sediment and in suspended sediment correlated with total recoverable concentrations in water.

Correlations between streambed-sediment data and the 90th-percentile water data were observed among many different elements. For example, 90th percentiles for total recoverable zinc correlated with chromium, copper, and molybdenum concentrations in streambed sediment at  $\rho = 0.51$  to  $0.56$ . Total recoverable copper concentrations correlated with aluminum, beryllium, boron, cobalt, copper, molybdenum, vanadium, and zinc in streambed sediments at  $\rho = 0.50$  to  $0.66$ . Total recoverable nickel correlated with aluminum, barium, beryllium, chromium, cobalt, copper, iron, molybdenum, vanadium, and zinc in streambed sediments at  $\rho = 0.50$  to  $0.87$ . Total recoverable lead correlated with selenium, beryllium, chromium, copper, mercury, molybdenum, nickel, vanadium, and zinc in streambed sediments at  $\rho = 0.50$  to  $0.72$ .

Similar to the suspended sediment, many priority pollutants in streambed sediments correlated with phosphorus concentrations in water. Of the three data sets used for water, the largest correlation coefficients were for concurrent dissolved and total recoverable phosphorus concentrations in water; and for beryllium, chromium, cobalt, copper, molybdenum, nickel, and zinc ( $\rho > 0.50$ ) in streambed sediments. Chromium, copper, nickel, and zinc in streambed sediment correlated even more strongly with phosphorus in streambed sediment ( $\rho = 0.65$  to  $0.80$ ; Colman and Sanzalone, 1991). Large phosphorus concentrations in streambed sediment are associated with urban areas, as are many of the elements it significantly correlated with in streambed sediments. Phosphorus, however, was the only urban-associated element that was always present in concentrations above its minimum reporting level in

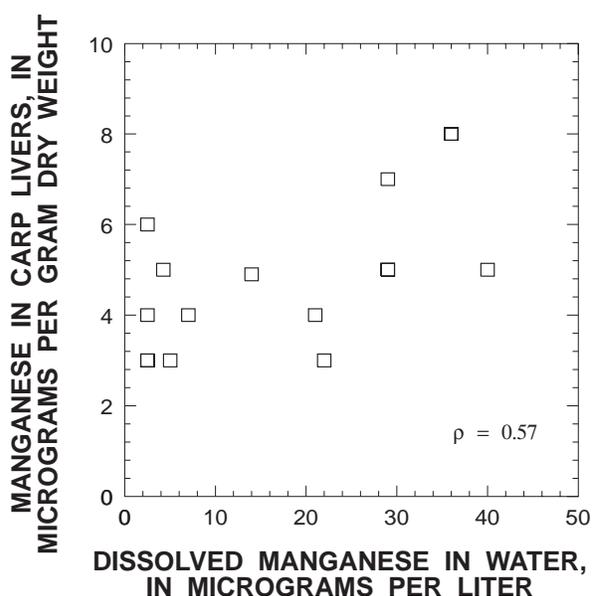
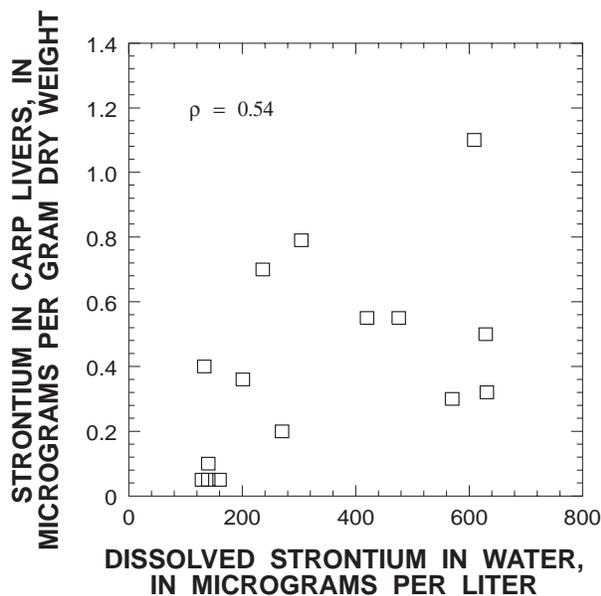
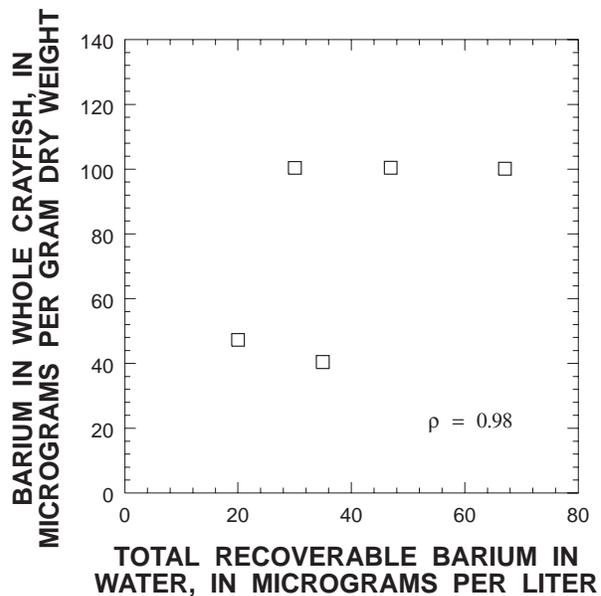
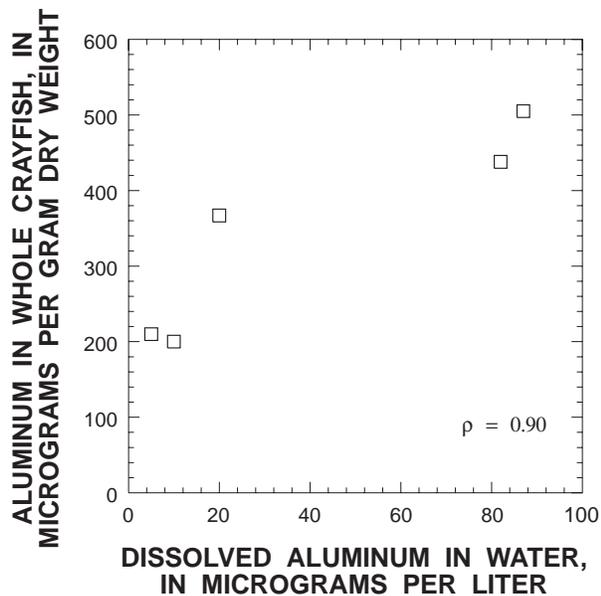
water. Thus, concentrations of phosphorus in water may serve as an indicator for the other urban-related elements typically found in concentrations below the current minimum reporting levels.

