

# **Trace Elements and Organic Chemicals in Stream-Bottom Sediments and Fish Tissues, Red River of the North Basin, Minnesota, North Dakota, and South Dakota, 1992-95**

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## FOREWORD

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

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

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

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

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

The goals of the NAWQA Program are being achieved through investigations of 60 of the Nation's most important river basins and aquifer systems, which are referred to as study units. These study units are distributed throughout the Nation and cover a diversity of hydrogeologic settings. More than two-thirds of the Nation's freshwater use occurs within the 60 study units and more than two-thirds of the people served by public water-supply systems live within their boundaries.

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

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

Robert M. Hirsch  
Chief Hydrologist



## Contents

|                                             |    |
|---------------------------------------------|----|
| Abstract .....                              | 1  |
| Introduction .....                          | 1  |
| Study area .....                            | 1  |
| Background .....                            | 3  |
| Sample media .....                          | 4  |
| Acknowledgments .....                       | 5  |
| Study methods .....                         | 5  |
| Sampling .....                              | 5  |
| Chemical and data analyses .....            | 5  |
| Quality control .....                       | 6  |
| Field samples .....                         | 6  |
| Laboratory quality control .....            | 6  |
| Sediment chemistry .....                    | 9  |
| Elemental composition .....                 | 9  |
| Organochlorines .....                       | 14 |
| Semivolatile organic compounds .....        | 14 |
| Trace elements in fish livers .....         | 19 |
| Trace elements in whole-fish samples .....  | 21 |
| Organochlorines in whole-fish samples ..... | 25 |
| Implications for resource quality .....     | 25 |
| Sediments .....                             | 25 |
| Fish tissues .....                          | 26 |
| Summary .....                               | 28 |
| References .....                            | 29 |

## Illustrations

|                                                                                                                                                    |    |
|----------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Figure 1. Map of study area, physiographic areas, and sites sampled for stream-bottom sediments and fish tissue .....                              | 2  |
| Figures 2-6. Graphs showing:                                                                                                                       |    |
| 2. Concentrations of selected elements plotted against aluminum concentrations in stream-bottom sediments .....                                    | 10 |
| 3. Concentrations of selected elements plotted against aluminum concentrations in stream-bottom sediments .....                                    | 13 |
| 4. Loadings for first two principal components, from principal component analysis of element concentrations in stream-bottom sediments .....       | 15 |
| 5. Loadings for first and third principal components, from principal component analysis of element concentrations in stream-bottom sediments ..... | 16 |
| 6. Groupings of sites, based on site scores from principal component analysis of element concentrations in stream-bottom sediments .....           | 17 |
| 7. Map showing distribution of total polycyclic aromatic hydrocarbon concentrations in stream-bottom sediments .....                               | 20 |

## Illustrations—continued

Figures 8-9. Graphs showing:

|                                                                                                                                            |    |
|--------------------------------------------------------------------------------------------------------------------------------------------|----|
| 8. Ratios of light to heavy polycyclic aromatic hydrocarbon concentrations versus total PAH concentrations in stream-bottom sediments..... | 21 |
| 9. Selected trace element concentrations in fish tissue samples.....                                                                       | 24 |

### Tables

|                                                                                                                                                                  |    |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| 1. Chemical elements determined in less than 63-micrometer stream-bottom sediments and fish tissues, with method reporting limits.....                           | 3  |
| 2. Organochlorines determined in less than 2-millimeter stream-bottom sediments and whole-fish composite samples, with method reporting limits.....              | 7  |
| 3. Semivolatile organic chemicals determined in less than 2-millimeter stream-bottom sediments.....                                                              | 8  |
| 4. Summary of surrogate-recovery data for organic chemical analyses of stream-bottom sediments.....                                                              | 9  |
| 5. Summary of element concentrations in 43 stream-bottom sediment samples, and correlation with aluminum concentration.....                                      | 11 |
| 6. Summary of concentrations of organic chemicals in stream-bottom sediments.....                                                                                | 18 |
| 7. Selected fish-sample data: location, common name, mean weight and length, and concentrations of selected chemical constituents in composite fish samples..... | 22 |
| 8. Comparison of selected chemical constituents in stream-bottom sediments with concentrations thought to adversely affect aquatic biota.....                    | 27 |

### Conversion Factors

| <u>Multiply</u>                     | <u>By</u> | <u>To obtain</u>  |
|-------------------------------------|-----------|-------------------|
| centimeter (cm)                     | 0.3937    | inch              |
| millimeter (mm)                     | .03937    | inch              |
| meter (m)                           | 3.281     | foot              |
| kilometer (km)                      | .6214     | mile              |
| square kilometer (km <sup>2</sup> ) | .3861     | square mile       |
| kilogram                            | 2.205     | pound avoirdupois |

Concentrations of substances in sediments and fish are given in weight percent, micrograms per gram ( $\mu\text{g/g}$ ), or nanograms per gram ( $\text{ng/g}$ ). A microgram is a millionth of a gram; a nanogram is a billionth of a gram.

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## Abstract

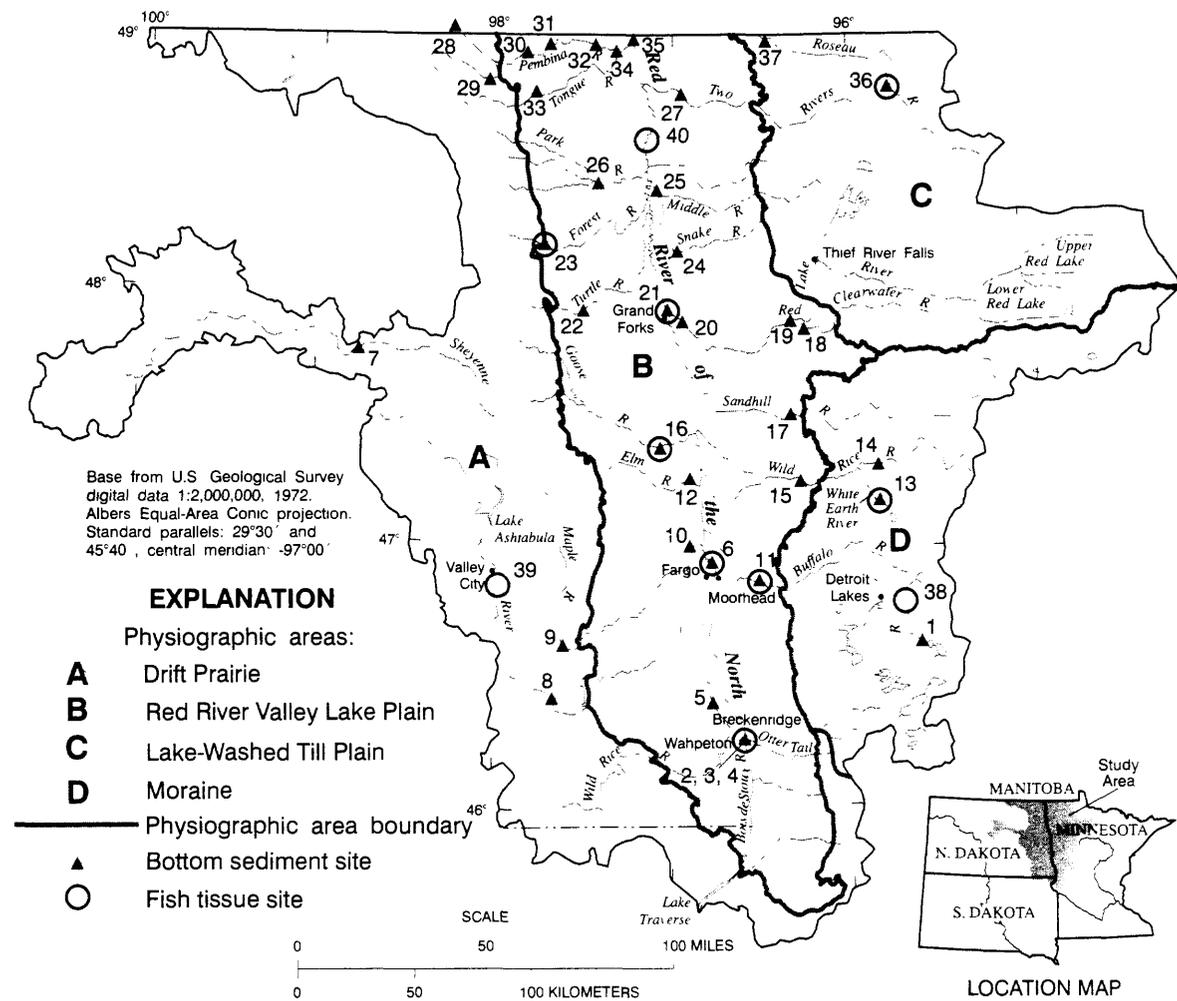
Stream-bottom sediment and fish-tissue samples from the Red River of the North Basin, were analyzed for a large suite of chemical elements and organic chemicals. Cadmium, lead, and mercury were widespread in sediments, at concentrations not indicative of acute contamination. Mercury, the element of greatest health concern in the region, was detected at low concentrations in 38 of 43 sediment samples (<0.02-0.13 micrograms per gram) and all of eleven fish-liver samples (0.03-0.6 micrograms per gram dry weight, or 0.0066-0.13 micrograms per gram wet weight). Concentrations of many elements appeared to be controlled by mineral rather than anthropogenic sources. DDT and its metabolites were the most frequently detected synthetic organochlorines: *p,p'*-DDE was detected in 9 of 38 sediment samples (concentration range: <1-16 nanograms per gram) and also frequently in whole-fish samples. Total DDT (the sum of DDT and its metabolites) concentrations ranged from <5 to 217 nanograms per gram, and at least one component of total DDT was detected in 19 of 23 fish samples. Concentrations of DDT and its metabolites in stream sediments were significantly higher in the intensively cropped Red River Valley Lake Plain, compared to upland areas, probably because of greater historical DDT usage in the lake plain. Several polycyclic aromatic hydrocarbons were detected in stream-bottom sediments. Although the potentially toxic chemicals measured in this study were at low levels, relative to more contaminated areas of the Nation, maximum concentrations of some chemicals are of concern because of their possible effects on aquatic biota and human health.