Correlations ( $\rho > 0.5$ ) were observed between some element concentrations in biota and concentrations of elements in water and sediment components from the upper Illinois River Basin; however, correlations for boron, beryllium, chromium, lead, molybdenum, nickel, and silver were hindered by insufficient data or many data below the minimum reporting level. The variety of mollusk and plant species collected at sites resulted in insufficient data for any one species. In addition, limited overlap of sites sampled for organic carbon and element concentrations in suspended sediment precluded examination of correlations with element concentrations in tissues of all biota except common carp.

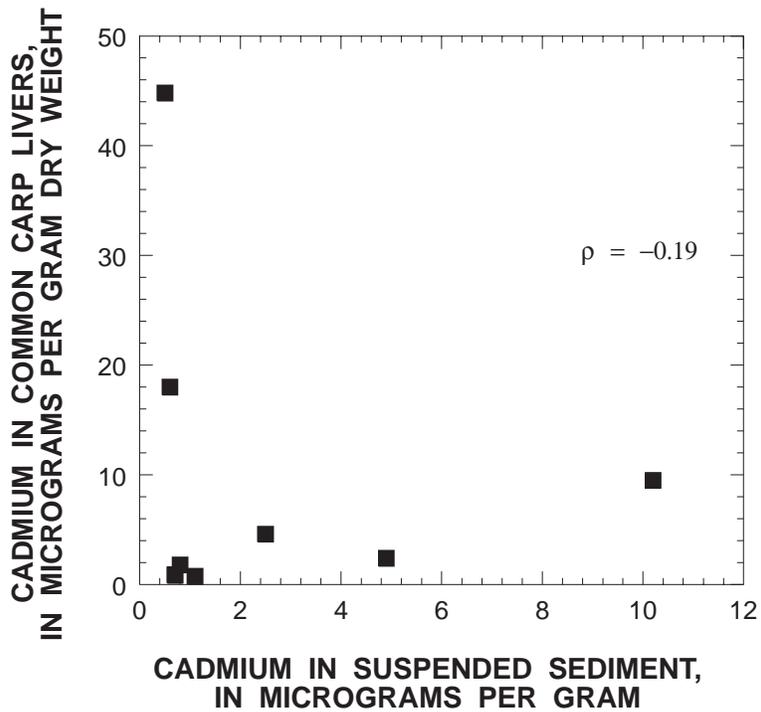
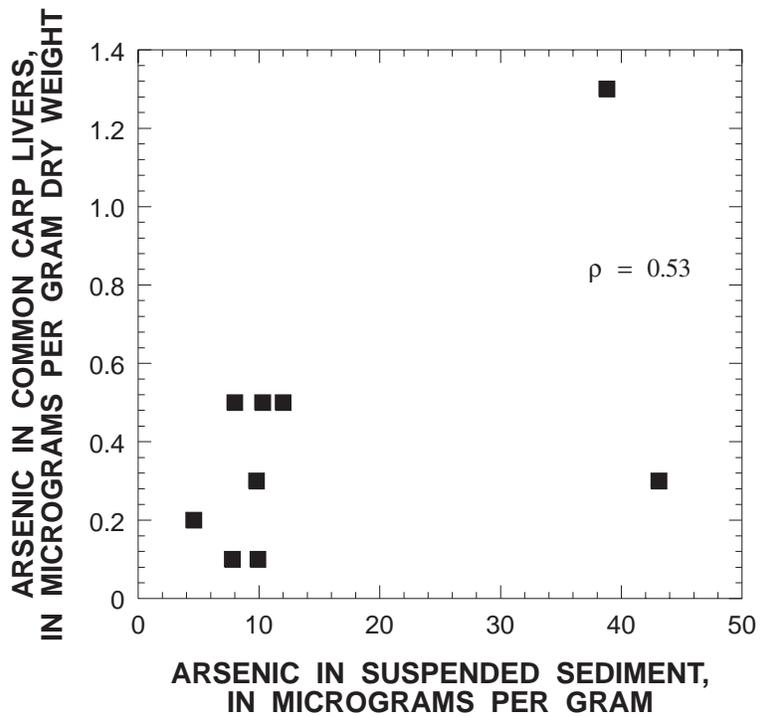
Correlations were found between concentrations of aluminum, barium, manganese, and strontium in biota and water (fig. 24). Aluminum concentrations in whole crayfish were found to be positively correlated with dissolved concentrations of this element in water ( $\rho = 0.90$ ). Barium concentrations in whole crayfish were positively correlated with total recoverable barium in water ( $\rho = 0.98$ ). Manganese concentrations in common carp and white sucker livers were positively correlated with concentrations of dissolved manganese ( $\rho = 0.57$  and  $0.55$ , respectively). Positive correlations were found between concentrations of strontium in common carp livers and in dissolved concentrations in water ( $\rho = 0.54$ ). Most of the total recoverable strontium was in the dissolved phase, where it is available for uptake. Fish may be accumulating the strontium directly from the water and sediment or by ingestion of plants, which readily take up this element (Kabata-Pendias and Pendias, 1984).

Concentrations of arsenic in suspended sediment were positively correlated ( $\rho = 0.53$ ) with concentrations of arsenic in common carp livers (fig. 25). The largest arsenic load and yield of the eight NAWQA fixed sites was found at the Fox River at Algonquin (site 89), an agricultural site, and arsenic concentrations in common carp livers from the Fox River tributaries were relatively large as a group. This relation indicates that arsenic in suspended sediments may be a source of arsenic in carp.

Concentrations of cadmium in common carp livers and suspended sediment may also be correlated, although the correlation is confounded by



**Figure 24.** Relations of concentrations of selected elements in tissue to concentrations in water from the upper Illinois River Basin, 1989–90 ( $\rho$  = Spearman's ranked correlation coefficient).



**Figure 25.** Relations of concentrations of selected elements in tissue to concentrations in suspended sediment from the upper Illinois River Basin, 1989–90 ( $\rho$  = Spearman's ranked correlation coefficient).

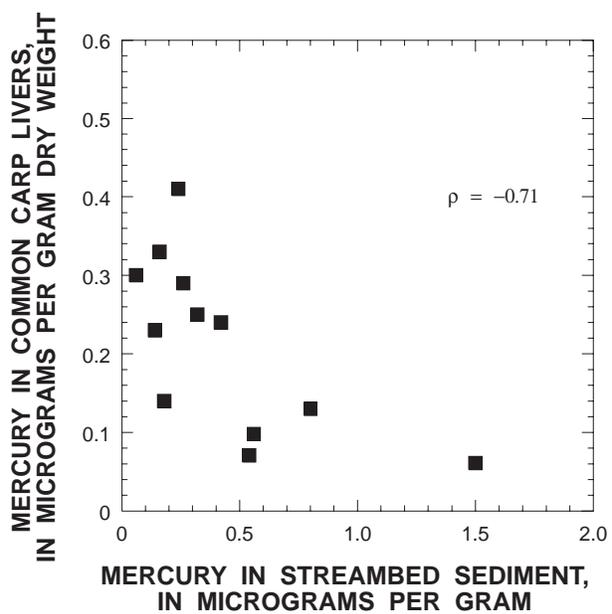
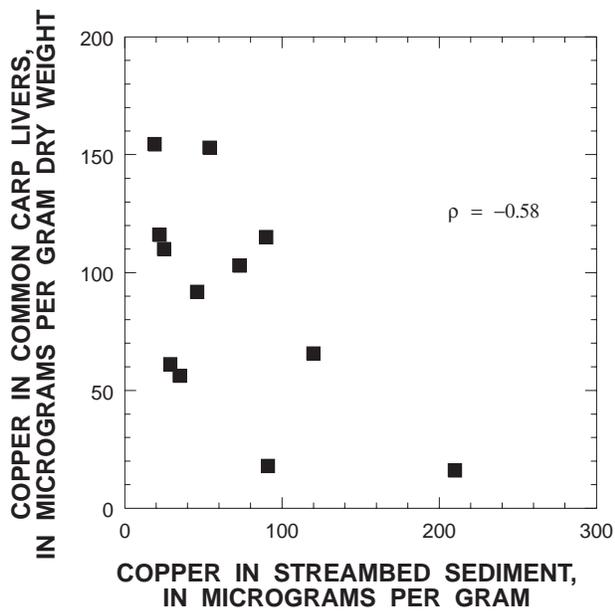
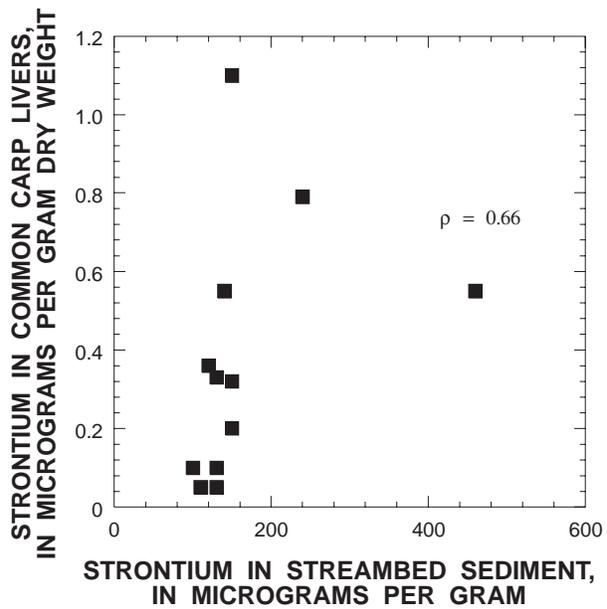
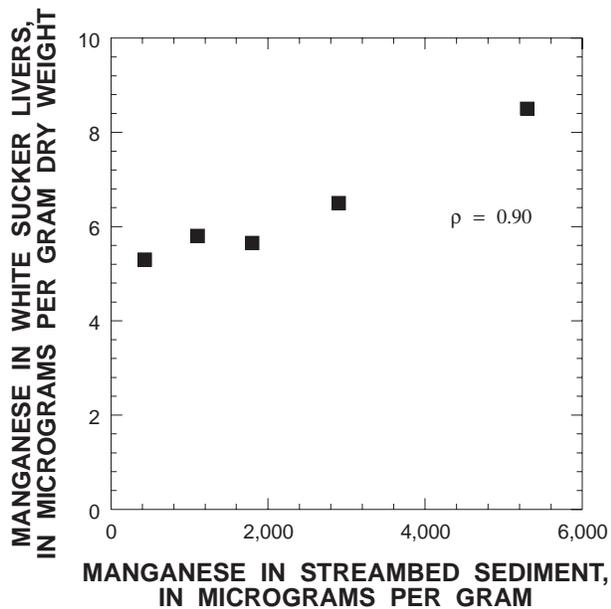
two outliers (fig. 25). These two outliers represent the large concentrations in carp livers from the Fox River at Dayton (site 99) and the Iroquois River near Chebanse (site 28). Without these outliers, the correlation coefficient between cadmium in carp livers and in suspended sediment increases from  $\rho = -0.19$  to 0.74, indicating that large concentrations of cadmium in livers of common carp were positively correlated with large concentrations in suspended sediment. Other researchers have found positive correlations for concentrations of cadmium in fish livers and concentrations in water or sediment (Benoit and others, 1976; Boyer, 1984; Klaverkamp and others, 1991).