## Introduction

Trace elements, organochlorines, polycyclic aromatic hydrocarbons (PAHs), and other organic contaminants have entered aquatic environments as a result of modern industrial and agricultural activities. Many of these hydrophobic contaminants are toxic, and therefore are water-quality concerns if present at sufficient concentrations. This report summarizes analyses of stream-bottom sediments and fish tissues collected from streams of the Red River of the North (Red River) Basin to assess the presence and distribution of many of these contaminants. This study is one aspect of the U.S. Geological Survey's National Water-Quality Assessment (NAWQA) of the Red River Basin. The Red River Basin is one of 60 NAWQA study units across the Nation. Other parts of the study include stream-water quality, aquatic ecology, and ground-water quality, and will be combined to provide multiple lines of evidence (Gurtz, 1994) for assessment of the aquatic resources in the Red River Basin (Stoner and Lorenz, 1996).

## Study Area

The land surface of the Red River Basin, largely composed of unconsolidated sediments, is a remnant of the most recent glaciation. Lorenz and Stoner (1997) delineated physiographic areas for the U.S. portion of the Red River Basin (fig. 1), which is the focus of this study (some Canadian drainage from the Pembina River Basin also is included). Approximately 80 percent of the Red River Valley Lake Plain, a glacial lake bed, is cultivated. Extensive drainage has converted large areas of poorly drained lands, including wetlands, to cropland. West of the Red River Valley Lake Plain is the Drift Prairie, an area of low, rolling hills and prairie with many prairie-pothole wetlands. Cretaceous marine sediments crop out in some river valleys in this area, especially the Pembina River valley (Bluemle, 1977). East of the Lake Plain are the Moraine, an area of rolling hills with forests, lakes, and wetlands; and the Lake-Washed Till Plain, a flat area of extensive wetlands. Agriculture in the upland areas is a mixture of cropland and livestock production; cropland accounts for substantially less land use than in the Red River Valley Lake Plain.



- |                                                       |                                                          |
|-------------------------------------------------------|----------------------------------------------------------|
| 1 Otter Tail River near Perham, Minn.                 | 21 Red River of the North at Grand Forks, N. Dak.        |
| 2 Otter Tail River at Breckenridge, Minn.             | 22 Turtle River near Arvilla, N. Dak.                    |
| 3 Bois de Sioux River near Wahpeton, N. Dak.          | 23 Forest River near Fordville, N. Dak.                  |
| 4 Red River of the North at Wahpeton, N. Dak.         | 24 Snake River above Alvarado, Minn.                     |
| 5 Wild Rice River near Abercrombie, N. Dak.           | 25 Snake River near Big Wood, Minn.                      |
| 6 Red River of the North downstream of Fargo, N. Dak. | 26 Park River at Grafton, N. Dak.                        |
| 7 Sheyenne River near Warwick, N. Dak.                | 27 South Branch Two Rivers at Hallock, Minn.             |
| 8 Sheyenne River at Lisbon, N. Dak.                   | 28 Pembina River near Windygates, Manitoba               |
| 9 Maple River near Enderlin, N. Dak.                  | 29 Little South Pembina River near Walhalla, N. Dak.     |
| 10 Sheyenne River near Harwood, N. Dak.               | 30 Pembina River at Walhalla, N. Dak.                    |
| 11 Buffalo River near Glyndon, Minn.                  | 31 Pembina River above Neche, N. Dak.                    |
| 12 Elm River near Grandin, N. Dak.                    | 32 Pembina River below Neche, N. Dak.                    |
| 13 White Earth River near Waubun, Minn.               | 33 Tongue River near Hallson, N. Dak.                    |
| 14 Wild Rice River near Mahanomen, Minn.              | 34 Pembina River above Pembina, N. Dak.                  |
| 15 Wild Rice River at Twin Valley, Minn.              | 35 Red River of the North at Pembina, N. Dak.            |
| 16 Goose River at Hillsboro, N. Dak.                  | 36 Roseau River below South Fork near Malung, Minn.      |
| 17 Sand Hill River at Fertile, Minn.                  | 37 Roseau River below State Ditch 51 near Caribou, Minn. |
| 18 Clearwater River at Red Lake Falls, Minn.          | 38 Otter Tail River near Detroit Lakes, Minn.            |
| 19 Red Lake River at Red Lake Falls, Minn.            | 39 Sheyenne River at Valley City, N. Dak.                |
| 20 Red Lake River at East Grand Forks, Minn.          | 40 Red River of the North near Drayton, N. Dak.          |

**Figure 1. Study area, physiographic areas, and sites sampled for stream-bottom sediments and fish tissue (fish tissue site names are underlined).**

About 511,000 people (U.S. Bureau of Census, 1991) live in this 90,600 km<sup>2</sup> basin, with about one-third of the population concentrated in the Fargo-Moorhead and Grand Forks-East Grand Forks areas. Heavy industry is sparse in the region. See Stoner and others (1993) for a more complete review of the environmental setting of the Red River Basin.

### Background

Various elements may be useful to distinguish sediment sources or types because elements are not equally distributed geographically. Background concentrations of many elements measured, such as calcium, aluminum, and various trace and rare-earth elements, reflect the compositions of geologic parent materials. Some conservative (relatively nonreactive) elements such as Al, Fe, and Ti (names and symbols of elements are listed in table 1) have been used to help evaluate variations in trace element contents of sediments (Horowitz, 1991, p. 88; Kennicutt and others, 1994).

Trace elements occur naturally in the environment, but their concentrations may be substantially altered by industrial discharges, combustion of fossil fuels, and mining. Nriagu and Pacyna (1988) reported that human activities result in substantial inputs to the environment of As, Cd, Cr, Cu, Hg, Mn, Ni, Pb, Sb, Se, Sn, V, and Zn. Lead has been widely used as a gasoline additive. Other heavy metals (Cd, Cr, Cu, Hg, Mn, Ni, Sb, Sn, and Zn) are used in association with metal works such as plating or in the manufacture of alloys.

Organochlorine insecticides and other complex (heavy), chlorinated organic chemicals such as polychlorinated biphenyls (PCBs) are synthetic; that is, they do not occur naturally. Many organochlorines, such as DDT and its metabolites DDE and DDD, are resistant to biological degradation and persist in the environment for years. Many of these compounds can concentrate in and harm biota. As a result, many of these compounds have been banned from agricultural or industrial use in the United States and Canada since the 1970's. However, some organochlorines are still used abroad. Global atmospheric transport results in continued deposition of these compounds in regions where they are no longer used (see, for example, Kurtz, 1990). Many of these compounds have been designated as priority pollutants by the U.S. Environmental Protection Agency (USEPA). (Priority pollutants are defined in Federal Register, 46 CRF, p. 2264, Jan. 8, 1981, and in texts on water pollution or treatment such as Viessman and Hammer, 1985). Priority pollutants are closely

Table 1.—Chemical elements determined in less than 63-micrometer stream-bottom sediments and fish tissues, with method reporting limits [% , percent, by weight; µg/g, micrograms per gram; NA, not analyzed. Concentrations are given in dry weight basis.]

| Element          | Method reporting limit |              |
|------------------|------------------------|--------------|
|                  | Sediments              | Fish tissues |
| Aluminum, Al     | 0.05 %                 | 1.0 µg/g     |
| Antimony, Sb     | .1 µg/g                | .1 µg/g      |
| Arsenic, As      | .1 µg/g                | .1 µg/g      |
| Barium, Ba       | 1.0 µg/g               | .1 µg/g      |
| Beryllium, Be    | 1.0 µg/g               | .1 µg/g      |
| Bismuth, Bi      | 10.0 µg/g              | NA           |
| Boron, B         | NA                     | .2 µg/g      |
| Cadmium, Cd      | .1 µg/g                | .1 µg/g      |
| Calcium, Ca      | .05 %                  | NA           |
| Cerium, Ce       | 4.0 µg/g               | NA           |
| Chromium, Cr     | 1.0 µg/g               | .5 µg/g      |
| Cobalt, Co       | 1.0 µg/g               | .1 µg/g      |
| Copper, Cu       | 1.0 µg/g               | .5 µg/g      |
| Europium, Eu     | 2.0 µg/g               | NA           |
| Gallium, Ga      | 4.0 µg/g               | NA           |
| Gold, Au         | 8.0 µg/g               | NA           |
| Holmium, Ho      | 4.0 µg/g               | NA           |
| Iron, Fe         | .05 %                  | 1.0          |
| Lanthanum, La    | 2.0 µg/g               | NA           |
| Lead, Pb         | 4.0 µg/g               | .1 µg/g      |
| Lithium, Li      | 2.0 µg/g               | NA           |
| Magnesium, Mg    | .005 %                 | NA           |
| Manganese, Mn    | 4.0 µg/g               | .1 µg/g      |
| Mercury, Hg      | .02 µg/g               | .02 µg/g     |
| Molybdenum, Mo   | 2.0 µg/g               | .1 µg/g      |
| Neodymium, Nd    | 4.0 µg/g               | NA           |
| Nickel, Ni       | 2.0 µg/g               | .1 µg/g      |
| Niobium, Nb      | 4.0 µg/g               | NA           |
| Phosphorus, P    | .005 %                 | NA           |
| Potassium, K     | .05 %                  | NA           |
| Scandium, Sc     | 2.0 µg/g               | NA           |
| Selenium, Se     | .1 µg/g                | .1 µg/g      |
| Silver, Ag       | .1 µg/g                | .1 µg/g      |
| Sodium, Na       | .005 %                 | NA           |
| Strontium, Sr    | 2.0 µg/g               | .1 µg/g      |
| Sulfur, S        | .05 %                  | NA           |
| Tantalum, Ta     | 40.0 µg/g              | NA           |
| Thorium, Th      | 4.0 µg/g               | NA           |
| Tin, Sn          | 5.0 µg/g               | NA           |
| Titanium, Ti     | .005 µg/g              | NA           |
| Uranium, U       | .05 µg/g               | .1 µg/g      |
| Vanadium, V      | 2.0 µg/g               | .1 µg/g      |
| Yttrium, Y       | 2.0 µg/g               | NA           |
| Ytterbium, Yb    | 1.0 µg/g               | NA           |
| Zinc, Zn         | 4.0 µg/g               | .5 µg/g      |
| Organic carbon   | .01 %                  | NA           |
| Carbon org+inorg | .01 %                  | NA           |
| Inorganic carbon | .01 %                  | NA           |

monitored because of their potential for harmful environmental and human effects.

PAHs occur naturally, mainly in fossil fuels, and are also formed during fossil-fuel combustion. Environmental concentrations of many PAHs have substantially increased over the last century (LaFlamme and Hites, 1978; Wakeham and others, 1980). Concern over PAH contamination stems from their toxicity, including, at high concentrations, carcinogenicity to fish (Balch and others, 1995, and references therein). Sixteen PAHs are USEPA priority pollutants.

Determining sources of chemicals, particularly those that have both natural and anthropogenic sources, may be difficult for riverine environments. Processes that affect the fate and movement of chemicals, biota, and sediments in streams vary greatly in time and space. Natural versus anthropogenic contributions may be inferred from statistical relationships and available literature (Kennicutt and others, 1994), but cannot be determined quantitatively. In contrast, lake and peatland sediments, which are in more stable depositional environments, have been widely considered to be chemical sinks to more quantitatively determine anthropogenic enrichment of chemicals (Engstrom and others 1994; Hites and others, 1980).

Historical contaminant data for stream-bottom sediments and fish are somewhat limited for the Red River Basin. The U.S. Fish and Wildlife Service measured selected organochlorines and trace elements in fish from the Red River at Noyes, Minn. approximately biennially from 1969 to 1986 (Henderson and others, 1969; Henderson and others, 1971; Schmitt and others, 1981; Schmitt and others, 1983; Schmitt and others, 1985; Schmitt and others, 1990; Schmitt and Brumbaugh, 1990). Goldstein (1995) reviewed these data for the Red River site. Various other Federal and state monitoring agencies have measured organochlorine compounds in fish and sediments (summarized by Tornes and Brigham, 1994). These data indicate a general decrease, over the past two decades, of concentrations of DDT and its metabolites in fish from the Red River. The most rapid decreases came in the 1970's, directly following restrictions on the use of DDT. Measurements in the mid-1980's through 1992 show that DDT levels in fish are low but detectable, and do not appear to be appreciably decreasing (summarized by Tornes and Brigham, 1994; Brigham, 1994). Levels of lead in fish have also decreased nationally (Schmitt and Brumbaugh, 1990) and in the Red River (reviewed by Goldstein, 1995), consonant with the decrease in usage of lead additives in gasoline.

Mercury is the element of greatest concern in game fish, and has prompted health advisories regarding consumption of large game fish (Minnesota Department of Health, 1996; North Dakota Department of Health, 1995). From analyses of sediment cores from rural Minnesota lakes, Swain and others (1992) concluded that deposition of mercury has increased about three-fold over the last century. Increased mercury deposition, which has occurred to some degree globally, has largely been attributed to mercury released from coal combustion and other industrial sources.

## Sample Media

Stream-bottom sediments and fish tissues were sampled for several reasons. Hydrophobic chemicals are easier to detect in solid phases (sediments, tissues) because they tend to concentrate in solid phases relative to the dissolved phase (Foreman and others, 1995; Leiker and others, 1995). Hydrophobic chemicals accumulate in sediments and fish over time, whereas concentrations in water may fluctuate greatly, possibly being high or detectable only transiently. Sediments are an integral part of the aquatic ecosystem. Microbiota live on sediment and use various components of sediment as a substrate for growth. Many benthic organisms live in the interstices of sediments, and are consumed by larger invertebrates and fish. Thus, sediment-bound contaminants may enter aquatic food chains. Game fish are an important aquatic resource in the Red River Basin, so an understanding of contaminants in fish is of interest for public health reasons.

Two different tissue types were analyzed: whole bodies were analyzed for organic chemicals, and fish livers were analyzed for trace elements (following the guidelines of Crawford and Luoma, 1993). Because the liver helps deplete excessive levels of metals (and other chemicals) from organisms, this organ often has higher concentrations of chemicals than other organs, and may be a good indicator organ for metal contaminants.

The relations between concentrations of various elements in liver tissue and muscle (fillet) tissue probably varies by element, fish species, and the level of contamination. A review by Goldstein and others (1996) noted that at mercury concentrations less than about 0.5  $\mu\text{g/g}$  (wet weight basis), mercury levels are typically lower in fish liver than muscle tissue. This observation also held for common carp (*Cyprinus carpio*) in the Red River (Goldstein and others, 1996). At higher concentrations, mercury levels in fish liver exceed those in muscle tissue (reviewed by Goldstein and others,

1996). Comparative data for other elements are not available for fish from the Red River Basin.

## Acknowledgments

We thank Larry Lane of the Mississippi State Chemical Laboratory for analyzing organochlorines in the 1994 fish samples and providing documentation of the method. We also thank the following U.S. Geological Survey Personnel: Robert Borgstede for illustrations; David Lorenz for maps; Shelley Morrison and Julie Tapper for preparing portions of this manuscript; and Ginger Amos, Janet Heiny, Stephen Komor, Charles Wong, and Laurel Woodruff for reviews of the manuscript.

## Study Methods

### Sampling

Bottom-sediment samples were collected from tributaries and from the mainstem of the Red River (fig. 1), using the guidelines of Shelton and Capel (1994). Briefly, the surface 2-4 cm of sediments scooped from about five depositional zones (areas where fine-grained sediments accumulate) at each site were composited, stirred, and separated into two portions. One portion, for analysis of organic chemicals, was sieved with a 2-mm stainless steel sieve. The other portion, for analysis of major and trace elements, was sieved with an acid-cleaned 63-micrometer ( $\mu\text{m}$ ) Nylon sieve, using less than 250 milliliters (mL) native stream water to aid in sieving. The supernatant water was decanted prior to shipping samples to the laboratory.

Sediments typically were sampled once at each site during 1992-95. Several sites were sampled two or more times. Multiple sampling at the same site consisted of one of the following: Intrasite-variability samples, whereby sediments from two or three depositional areas at a site were sampled and analyzed separately (rather than compositing); short-term temporal-variability samples, which were collected at the same site during the same year; and long-term (between-year) variability samples, which were collected at the same site, but during different years. Intrasite and short-term variability samples are considered only in the quality control section of this report. Samples from different years at the same site are treated as independent samples, included in all data analyses.

Fish were collected (sites shown in fig. 1) by electroshocking with pulsed direct current; sorted by species and size, and composited in the field. Detailed methods are given by Crawford and Luoma (1993).

Briefly, five to nine similarly sized individuals were weighed, measured, sexed, and frozen on dry ice. Livers from five to nine other fish were excised, composited in the field, and frozen. Frozen samples were shipped for analysis within 24 hours of collection.

Clean sampling procedures minimized the potential for contamination of samples. Sediment-sampling equipment was cleaned, before use, with a 1-percent Liquinox solution, then rinsed with deionized water and methanol. Equipment used solely for trace element sediment samples was also cleaned with 7 percent nitric acid. Whole fish were wrapped in aluminum foil, and sealed in plastic bags. Fish livers were placed in clean, self-sealing plastic bags. Field personnel wore clean, disposable latex gloves during sample collection and handling.

### Chemical and Data Analyses

Sediment samples for analysis of chemical elements were analyzed at the U.S. Geological Survey's Branch of Geochemistry Laboratory in Denver, Colo. Numerous laboratory analytical and quality-control procedures were used. These have been summarized by Arbogast (1990) and Heiny and Tate (1997). Briefly, dried samples were subjected to complete, strong-acid digestion, and were analyzed by a variety of atomic spectroscopy methods.

Organic chemicals in sediment samples were analyzed at the U.S. Geological Survey's National Water Quality Laboratory (NWQL) in Arvada, Colo. Briefly, samples were solvent extracted. Extracts were dried, reduced in volume, and potential interferences were removed using gel-permeation chromatography (GPC). One aliquot was analyzed for organochlorines by gas chromatography with electron-capture detection (GC-ECD) (Foreman and others, 1995). The other was analyzed for PAHs and other semivolatile compounds by gas chromatography with mass-spectrometry detection (Furlong and others, 1996).

Composite whole-fish samples from the 1992 sampling were analyzed for organochlorines at the NWQL, using methods of Leiker and others (1995). Briefly, methylene chloride extracts of homogenized composite samples were cleaned using GPC, exchanged into hexane, chromatographically separated into two fractions, concentrated, and analyzed by GC-ECD.