Positive correlations were found between some element concentrations in tissues and streambed sediments (fig. 26). Manganese concentrations in livers of white sucker were positively correlated with concentrations of this element in streambed sediment ( $\rho = 0.90$ ). Strontium in common carp livers positively correlated with strontium in streambed sediment ( $\rho = 0.66$ ). Although correlations were not evident, copper and nickel concentrations in biota from the North Branch Chicago River at Niles (site 45) reflected large concentrations of these elements in streambed sediments (tables A1 and A3). Concentrations of copper in waterweed and crayfish from this site were the largest found in aquatic plants and crayfish (48.6 and 185  $\mu\text{g/g}$ , respectively). A composite sample of streambed sediments from this site contained 120  $\mu\text{g/g}$  copper, one of the three largest concentrations of copper found in the basin during the 1990 sampling. In addition, nickel concentrations in waterweed from this site were also the largest concentrations found in plants in the basin (36  $\mu\text{g/g}$ ), and nickel in streambed sediments from this site in 1990 were at the second largest concentration found (53  $\mu\text{g/g}$ ) that year.

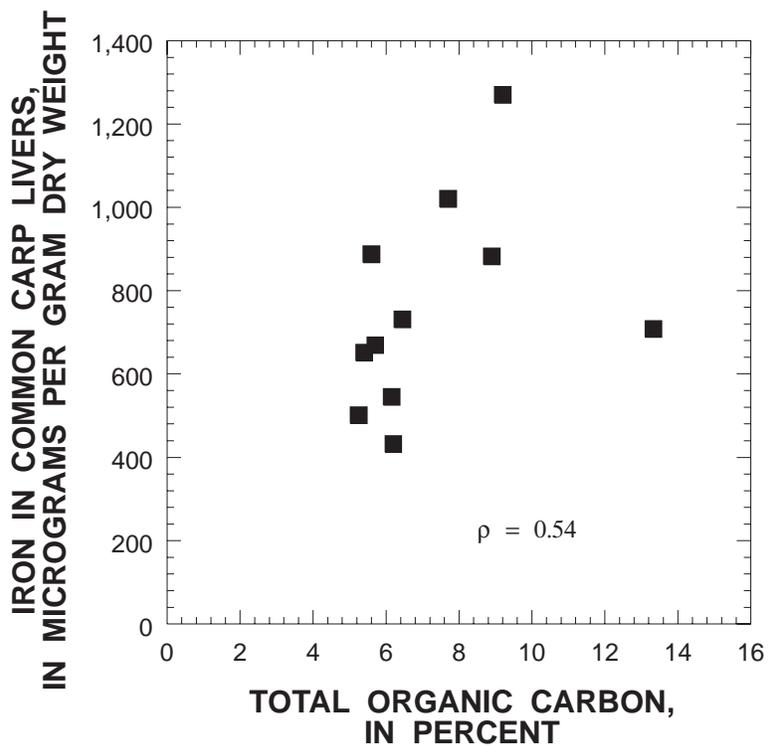
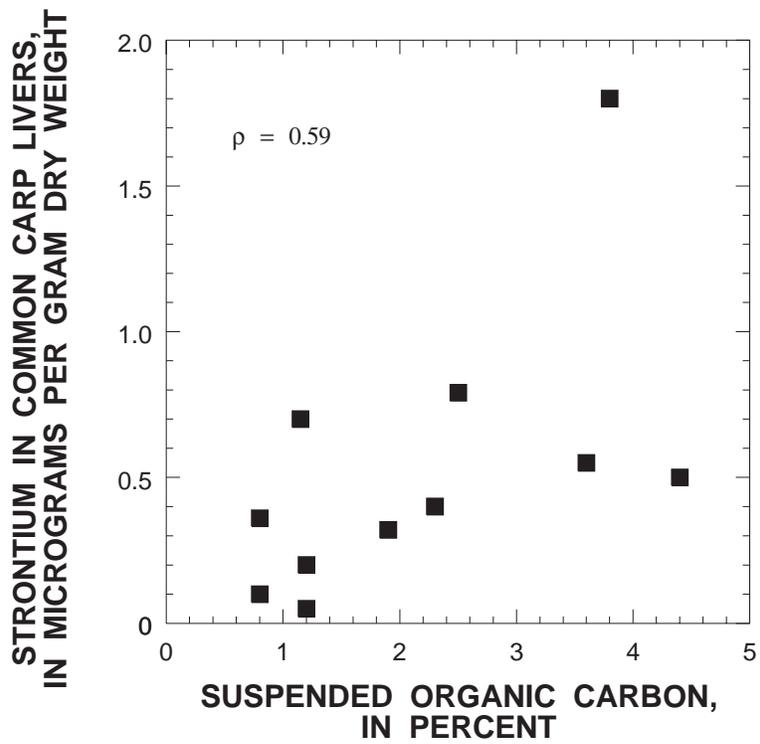
Negative correlations were found for copper and mercury ( $\rho = -0.58$  and  $-0.71$ , respectively) between concentrations in common carp livers and in streambed sediment. As mentioned earlier, copper and mercury were positively correlated with each other in carp livers ( $\rho = -0.56$ ). Two replicate carp-liver samples from Big Rock Creek (site 94) in 1990 contained relatively large copper concentrations (130 and 179  $\mu\text{g/g}$ ). Yet, streambed sediment from this small tributary to the Fox River had copper concentrations of 19  $\mu\text{g/g}$ , which is one of the smallest concentrations of copper in the Fox River Basin.

Livers of common carp from the Des Plaines River above Brandon Road Dam at Joliet (site 58) had the smallest concentrations of copper and mercury in both sample years. Streambed sediments collected below the dam had the largest concentrations of these elements in 1990. Wiener and others (1984) found no significant relation between mercury concentrations in unsieved streambed sediments and common carp livers from the upper Mississippi River. Analysis of methylmercury in streambed sediment samples might aid interpretations of mercury concentrations in fish livers from the upper Illinois River Basin. Harrison and Klaverkamp (1990) also found a negative correlation between concentrations of mercury in northern pike livers and unsieved lakebed sediments; copper concentrations in white sucker livers negatively correlated to copper concentrations in these sediments.

Concentrations of suspended organic carbon were positively correlated with concentrations of strontium in carp livers ( $\rho = 0.59$ ) and were negatively correlated with cadmium, copper, and selenium ( $\rho = -0.63$ ,  $-0.51$ , and  $-0.74$ , respectively) in carp livers (fig. 27). The outlier in the strontium data was from the Du Page River at Shorewood (site 69). The two outliers in the cadmium data represent the Iroquois River near Chebanse (site 28) and the Fox River at Dayton (site 99). Total organic carbon was positively correlated with concentrations of iron in carp livers ( $\rho = 0.54$ ). Organic carbon compounds (such as humic and fulvic acids) are known to bind certain trace elements. This binding has generally been thought to render elements unavailable for uptake by biota (Spacie and Hamelink, 1985); however, Winner (1985) found that 7-day-old *Daphnia pulex* accumulated significantly more copper in the presence of humic acid than in an environment without humic acid. Recent work with two marine bivalves by Decho and Luoma (1994) indicates that organic carbon compounds may slightly enhance uptake of cadmium but reduce the availability of chromium. Positive correlations between trace elements in tissues and organic carbon concentrations in this study indicate that organic matter may have enhanced the uptake of an element to biota, whereas negative correlations might indicate that organic matter functioned as a binding agent that made an element less available to biota.



**Figure 26.** Relations of concentrations of selected elements in tissue to concentrations in streambed sediment from the upper Illinois River Basin, 1989–90 ( $\rho$  = Spearman's ranked correlation coefficient).



**Figure 27.** Relations of concentrations of selected elements in biota to organic carbon concentrations in the upper Illinois River Basin, 1989–90 ( $\rho$  = Spearman's ranked correlation coefficient).

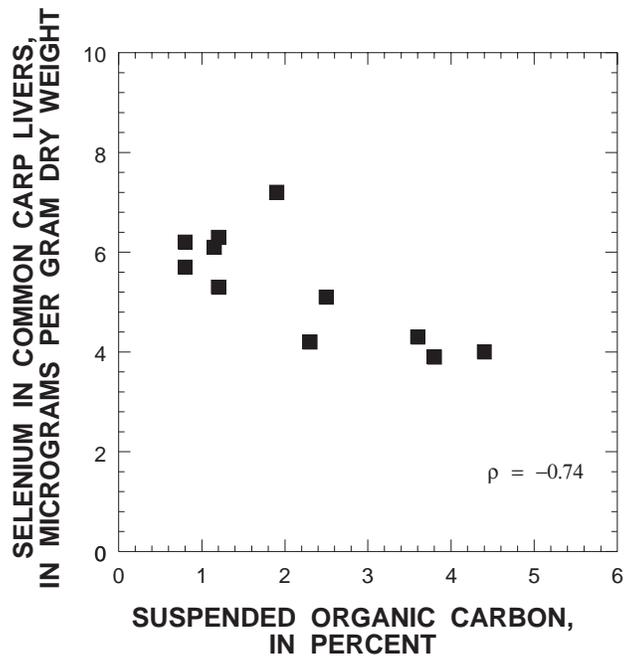
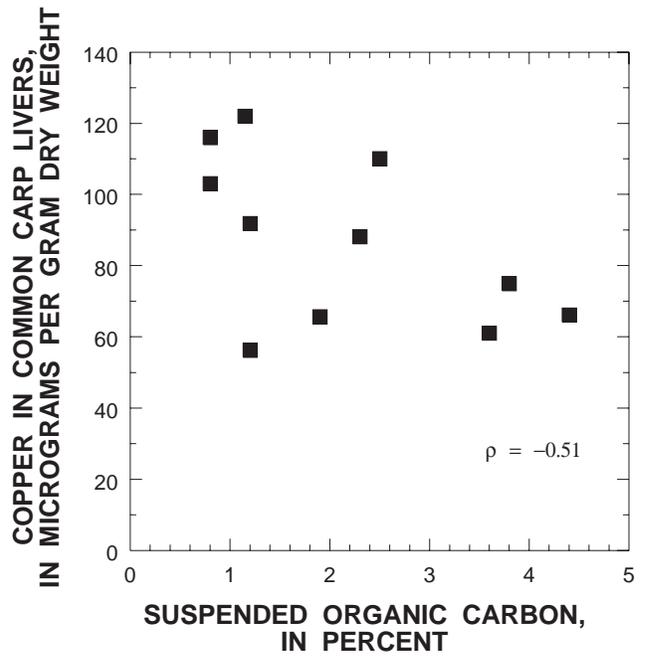
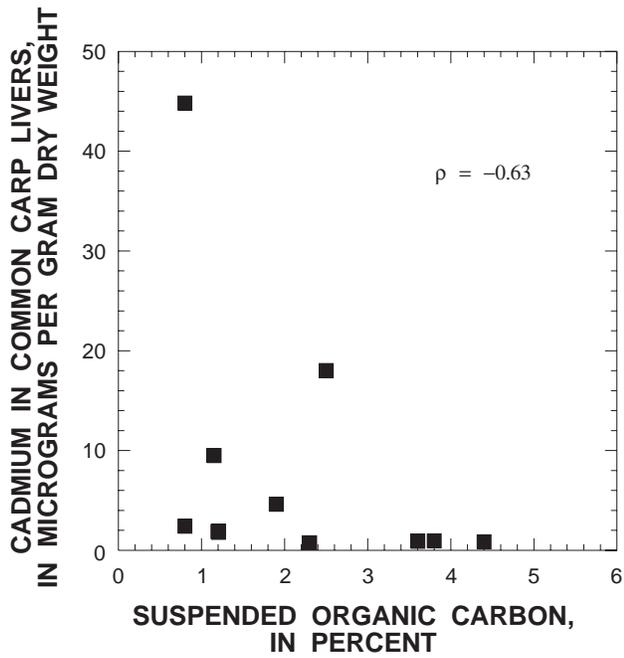