From the 1994 sampling, composite whole-fish samples were analyzed for organochlorines at the Mississippi State Chemical Laboratory, Mississippi State, Miss. The method is summarized as follows

(Larry Lane, Miss. State Chemical Laboratory, written commun., 1995):

Five gram tissue samples are thoroughly mixed with anhydrous sodium sulfate and Soxhlet extracted with hexane for seven hours. The extract is concentrated by rotary evaporation; transferred to a tared test tube, and further concentrated to dryness for lipid determination. The weighed lipid sample is dissolved in petroleum ether and extracted four times with acetonitrile saturated with petroleum ether. Residues are partitioned into petroleum ether which is washed, concentrated, and transferred to a glass chromatographic column containing 20 grams of Florisil. The column is eluted with 200 mL 6% diethyl ether/94% petroleum ether (Fraction I) followed by 200 mL 15% diethyl ether/85% petroleum ether (Fraction II). Fraction II is concentrated to appropriate volume for quantification by gas chromatography. Fraction I is concentrated and transferred to a silicic acid chromatographic column for additional cleanup required for separation of PCBs from other organochlorines. Three fractions are eluted from the silicic acid column. Each is concentrated to appropriate volume for quantification of residues by megabore column, electron capture gas chromatography. PCBs are found in Fraction II.

Fish livers (1992 samples) and whole-fish composites (1994 samples) were analyzed at the NWQL for chemical elements following strong-acid digestion, using methods summarized by Hoffman (1996) and by Heiny and Tate (1997).

Tables 1-3 list the analytes measured in this study.

Data were analyzed using principal component analysis and correlation analysis (SAS version 6.07, SAS Institute, Cary, North Carolina). Correlation is a measure of the strength of the linear relation between two variables (SAS Institute, 1989), whereas principal component analysis examines relations among several variables (SAS Institute, 1989). Principal component analysis was performed using the Pearson correlation matrix (SAS Institute, 1989).

### Quality Control

Quality-control samples are analyzed to assess bias and variability of the process of sample collection, handling, shipping, and analysis. To assess data quality, we collected a limited number of field QC samples, and mainly relied on laboratory quality-control data.

### Field samples

No true replicate sediment samples were collected. Rather, sediments were resampled at some sites a few weeks apart, or in some cases, during different years. Results were used to assess whether sampling at a given time affects the measured composition of the sediments. In general, sites that were resampled showed similar sediment composition. A notable exception was niobium in bottom sediments, which appeared to increase in concentration over the period 1993-95 at the Pembina and Red Rivers. However, reported niobium concentrations in standard reference materials also increased during that time period, indicating difficulty in obtaining consistent, precise measurements of that element (Richard Sanzolone, U.S. Geological Survey Branch of Geochemistry Laboratory, oral commun., 1996).

Two sets of duplicate, composite fish-liver samples were collected. Duplicate white sucker (*Catostomus commersoni*) liver samples yielded similar concentrations of all detected elements, whereas one of the liver samples from common carp had systematically higher element concentrations than its paired sample. For elements detected at concentrations greater than 5 times the method reporting limit (Co, Cu, Fe, Mn, Mo, Se, Sr, and Zn for white suckers; Cd, Cu, Fe, Mn, Hg, Mo, Se, V, and Zn for carp), relative percent differences ranged from 0-5.9 percent and 1.9-2.7 percent for white sucker and carp duplicates, respectively. At lower concentrations, relative percent differences for concentrations of detected elements (Cr, Hg, Ag, and B for white suckers; As, Ag, and Sr for carp) ranged from 14-33 percent and 25-50 percent for white sucker and carp duplicates, respectively. Duplicate whole-carp composite samples had similar levels of *p,p'*-DDE (12 and 16 ng/g), which was the only organochlorine detected in these samples.

### Laboratory quality control

For element chemistry, the Branch of Geochemistry Laboratory and the NWQL routinely analyze numerous quality-control samples, including blanks, replicates, reagent spikes, and standard reference materials. Both laboratories participate in interlaboratory comparisons of unknown and standard reference samples. In 1994 and 1995 interlaboratory comparisons (summarized in Willie and Berman, 1995), the Branch of Geochemistry Laboratory rated "superior" in 1994 and "good" for 1995 for accuracy and precision of bed sediment analyses (Richard Sanzolone, U.S. Geological Survey, oral commun., 1996). The NWQL has rated from "fair" to "superior" from 1993-95 for analysis of biological tissues (Kim Pirkey, U.S. Geological Survey, oral

Table 2.—Organochlorines determined in less than 2-millimeter stream-bottom sediments and whole-fish composite samples, with method reporting limits

[Concentrations are expressed on a dry-weight basis for sediments, and a wet-weight basis for fish tissues; NWQL, U.S. Geological Survey National Water Quality Laboratory; Miss. State, Mississippi State Chemical Laboratory; NA, not analyzed.]

| Chemical                                         | Method reporting limit (nanograms per gram) |                   |                          |
|--------------------------------------------------|---------------------------------------------|-------------------|--------------------------|
|                                                  | Bottom sediments (NWQL)                     | Whole fish (NWQL) | Whole fish (Miss. State) |
| Aldrin                                           | 1                                           | 5                 | NA                       |
| <i>cis</i> -chlordane                            | 1                                           | 5                 | 10                       |
| <i>trans</i> -chlordane                          | 1                                           | 5                 | 10                       |
| Chloroneb                                        | 5                                           | NA                | NA                       |
| DCPA (dacthal)                                   | 5                                           | 5                 | NA                       |
| <i>o,p'</i> -DDD                                 | 1                                           | 5                 | 10                       |
| <i>p,p'</i> -DDD                                 | 1                                           | 5                 | 10                       |
| <i>o,p'</i> -DDE                                 | 1                                           | 5                 | 10                       |
| <i>p,p'</i> -DDE                                 | 1                                           | 5                 | 10                       |
| <i>o,p'</i> -DDT                                 | 2                                           | 5                 | 10                       |
| <i>p,p'</i> -DDT                                 | 2                                           | 5                 | 10                       |
| Dieldrin                                         | 1                                           | 5                 | 10                       |
| Endosulfan I                                     | 1                                           | NA                | NA                       |
| Endrin                                           | 2                                           | 5                 | 10                       |
| Heptachlor                                       | 1                                           | 5                 | NA                       |
| Heptachlor epoxide                               | 1                                           | 5                 | 10                       |
| Hexachlorobenzene                                | 1                                           | 5                 | 10                       |
| $\alpha$ -hexachlorocyclohexane ( $\alpha$ -HCH) | 1                                           | 5                 | 10                       |
| $\beta$ -hexachlorocyclohexane ( $\beta$ -HCH)   | 1                                           | 5                 | 10                       |
| $\delta$ -hexachlorocyclohexane ( $\delta$ -HCH) | NA                                          | NA                | 10                       |
| Isodrin                                          | 1                                           | NA                | NA                       |
| Lindane ( $\gamma$ -HCH)                         | 1                                           | 5                 | 10                       |
| <i>o,p'</i> -methoxychlor                        | 5                                           | 5                 | NA                       |
| <i>p,p'</i> -methoxychlor                        | 5                                           | 5                 | NA                       |
| Mirex                                            | 1                                           | 5                 | 10                       |
| <i>cis</i> -nonachlor                            | 1                                           | 5                 | 10                       |
| <i>trans</i> -nonachlor                          | 1                                           | 5                 | 10                       |
| Oxychlordane                                     | 1                                           | 5                 | 10                       |
| PCBs, total                                      | 50                                          | 50                | 50                       |
| Pentachloroanisole                               | 1                                           | 5                 | NA                       |
| <i>cis</i> -permethrin                           | 5                                           | NA                | NA                       |
| <i>trans</i> -permethrin                         | 5                                           | NA                | NA                       |
| Toxaphene                                        | 200                                         | 200               | 50                       |

Table 3.—Semivolatile organic chemicals determined in less than 2-millimeter stream-bottom sediments

| Polycyclic aromatic hydrocarbons:                                                                     |                                  |                                    |
|-------------------------------------------------------------------------------------------------------|----------------------------------|------------------------------------|
| acenaphthene                                                                                          | 1,2-dimethylnaphthalene          | 1-methylpyrene                     |
| acenaphthylene                                                                                        | 1,6-dimethylnaphthalene          | naphthalene                        |
| anthracene                                                                                            | 2-ethylnaphthalene               | phenanthrene                       |
| benz[ <i>a</i> ]anthracene                                                                            | fluoranthene                     | 2,6-dimethylnaphthalene            |
| benzo[ <i>a</i> ]pyrene                                                                               | fluorene                         | phenanthridine                     |
| benzo[ <i>b</i> ]fluoranthene                                                                         | indeno[1,2,3- <i>c,d</i> ]pyrene | pyrene                             |
| benzo[ <i>g,h,i</i> ]perylene                                                                         | 2-methylantracene                | 2,3,6-trimethylnaphthalene         |
| benzo[ <i>k</i> ]fluoranthene                                                                         | 4,5-methylenephenanthrene        |                                    |
| chrysene                                                                                              | 1-methylfluorene                 |                                    |
| dibenz[ <i>a,h</i> ]anthracene                                                                        | 1-methylphenanthrene             |                                    |
| Heterocyclic compounds and Polycyclic aromatic hydrocarbons derivatives:                              |                                  |                                    |
| acridine                                                                                              | 2-chloronaphthalene              | isoquinoline                       |
| anthraquinone                                                                                         | carbazole                        | quinoline                          |
| benzo[ <i>c</i> ]cinnoline                                                                            | dibenzothiophene                 | phenanthridine                     |
| 2,2'-biquinoline                                                                                      |                                  |                                    |
| Monoaromatic compounds, including nitrated, chlorinated, and phenolic compounds and phthalate esters: |                                  |                                    |
| C <sub>8</sub> -alkylphenol                                                                           | di- <i>n</i> -butylphthalate     | 2,4-dinitrotoluene                 |
| azobenzene                                                                                            | 1,2-dichlorobenzene              | 2,6-dinitrotoluene                 |
| bis(2-ethylhexyl)phthalate                                                                            | 1,3-dichlorobenzene              | nitrobenzene                       |
| butylbenzylphthalate                                                                                  | 1,4-dichlorobenzene              | pentachloronitrobenzene            |
| 4-chloro-3-methylphenol                                                                               | diethylphthalate                 | phenol                             |
| 2-chlorophenol                                                                                        | dimethylphthalate                | 1,2,4-trichlorobenzene             |
| <i>p</i> -cresol                                                                                      | di- <i>n</i> -octylphthalate     | 3,5-xyleneol                       |
| Other base-neutral-acid extractable organic compounds:                                                |                                  |                                    |
| 4-bromophenyl phenyl ether                                                                            | isophorone                       | N-nitrosodi- <i>n</i> -propylamine |
| 4-chlorophenyl phenyl ether                                                                           | bis(2-chloroethoxy) methane      | N-nitrosodiphenylamine             |

oral commun., 1996). Neither laboratory participated in the 1992 comparison, which is when many of the samples were submitted for analysis.