Figure 27. Continued.

## SUMMARY AND CONCLUSIONS

The U.S. Geological Survey, as part of a pilot National Water-Quality Assessment project, examined 22 major and trace elements in water, sediment, and biota in the upper Illinois River Basin. The 22 elements include aluminum, antimony, arsenic, barium, beryllium, boron, cadmium, chromium, cobalt, copper, iron, lead, manganese, mercury, molybdenum, nickel, phosphorus, selenium, silver, strontium, vanadium, and zinc. The distributions and correlation of these elements in and among each of the three aquatic components were identified, although conclusions were hindered because of the large amount of concentration data below the minimum reporting level.

Several concentrations of the priority pollutants exceeded water-quality criteria at urban sites from 1978 through 1986 and from 1987 through 1990, and the number of concentrations that exceeded these criteria were approximately the same at similar sites between these periods. The results from this study were not adequate to evaluate whether these concentrations above the criteria affect the propagation and distribution of biological communities. An ecological survey was done at the same time as the synoptic survey for biota. Results of the ecological survey may provide some insight into the relation between water chemistry and the health of aquatic organisms in the upper Illinois River Basin.

Mean annual loads and yields of urban-associated elements at urban sites typically were one order of magnitude larger than loads and yields of the same elements at agricultural sites. In the Chicago area, yields of lead from streams were similar to yields of lead from atmospheric deposition; however, yields of other priority pollutants, such as copper and zinc, were much greater in streams than in atmospheric deposition.

Although the Chicago area contains some of the most intensively used urban and industrial land, concentrations of many of the priority pollutants in water were below the minimum reporting level. This limited the amount of analysis that could be done with these pollutants. Better analytical techniques with smaller minimum reporting levels would be necessary to evaluate the occurrence and distribution of trace elements in water, especially outside of urban areas. Minimum reporting levels for some elements were barely low enough to classify concentrations that

were above water-quality criteria.

Correlations among elements in water were site specific for many elements, but correlations for grouped data from eight NAWQA fixed sites were similar to those for grouped data from 40 NAWQA and Illinois Environmental Protection Agency sites. Differences in correlations probably depended on the source of an element and on site-specific geochemical and biological processes. Total and dissolved concentrations correlated only for boron and strontium. Total and dissolved concentrations correlated for arsenic, barium, chromium, and nickel, but correlation coefficients differed significantly among sites. No correlation was found among dissolved and total recoverable concentrations for aluminum, copper, iron, and lead.

From 1978 through 1990, barium, boron, iron, manganese, and strontium concentrations in water decreased at many sites in the upper Illinois River Basin, and strontium concentrations in water increased at a number of other sites. Downward trends in streamflow were observed at two sites; these were not the same sites where concentrations of these elements decreased. More significant downward trends in streamflow were expected as a result of drought conditions from 1987 through 1989. Trends in barium and strontium concentrations are probably caused by changes in ground-water sources utilized as water supplies in the Fox and Du Page River Basins. The lack of expected downward trends in lead may be because of the release of lead from the stream sediments to the water column, which would maintain concentrations in water long after the initial source of the lead was removed.

All of the priority pollutants except arsenic were enriched in streambed sediments from urban areas relative to agricultural areas. The pattern of enrichment for many of these priority pollutants in streambed sediments continues for many miles down the Illinois River, although concentrations are reduced by sediment originating from the Fox and Kankakee River Basins. In addition, several of the priority pollutants were enriched in sediment from high-order streams relative to low-order streams. Correlation of the priority pollutants in sediments indicates that streams contain a well-mixed variety of elements from municipal wastewater-treatment plants, combined sewer overflows in Chicago, industrial point sources, and urban runoff from streets, parking lots, and buildings.

Significant seasonal variations in element concentrations in suspended sediment indicate that the amount of elements transported in a stream depends on more than just the suspended-sediment concentration. Other geochemical or biochemical processes seem to affect the concentrations of elements in the suspended sediment. Understanding these processes is essential to developing adequate sediment-quality criteria.

The widespread effects of human activity on water resources in the upper Illinois River Basin made it difficult to identify reference sites where background concentrations of one or more elements could be found in all components, especially biota. Because of variation in concentrations among species and, at times, within different populations of a single species, information on background concentrations of elements in biota is critical in assessment of environmental effects on water quality. Some streams that were selected as reference sites on the basis of retrospective information and habitat were later identified as having elevated concentrations of several elements. Fortunately, concentrations of some elements were relatively small at one or more sites compared to other sites in the upper Illinois River Basin, even if those sites may have been enriched in other elements. This allowed for estimation of some "background" concentrations for the purposes of this study; however, these concentrations do not represent natural background concentrations because effects of human activity in the basin are widespread.

Element concentrations seem to be somewhat enriched in biota from several sites in the upper Illinois River Basin compared to other sites in and outside of the basin. In addition, biota from some urban sites, such as the North Branch Chicago River (site 45), North Shore Channel (site 46), Little Calumet River (site 53), and Salt Creek (site 38) were enriched with respect to more than one element. Studies of the effects of elevated concentrations of priority pollutants on biological development and diversity need to take into account the synergistic effects of these elements.

Whether elevated concentrations of some elements in biota from the upper Illinois River Basin resulted in toxicity to the biota is not known. Toxicity data from biota exposed to elements under field conditions are uncommon and may not be applicable to biota from the basin. The inherent variability of natural systems and limitations in the ability to detect responses of biota to element exposures in

nature has resulted in a lack of criteria for maximum tissue concentrations necessary to protect aquatic life (Luoma and Carter, 1991).

Correlations were observed between element concentrations in tissues of biota. Correlations of copper, mercury, and zinc concentrations were strongly positive with each other in white sucker and common carp livers; copper and zinc also were positively correlated in crayfish. In addition, aluminum, chromium, iron, and vanadium were positively correlated in crayfish. Correlations of these sediment-associated elements indicate a common source and mode of element accumulation in these biota.

Although statistical comparisons were not possible, patterns of element concentrations in biota indicate land-use relations. Arsenic was enriched in biota collected from sites representing agricultural land uses only, whereas chromium, lead, nickel, and strontium were enriched in biota collected from urban sites only. This pattern may indicate that these land uses are important sources of the element to biota in the basin. In contrast, elevated concentrations of barium, cadmium, copper, mercury, selenium, and zinc were observed at agricultural and urban sites.

Differences in element concentration among biota from sites in the upper Illinois River Basin support the collection of more than one species at a site in water-quality investigations. Concentrations of most elements were measurable in bivalves. In contrast, fish livers generally contained the smallest concentrations of all biota for aluminum, arsenic, barium, boron, chromium, manganese, strontium, and vanadium. Fish livers, however, generally contained the largest concentrations of copper, mercury, selenium, and zinc in biota from the basin. Fish livers also were adequate bioindicators of cadmium bioavailability, and carp livers generally contained the largest concentrations in biota. Whole crayfish may not be adequate bioindicators of cadmium for the upper Illinois River Basin. Submersed aquatic plants had fewer concentrations below the minimum reporting levels for element concentrations than all other biota collected in the basin. Caddisflies and wild celery from Salt Creek, an urban/industrial stream, accumulated concentrations of most elements well above minimum reporting levels, including concentrations of some elements (chromium, nickel, and lead) that were near or below such levels in three other types of biota collected at this site. Thus, any one species of biota

may not accumulate all elements of concern and, therefore, may not be a good bioindicator for some elements.

Results of sampling for water, sediment, and biota in the upper Illinois River Basin indicate that many major and trace elements are elevated or enriched in these components. Although concentrations of some priority pollutants were distinctly enriched in urban areas in all components, many of the pollutants were enriched in only the sediment component. In addition, arsenic concentrations in all components were enriched in agricultural areas.

Determining correlations among the three components was hindered by the amount of concentration data below minimum reporting levels. Correlations among elements in water and sediment differed among sites in many cases. In addition, correlations among biota and water and sediment were limited because of the number of different species sampled and insufficient amounts of data.

The largest arsenic concentrations in water, sediment, and biota were found at sites in the Kankakee River Basin. Agricultural use of arsenic-based chemicals (insecticides, herbicides, algicides, and desiccants) has resulted in the largest anthropogenic source of arsenic in the environment (Woolson, 1975). Agriculture use, however, does not fully explain the larger concentrations of arsenic in the Kankakee River Basin because the Iroquois River, a tributary to the Kankakee River, drains an area with a greater percentage of agricultural land yet has smaller concentrations of arsenic in all three components. Arsenic concentrations in the Kankakee River seem to be affected by more than just the source of the arsenic. The predominance of arsenic in the Kankakee River Basin is enhanced by properties of the geochemical substrate, such as the particle size of sediments. The lack of fine-grained sediment in the Kankakee River Basin may have allowed more arsenic to be associated with iron and manganese coatings, which may have allowed the arsenic to become more bioavailable. Although concentrations of arsenic in water are below water-quality criteria, the apparent enrichment of arsenic in biota from the Kankakee River warrants further study.

The distribution of barium and strontium concentrations differed among the three components. For example, elevated strontium concentrations were found in water and biota in the Du Page and Fox River Basins, whereas concentrations of strontium in stream-bed sediment were elevated in the Fox River Basin but not in the Du Page River Basin. Large concentrations of barium in water were observed in the Fox and Du Page River Basins, but concentrations in sediments were not large in these basins. Elevated concentrations of barium and strontium in water seem to be related to ground-water sources in the Fox and Du Page River Basins.

Correlations of concentrations in streambed sediment and other components were limited by a lack of particle-size data to determine the proportion of fine-fraction sediments in total streambed sediments at a given location. Large concentrations of contaminants in fine-fraction sediments might be less available to biota and to the water column if these sediments were only a small percentage of the sediments at a location. Between-site differences in particle-size distribution of streambed sediments may help explain why correlations between concentrations of some elements in water, sediment, and biota were not observed in this study.

Phosphorus concentrations in water correlated with priority pollutants in streambed sediments. This relation means that elevated phosphorus concentrations in water could be used to indicate water that contains large concentrations of priority pollutants. This indication could be important where elements that are known to bioaccumulate are found below the minimum reporting level.

Significant correlations were observed among alkalinity and other buffer-related elements in water and priority pollutants in suspended sediment and streambed sediment. Thus, the buffering capacity of the water seems to have affected concentrations of priority pollutants in the sediment.