For organic chemical analyses, laboratory quality assurance procedures and summaries of method performance are given for bottom-sediment analyses by Foreman and others (1995) and Furlong and others (1996); and for fish-tissue analyses by Leiker and others (1995). As part of assessing method performance (bias and precision), laboratory analysts added surrogates, chemicals with similar properties to the analytes of

interest, to each sample prior to analysis. Reagent-spike samples and reagent-blank samples also were analyzed with each set of samples. For bottom-sediment analyses, low and variable recoveries of surrogates (table 4) and spikes (National Water Quality Laboratory, U.S. Geological Survey, written commun., 1994) plagued early analyses, affecting eleven samples from this study (Foreman and others, 1995, p. 75-78). Analytical recoveries in these samples typically were about half the recoveries observed later in the study, after improvements to the methods were made. Therefore, the

Table 4.—Summary of surrogate-recovery data for organic chemical analyses of stream-bottom sediments.

[*d6*, *d14*, and *d5* indicate hexa-, tetradeca-, and pentadeuterated compounds, respectively; recovery statistics based on 38 samples.]

| Surrogate                                  | Percent recovery |      |         | Surrogate                       | Percent recovery |      |         |
|--------------------------------------------|------------------|------|---------|---------------------------------|------------------|------|---------|
|                                            | Minimum          | Mean | Maximum |                                 | Minimum          | Mean | Maximum |
| Organochlorines:                           |                  |      |         | Semivolatile organic compounds: |                  |      |         |
| $\alpha$ -hexachlorocyclohexane, <i>d6</i> | 35               | 68   | 120     | terphenyl, <i>d14</i>           | 37               | 68   | 130     |
| octachlorobiphenyl                         | 13               | 63   | 110     | 2-fluorobiphenyl                | 23               | 51   | 93      |
| 3,5-dichlorobiphenyl                       | 15               | 58   | 110     | nitrobenzene, <i>d5</i>         | 21               | 55   | 130     |

range of recoveries is quite large. Reported concentrations of the compounds of interest are not corrected for surrogate recovery. Low recoveries result in low-biased concentration data, and analytes that occur at concentrations slightly greater than reporting limits might not be detected in a given sample if analytical recoveries are low.

Coelution and thermal degradation of some DDT compounds occasionally resulted in poor recovery of these compounds, and sometimes deletion of poor-quality data (Leiker and others, 1995). One surrogate (3,5-dichlorobiphenyl) was added to each fish sample prior to analysis. Recoveries of this surrogate ranged from 30 to 90 percent, with a mean of 66 percent.

One duplicate analysis of a fish-tissue sample by the Mississippi State Chemical Laboratory (1994 data) showed similar concentrations of the four detected organochlorines. An associated spiked sample had recoveries of 71-105 percent (mean=97 percent) for the organochlorines analyzed. Lipid determinations tended to be higher than those reported by the NWQL; lipid determinations are influenced by the solvent used for extraction.

### Sediment Chemistry

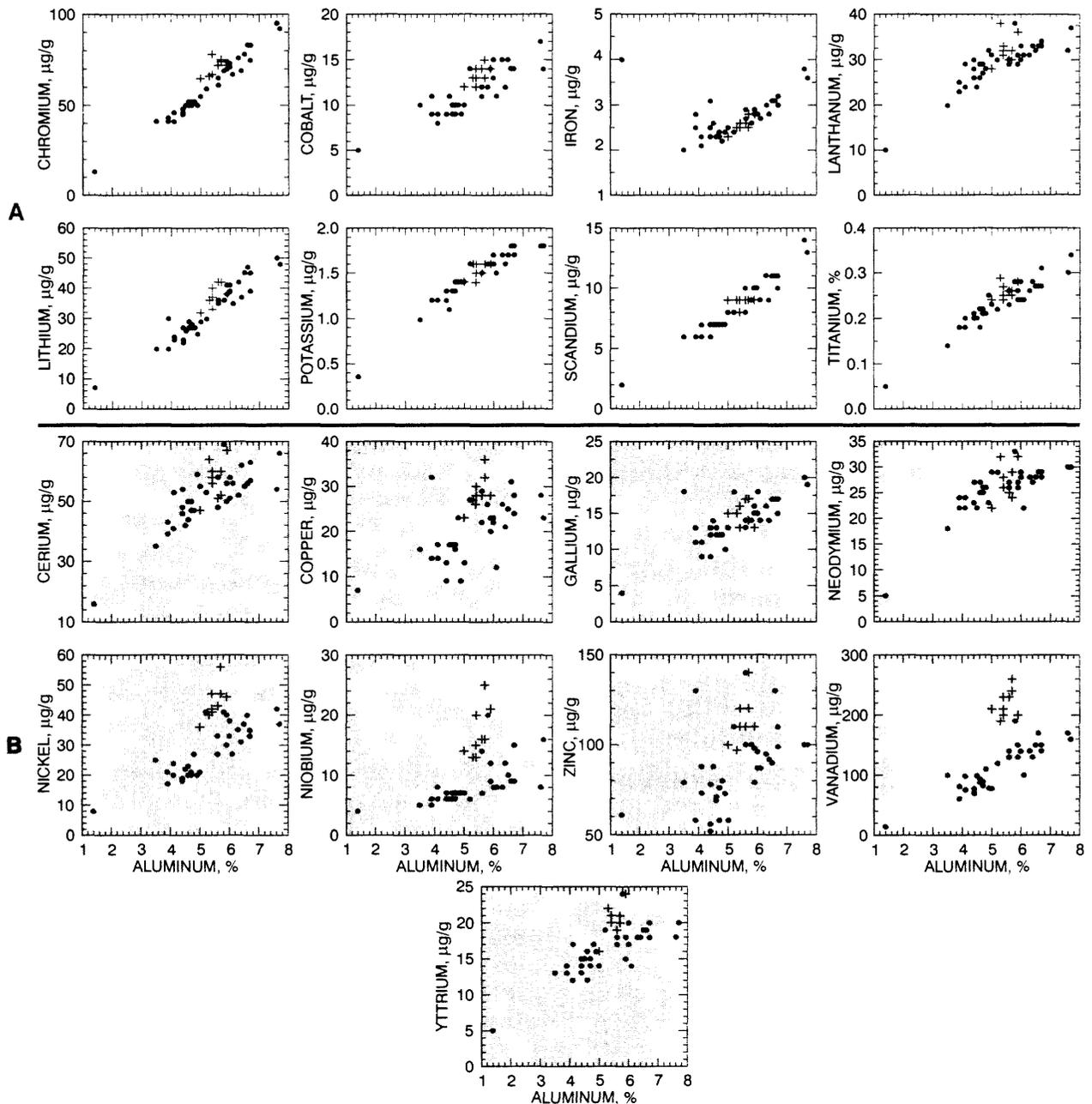
Elemental composition and PAH data for the 1992-94 samples, and organochlorine data for all samples, were summarized by Brigham and Tornes (1996). This section expands on the earlier presentation and includes elemental and PAH data from the 1995 samples. An error in europium data was identified after publication of the earlier paper; all europium data in samples from this study are now reported as less than 2  $\mu\text{g/g}$ . Data for several other parameters have been updated by the NWQL since the publication of the earlier paper.

### Elemental Composition

Measured concentrations of eight trace elements (Cr, Co, Fe, La, Li, K, Sc, and Ti) strongly correlate ( $r \geq 0.74$ )

with aluminum concentrations (fig. 2A; table 5). Nine more trace elements (Ce, Cu, Ga, Nd, Ni, Nb, V, Y, and Zn) moderately correlate ( $0.43 \leq r \leq 0.67$ ) with aluminum (fig. 2B). This suggests that the concentrations of these elements are controlled by the abundance of aluminosilicates or clay minerals. Chromium, which may be enriched in some waters by industrial pollution, shows a very strong correlation ( $r=0.95$ ) with aluminum, which likely precludes contamination as a source of chromium in Red River Basin stream-bottom sediments. [Note: all correlations exclude the sample from the Otter Tail River near Perham, Minn., which is an outlier. This sample had the lowest aluminum content (figs. 2 and 3).]

Most of the elements with strong or moderate correlations with Al (excluding Co, Cu, Ga, Fe, and Ni) are lithophiles (elements that are concentrated in the silicate phase upon mineral formation) (Brownlow, 1979). Thus, abundance of aluminosilicates (especially clay minerals) probably controls concentrations of these elements. Semiquantitative mineralogic analyses of 20 samples from this study show the less than 63- $\mu\text{m}$  sediments to be composed predominantly of silicate minerals (clays, quartz, and plagioclase), with lesser amounts of carbonates (dolomite and calcite) and gypsum (unpublished data; analyses by William M. Last, University of Manitoba, using methods of Last, 1996). It is possible that elements from anthropogenic sources adsorb to aluminosilicate minerals, and thus correlate with aluminum. However, this probably would not explain the strong correlations observed for most lithophilic elements. Any lack of uniformity of inputs, or lack of uniform exposure of sediments to anthropogenic inputs, would likely produce high outliers in the element-aluminum plots (fig. 2), and in normal probability plots of element concentrations (or log-transformed concentrations) (not shown herein). Such outliers were not observed for these elements. No significant correlations with Al, or with Ca and Mg (which are indicators of carbonate and evaporite



### EXPLANATION

- + Sample from Pembina River Basin (sites 28-34)
- Sample from Red River of the North Basin, excluding Pembina River Basin

µg/g = micrograms per gram, dry weight

% = percent, dry weight

**Figure 2. Concentrations of selected elements plotted against aluminum concentrations in stream-bottom sediments. [A - Selected elements that correlate highly ( $r \geq 0.74$ ) with aluminum. B - Selected elements that correlate moderately with aluminum ( $0.43 \leq r \leq 0.67$ ). All correlations exclude the sample with the lowest aluminum concentration, which is an outlier.]**

Table 5.—Summary of element concentrations in 43 stream-bottom sediment samples (less than 63-micrometer fraction), and correlation with aluminum concentration (correlation excludes Otter Tail River sample, which was an outlier).

[% , percent; µg/g, micrograms per gram; <, less than; N≥RL/N, number of values greater than or equal to the reporting limit/number of samples; r(Al), Pearson correlation coefficient with aluminum concentration; --, not calculated. NS, not statistically significant at the 95 percent confidence level.]

| Element, symbol          | Unit | Concentrations |        |         | N≥RL/N | r(Al) |
|--------------------------|------|----------------|--------|---------|--------|-------|
|                          |      | Minimum        | Median | Maximum |        |       |
| Aluminum, Al             | %    | 1.4            | 5.4    | 7.7     | 43/43  | --    |
| Antimony, Sb             | µg/g | .2             | .9     | 2.0     | 43/43  | NS    |
| Arsenic, As              | µg/g | 3.9            | 7.9    | 22      | 43/43  | NS    |
| Barium, Ba               | µg/g | 400            | 500    | 860     | 43/43  | 0.37  |
| Beryllium, Be            | µg/g | <1.0           | 1.0    | 2.0     | 37/43  | --    |
| Bismuth, Bi              | µg/g | <10            | <10    | <10     | 0/43   | --    |
| Cadmium, Cd              | µg/g | .2             | .6     | 2.8     | 43/43  | NS    |
| Calcium, Ca              | %    | 2.3            | 4.9    | 9.4     | 43/43  | -.52  |
| Cerium, Ce               | µg/g | 16             | 53     | 69      | 43/43  | .69   |
| Chromium, Cr             | µg/g | 13             | 66     | 95      | 43/43  | .95   |
| Cobalt, Co               | µg/g | 5.0            | 12     | 17      | 43/43  | .81   |
| Copper, Cu               | µg/g | 7.0            | 23     | 36      | 43/43  | .49   |
| Europium, Eu             | µg/g | <2.0           | <2.0   | <2.0    | 0/43   | --    |
| Gallium, Ga              | µg/g | <4.0           | 14     | 20      | 42/43  | .65   |
| Gold, Au                 | µg/g | <8.0           | <8.0   | <8.0    | 0/43   | --    |
| Holmium, Ho              | µg/g | <4.0           | <4.0   | <4.0    | 0/43   | --    |
| Iron, Fe                 | %    | 2.0            | 2.6    | 4.0     | 43/43  | .81   |
| Lanthanum, La            | µg/g | 10             | 30     | 38      | 43/43  | .76   |
| Lead, Pb                 | µg/g | 8.0            | 13     | 26      | 43/43  | NS    |
| Lithium, Li              | µg/g | 7.0            | 39     | 50      | 43/43  | .92   |
| Magnesium, Mg            | %    | .71            | 2.0    | 4.3     | 43/43  | NS    |
| Manganese, Mn            | µg/g | 610            | 1,400  | 5,100   | 3/43   | -.41  |
| Mercury, Hg              | µg/g | <.02           | .03    | .13     | 38/43  | NS    |
| Molybdenum, Mo           | µg/g | <2.0           | <2.0   | 2.0     | 1/43   | -     |
| Neodymium, Nd            | µg/g | 5.0            | 27     | 33      | 43/43  | .66   |
| Nickel, Ni               | µg/g | 8.0            | 33     | 56      | 43/43  | .62   |
| Niobium, Nb              | µg/g | <4.0           | 8.0    | 25      | 42/43  | .44   |
| Phosphorus, P            | %    | .08            | .09    | .23     | 43/43  | -.50  |
| Potassium, K             | %    | .36            | 1.5    | 1.8     | 43/43  | .93   |
| Scandium, Sc             | µg/g | 2.0            | 9.0    | 14      | 43/43  | .95   |
| Selenium, Se             | µg/g | .4             | .9     | 4.0     | 43/43  | NS    |
| Silver, Ag               | µg/g | .1             | .2     | .4      | 43/43  | NS    |
| Sodium, Na               | %    | .23            | .66    | .88     | 43/43  | NS    |
| Strontium, Sr            | µg/g | 130            | 160    | 230     | 43/43  | -.53  |
| Sulfur, S                | %    | .05            | .13    | .75     | 43/43  | -.56  |
| Tantalum, Ta             | µg/g | <40            | <40    | <40     | 0/43   | -     |
| Thorium, Th <sup>1</sup> | µg/g | <4.1           | 8.9    | 16.1    | 40/43  | .NS   |
| Tin, Sn                  | µg/g | <15            | <15    | <15     | 0/43   | --    |
| Titanium, Ti             | %    | .05            | .24    | .34     | 43/43  | .90   |
| Uranium, U               | µg/g | .86            | 2.86   | 9.75    | 43/43  | .32   |
| Vanadium, V              | µg/g | 14             | 130    | 260     | 43/43  | .52   |
| Yttrium, Y               | µg/g | 5.0            | 17     | 24      | 43/43  | .62   |
| Ytterbium, Yb            | µg/g | <1.0           | 2.0    | 2.0     | 42/43  | --    |
| Zinc, Zn                 | µg/g | 52             | 95     | 140     | 43/43  | .44   |
| Organic carbon           | %    | 1.07           | 2.15   | 17.3    | 43/43  | -.62  |
| Inorganic carbon         | %    | .57            | 1.79   | 3.90    | 43/43  | -.40  |

<sup>1</sup> Reporting limit varied from 2.7 to 4.1

minerals) are observed for As, Pb, Hg, Se, or Ag. Cadmium, which does not correlate with Al, has weak negative correlations with calcium and magnesium ( $r \sim 0.5$ ). Concentrations of these trace elements bear no (or weak) relations to aluminosilicate or carbonate minerals (selected plots shown in fig. 3A). These trace elements likely have different environmental sources or geochemical characteristics than clay or carbonate minerals. All of these trace elements have anthropogenic sources to the environment; natural geographic variability in geochemistry may also effect their distributions. For example, Mn, As, and Se undergo reduction-oxidation reactions, which greatly affect their solubility, and hence their concentrations in sediments.

The elements listed as having no correlation with Al, as well as Co, Cu, Ga, Fe, and Ni, are chalcophiles (elements that are concentrated in the sulfide phase upon mineral formation) (Brownlow, 1979). Several chalcophiles that correlate well with Al (Co, Cu, Ga, and Ni) may associate with aluminosilicate minerals via sulfide inclusion, isomorphic substitution, and/or adsorption to the mineral surface (Sposito, 1989, p. 11, p. 155).

Major elements associated with carbonate and evaporite minerals (Ca, Sr, and inorganic carbon) correlate negatively with aluminum content (table 5, fig. 3B). Calcium correlates very strongly with inorganic carbon ( $r > 0.9$ ), and moderately with Mg, Na, and organic carbon. Most of the inorganic carbon in these sediments can be accounted for by calcium carbonate. Very few statistically significant, positive correlations exist between calcium or magnesium and the trace elements measured in this study. This suggests that carbonate and evaporite minerals have little bearing, except as diluents, on the distributions of most trace elements. Sulfur also correlates negatively with Al.