Positive and negative correlations were observed among water or sediment and biota for some elements. Concentrations of aluminum and barium in crayfish positively correlated with concentrations of these elements in water and concentrations of manganese and strontium positively correlated with concentrations of these elements in common carp livers. Concentrations of arsenic and possibly cadmium in suspended sediment were positively correlated with concentrations of these elements in common carp

livers. Manganese in white sucker livers and strontium in common carp livers were positively correlated with concentrations of these elements in streambed sediments. These relations indicate that suspended and streambed sediments may be important sources of these elements to biota. Negative correlations were found between concentrations of copper and mercury in common carp livers and in streambed sediment. Concentrations of suspended organic carbon were positively correlated with concentrations of strontium in carp livers and were negatively correlated with cadmium, copper, and selenium in carp livers. Total organic carbon concentration positively correlated with iron concentrations in carp livers.

The small number of correlations found between element concentrations in tissues of biota and other components in this study emphasizes that water and sediment cannot be used as surrogates for biota, that concentrations in biota cannot presently be determined from concentrations in these components, and that bioaccumulation must be measured directly. This is because of the complex variety of chemical, physical, and biological variables affect the bioavailability of elements from water and sediment. Biota have been effectively used in several water-quality studies in the upper Illinois River Basin and elsewhere as indicators of bioavailability and as a complementary line of evidence with water and sediment data in interpretations of anthropogenic effects (Phillips, 1980; Steffek and Striegl, 1989).

Whereas element concentrations in water are instantaneous, concentrations in sediments and biota may provide indicators of water quality that are integrated over time. At sites where ambient concentrations fall below current analytical minimum reporting levels for water, concentrations in sediment and biota can provide valuable water-quality information. In the upper Illinois River Basin, total recoverable and dissolved concentrations of a number of elements in water were commonly near or below minimum reporting levels in water but were measurable, and at times elevated, in sediment and biota. These elements included the highly toxic priority pollutants arsenic, selenium, and zinc. Concentrations of mercury in sediment and biota were measurable and distinctly different among sites, even though many observations were below the minimum reporting levels for total recoverable and dissolved mercury in water. For these reasons, a combination of information from various components is clearly the

optimum for achieving the most complete understanding possible of water quality in the upper Illinois River Basin.

## CONSIDERATIONS FOR FUTURE NATIONAL WATER-QUALITY ASSESSMENT STUDIES

Results from the analysis of major and trace elements in water, sediment, and biota from the pilot NAWQA study of the upper Illinois River Basin indicate that the following considerations are important for future NAWQA studies.

### Sampling Design

1. **Objectives.**—Such objectives would ideally be set as early as possible in the project to maximize efficiency of sampling and usefulness of the data. Quantitative analysis of data collected in the pilot NAWQA synoptic surveys of sediment and biota in the upper Illinois River Basin was restricted because of multiple objectives in the design of the surveys.

2. **Overlap with data-collection network.**—The number of sites that overlap between surveys of different components must be carefully determined if the objectives of the project include (a) statistical comparisons of differences in constituents among water, sediment, and biota and (b) description of the accumulation and fate of the constituents through the aquatic system.

3. **Selection of reference sites.**—Review of retrospective data, information from local experts, and onsite reconnaissance are critical to selection of reference sites. Use of more than one reference site helps to ensure that background concentrations of all elements of interest are adequately identified.

4. **Number of species and organisms in samples.**—Comparability of biotic samples is enhanced if the number of species of biota collected in a basin (or program) is minimized and at least five individual organisms are included in each composite. Best results are obtained when individuals of a species are similar in size among sites and replicate composite samples are collected at a certain number of sites. These considerations have been addressed for the design of future NAWQA studies by Crawford and Luoma (1993).

5. **Types of biota.**—Ideally, at least two species of different types of biota would be collected at each site whenever possible. This strategy has been recommended for at least 50 percent of all sites in future NAWQA studies to aid assessment of the bioavailability of all elements that may be of concern (Crawford and Luoma, 1993).

6. **Collection of biota by subbasin or ecoregion.**—Collection of the same species of biota from at least five sampling locations in each subbasin or ecoregion would allow statistical comparison of element concentrations in biota among either subbasins or ecoregions in the basin.

#### Field and Laboratory Methods

1. **Consistency in sampling methods.**—Although project teams commonly think of potential improvements in methods during a project, consistency in sampling methods is essential for data comparability. For example, sediments collected during the biology synoptic sampling should be the same as those used during the sediment synoptic sampling if the data are to be compared.

2. **Consideration of sediment particle size.**—If the amount of an element in the sediment is of interest, then particle-size analysis could be considered for identifying the amount of the sample in the fine fraction. Particle-size analysis is inexpensive compared to other chemical analyses, and it is almost always useful in interpretation of element concentrations, even if simple verification of the presence of the element is the only objective of the sampling strategy.

3. **Partial digestion of sediment samples.**—Compared with total digestions, partial digestions provide more information about the concentrations of elements in adsorbed materials, which are important for assessing the amount that may be transported from the sediment to the water column. Partial digestions also are more useful for assessing the amount of an element that is available for biological uptake.

4. **Minimum reporting levels.**—Use of the most appropriate and state-of-the-art laboratory methods is necessary to achieve adequate minimum reporting levels and minimize the number of “less-than” values in a data set.

#### Ancillary Data

1. **Composition of soil and rock.**—Collection of comparable background information on concentrations of elements in soils, glacial materials, and bed-rock in the study area would be useful in classifying concentrations of elements in stream sediments. In the upper Illinois River Basin, background concentrations identified in previous studies could not be directly compared to samples collected during the NAWQA study.

2. **Geographic data and analysis.**—A geographic information system can be useful for analyzing large data bases and for integrating and displaying information from a wide variety of sources. Useful maps include, but are not limited to, land use, point sources, soils, surficial geology, and bedrock geology.

3. **Composition of ground water.**—If ground water significantly contributes to base flow, data on concentrations of major and trace elements in this component would be valuable for interpretation of element concentrations in the surface-water column. Analysis should be done to determine which sites (if any) can be eliminated and where new sites (if any) should be added. In the full-scale NAWQA program, surface-water and ground-water components will be integrated.

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