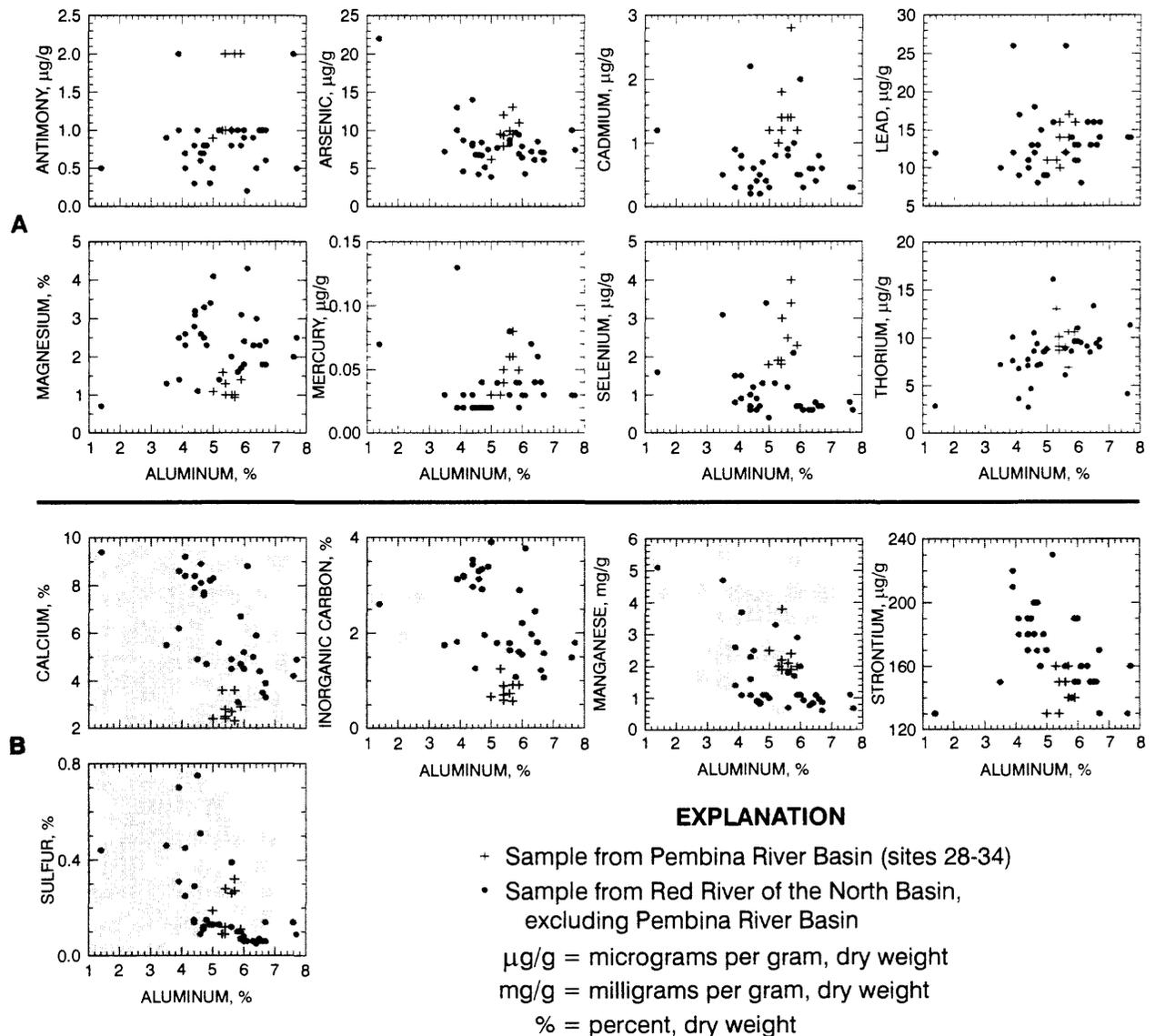
In the Pembina River Basin sediment samples, Nb and V concentrations are substantially higher than those that would be expected from their apparent relationship with Al in samples from the rest of the Red River Basin (fig. 2B). Excluding Pembina River Basin samples, these elements, as well as Ce, La, Nd, and Ni, correlate strongly with Al. The greater abundances of these elements, relative to Al, likely result from inputs of Cretaceous marine shales, which outcrop in the Pembina River Basin. Although Cretaceous shales also outcrop near the middle reaches of the Sheyenne River, samples from the Sheyenne River did not show the same geochemical patterns as Pembina River Basin samples. The sampling site near Warwick, N. Dak. is upstream of these outcrops; the Lisbon and Harwood sampling sites

are downstream, but are also below Lake Ashtabula, which would trap incoming sediments. Cd, Mn, and Se concentrations appeared enriched, relative to Al, in samples from tributaries in the Drift Prairie (including the Pembina River Basin) compared to samples from the Red River Valley Lake Plain and Minnesota tributaries.

Some of the Cretaceous marine shales in this region are black shales (Anna, 1986). Black shales are often enriched, relative to aluminum, in trace element content (see, for example, Calvert and others, 1996), which fits the pattern observed in this study (figs. 2 and 3). Analyses of Cretaceous shales by the North Dakota Geological Survey (Edward C. Murphy, North Dakota Geological Survey, written commun., 1996) show a wide range of trace-element concentrations, indicative of different shale types, including some with relatively high trace-element content.

There appears to be a dichotomy among the trace elements that have substantial anthropogenic inputs to the environment (listed in the introduction). Cr, Cu, Ni, and V appear to be associated with aluminosilicates, whereas As, Cd, Pb, Hg, and Se do not relate to aluminosilicates, carbonate, or evaporite minerals. Zinc relates relatively weakly to aluminosilicates. In addition to the previously mentioned geochemical considerations, atmospheric delivery from distant contamination sources may explain a portion of the concentrations of some of those elements that are not correlated with naturally occurring minerals. Ross (1994) noted that Cd, Hg, and Pb are distinguished from most other trace elements in that a high proportion of their total loads to soils are from atmospheric deposition. In contrast, relatively small amounts of the soil loads of Cr, Cu, Mn, Ni, and Zn are from atmospheric deposition. Also, sediment cores from lakes remote from industrial activity have shown little or no enrichment of Cu, Ni, Cr, and Se, but substantial enrichment (typically several times background concentrations) of As, Cd, Hg, Zn and especially Pb (Johnson, 1987; Johnson and others, 1986), which is attributable to an atmospheric contribution.

Chemical properties influence patterns of atmospheric deposition (reviewed by Ross, 1994). Elements that form relatively volatile species during combustion—As, Hg, and to a lesser extent Cd and Pb (Bertine and Goldberg, 1971)—would be expected to be transported farther in the atmosphere than less-volatile elements, which are largely deposited within several kilometers of their source (Klein and Russel, 1973). Mercury from industrial sources is known to be transported through the atmosphere and deposited in elevated amounts, relative to background levels,



**Figure 3. Concentrations of selected elements plotted against aluminum concentrations in stream-bottom sediments. (A - Selected elements that do not correlate with aluminum. B - Selected elements that correlate negatively with aluminum. Correlations exclude the sample with the lowest aluminum concentration, which is an outlier.)**

worldwide. These factors may have contributed to the variability in concentrations of some trace elements. However, this study was not designed to ascribe contaminants to their sources.

Principal component analysis (PCA), using data for elements that were detected in most or all samples, yields reasonable groupings of elements and sites. Elements that group together on principal component axes should have similar geochemical distributions, and possibly similar sources. From this analysis, the first three principal components (PC1, PC2, and PC3) accounted for 44, 19, and 8 percent, respectively, of the

total variance of the standardized data. Elements with negative PC1 scores are associated with carbonate minerals and organic matter, whereas those with positive PC1 scores include many heavy metals and trace elements, including those associated with aluminosilicates. A plot of PC2 versus PC1 (fig. 4) shows useful groupings of the elements. The upper left quadrant contains organic carbon, as well as elements that may be associated with organic matter (S and P). The upper right quadrant contains elements that are known to have substantial inputs to the environment due to human activity (Pb, Ag, Hg, As, Se, Sb, Cd, Cu, V.

Ni) (Nriagu and Pacyna, 1988). When present at high concentrations, many of these elements are toxic. The lower right quadrant contains elements associated with the composition of aluminosilicates (Al, Ti, Fe, K), as well as trace and rare-earth elements that are highly correlated with Al ( $r \geq 0.74$ ), and are likely trace constituents in aluminosilicate matrices (Ce, Cr, Co, La, Li, Nd, Sc, Th). The lower left quadrant includes Ca, Mg, Na, and inorganic carbon; this quadrant reflects carbonate and/or evaporite minerals.

It is unclear whether concentrations of the elements in the upper right quadrant of figure 4 are natural, or are elevated relative to natural, background levels. Principal component 3 (PC3) (fig. 5) further separates this group into elements with high (Pb, Hg, Ag, Cu, Sb, Zn), intermediate (U, As, Ni), and low (Se, Nb, Mn, Cd, Y, V) loadings. On the basis of lake-sediment core studies (examples discussed above), it is tempting to describe the first group (heavy metals with high PC3 loadings) as influenced by anthropogenic inputs, and the latter groups as primarily of natural origin. This interpretation is somewhat speculative, and does not strongly match findings from sediment-core studies.

Site scores, calculated from the first two principal components (fig. 6) form sensible groups. Sampling sites in the Drift Prairie, with lower aluminosilicate content and higher organic matter content, group in the upper left quadrant. Sites in the upland areas in Minnesota (the Moraine and the Lake-Washed Till Plain) have higher calcium carbonate content, and fall into the lower left quadrant. Lake Plain sites, dominated by detrital aluminosilicates, group in the lower right quadrant. Sites in the Pembina River Basin, with some contribution from trace-element-rich Cretaceous sediments, group in the upper right quadrant.

### Organochlorines

Most of the organochlorines analyzed in this study (table 2) were not detected in any samples. Three DDT-related compounds were detected. The DDT metabolite *p,p'*-DDE was the most frequently detected organochlorine, with a maximum concentration of 16 ng/g (table 6). In several samples for which *p,p'*-DDE data were censored (less than the reporting limit of 1 ng/g), laboratory reports indicated that traces of this compound were present (from about 0.3-0.9 ng/g). Less frequently detected were *p,p'*-DDD and *p,p'*-DDT. In several samples, *p,p'*-DDD and *p,p'*-DDT could not be quantified due to analytical interferences; these data were deleted from lab results.

In the agriculturally intensive Red River Valley Lake Plain, total DDT concentrations (the sum of DDT and its metabolites) were significantly higher ( $p < 0.05$ , Wilcoxon rank-sum test) than in the other physiographic areas. This suggests that past agricultural use of DDT is the dominant source of DDT and its metabolites. Stream sites in the upland areas had low or undetectable concentrations of any DDT compounds, which likely reflects lower historical usage in areas with less agriculture.

Capel and others (1996) noted that of 30 organochlorines analyzed in sediments, 26 were detected in at least one NAWQA study nationwide. The Red River Basin also had low concentrations of these analytes compared to other areas in the country.

### Semivolatile Organic Chemicals

Concentrations of PAHs and other semivolatile organic compounds are summarized in table 6. Laboratory reporting limits for many semivolatile organic chemicals varied considerably, by a factor of 50-100 for most compounds, during the course of this study. Higher reporting limits result from analytical interferences, which preclude accurate determination at low levels. For many samples, analytical data were censored at higher reporting limits than actual concentrations reported in other samples. These factors complicate quantitative interpretations of the data. To simplify discussion of these data in this report, all censored data were set equal to zero and all uncensored data were used as reported. Because of occasionally low recoveries and high reporting limits, these compounds could be more prevalent in the basin than indicated by table 6.

PAHs are widespread in sediments in the Red River Basin (fig. 7). Only at one site were no PAHs detected. Total PAH concentrations were quite low ( $< 100$  ng/g) at seven other sites. Fourteen PAHs were detected in at least 40 percent of the sediment samples; pyrene and fluoranthene were detected in nearly every sample. There was no clear relation between total PAH concentrations and physiography. The maximum concentration was observed at the Red River downstream of Fargo-Moorhead, the largest urban area. Relatively high concentrations were also observed at some rural sites. Higher ratios of light-to-heavy PAHs generally coincide with higher total PAH concentrations (fig. 8) (light and heavy refer to the number of carbon atoms in the compounds; see table 6). This probably reflects either differential weathering rates among the PAHs (light compounds weather faster)

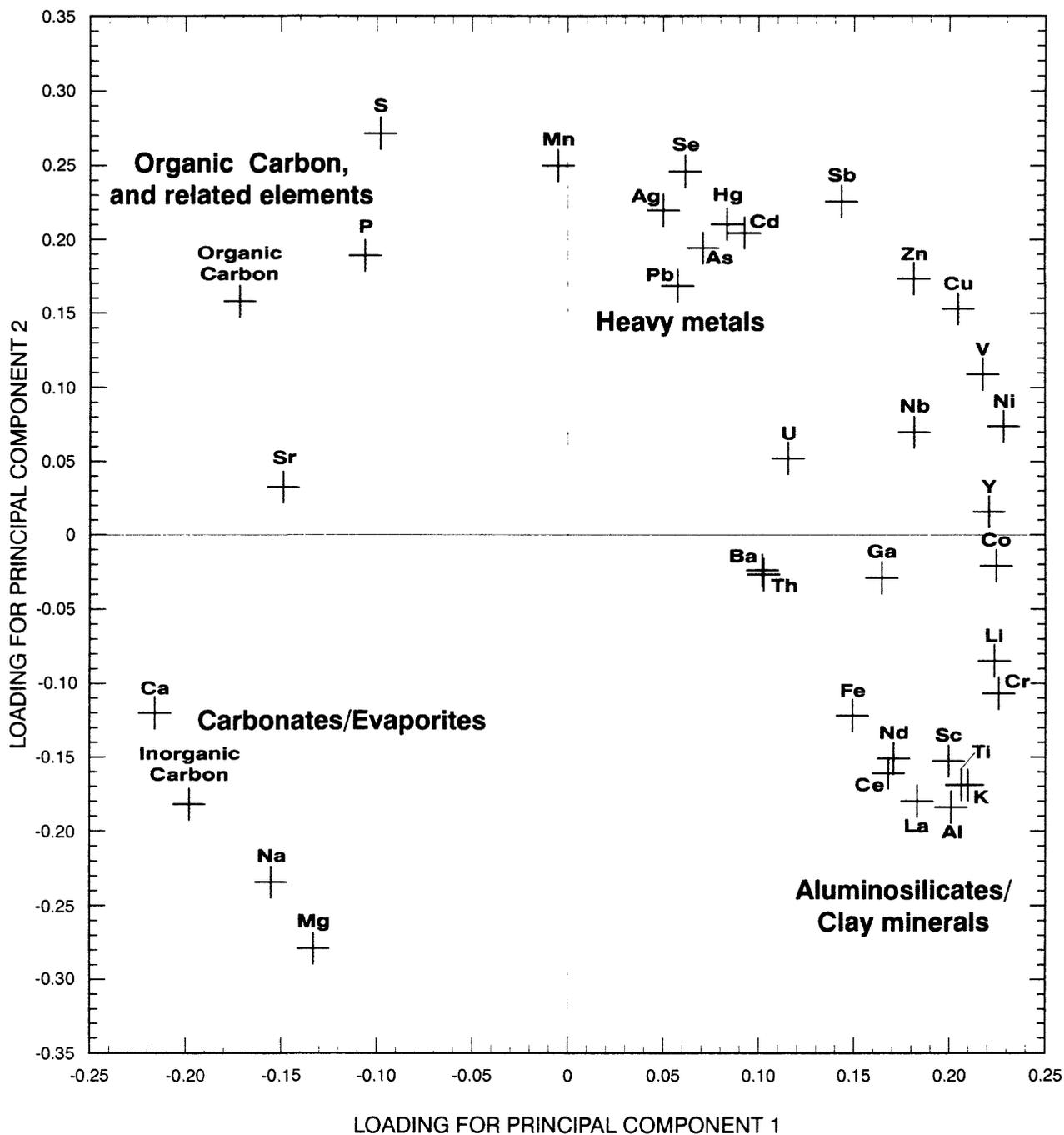
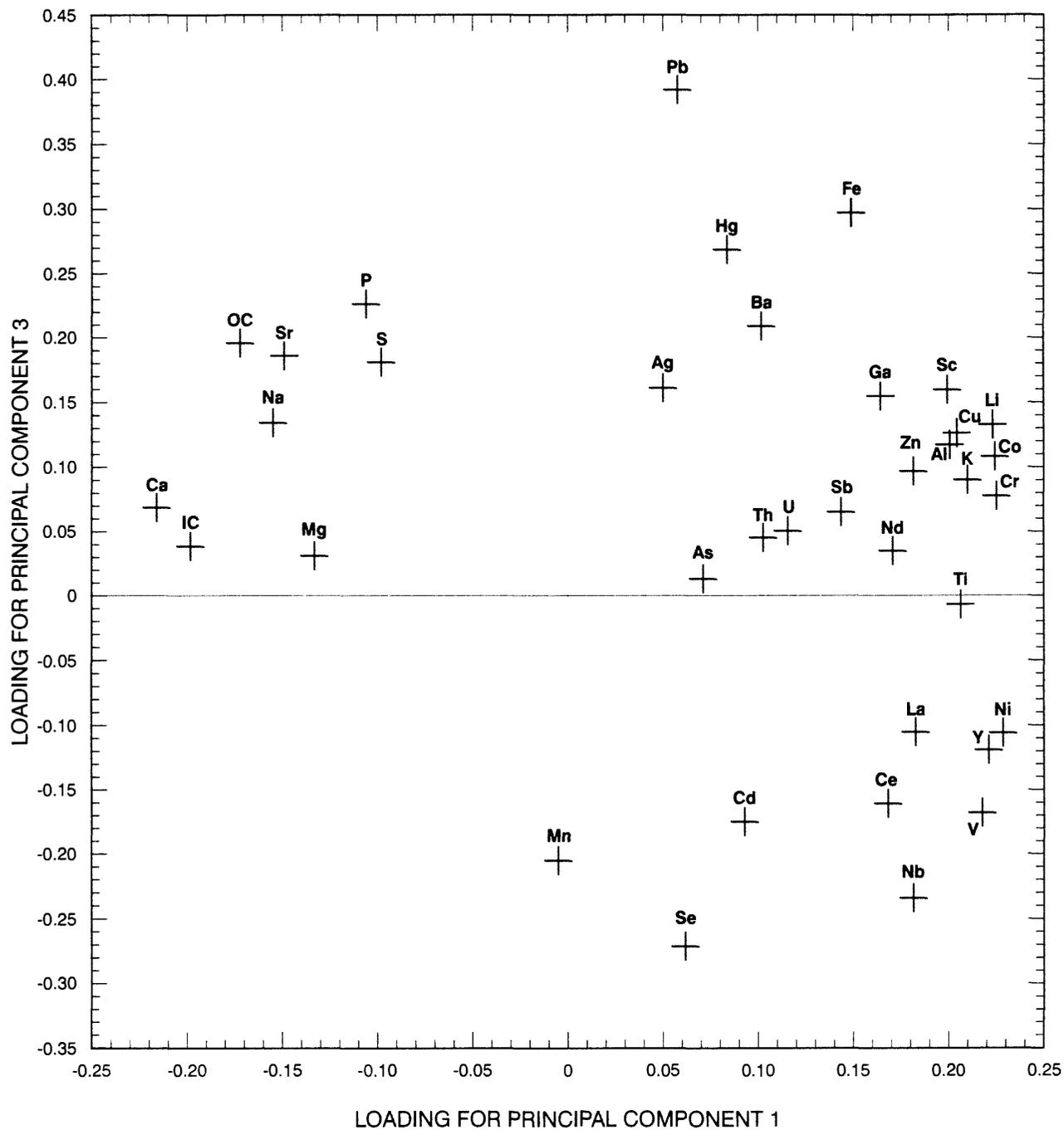


Figure 4. Loadings for first two principal components, from principal component analysis of element concentrations in stream-bottom sediments. (Element symbols are defined in table 1.)



**Figure 5. Loadings for first and third principal components, from principal component analysis of element concentrations in stream-bottom sediments. (Element symbols are defined in table 1.)**

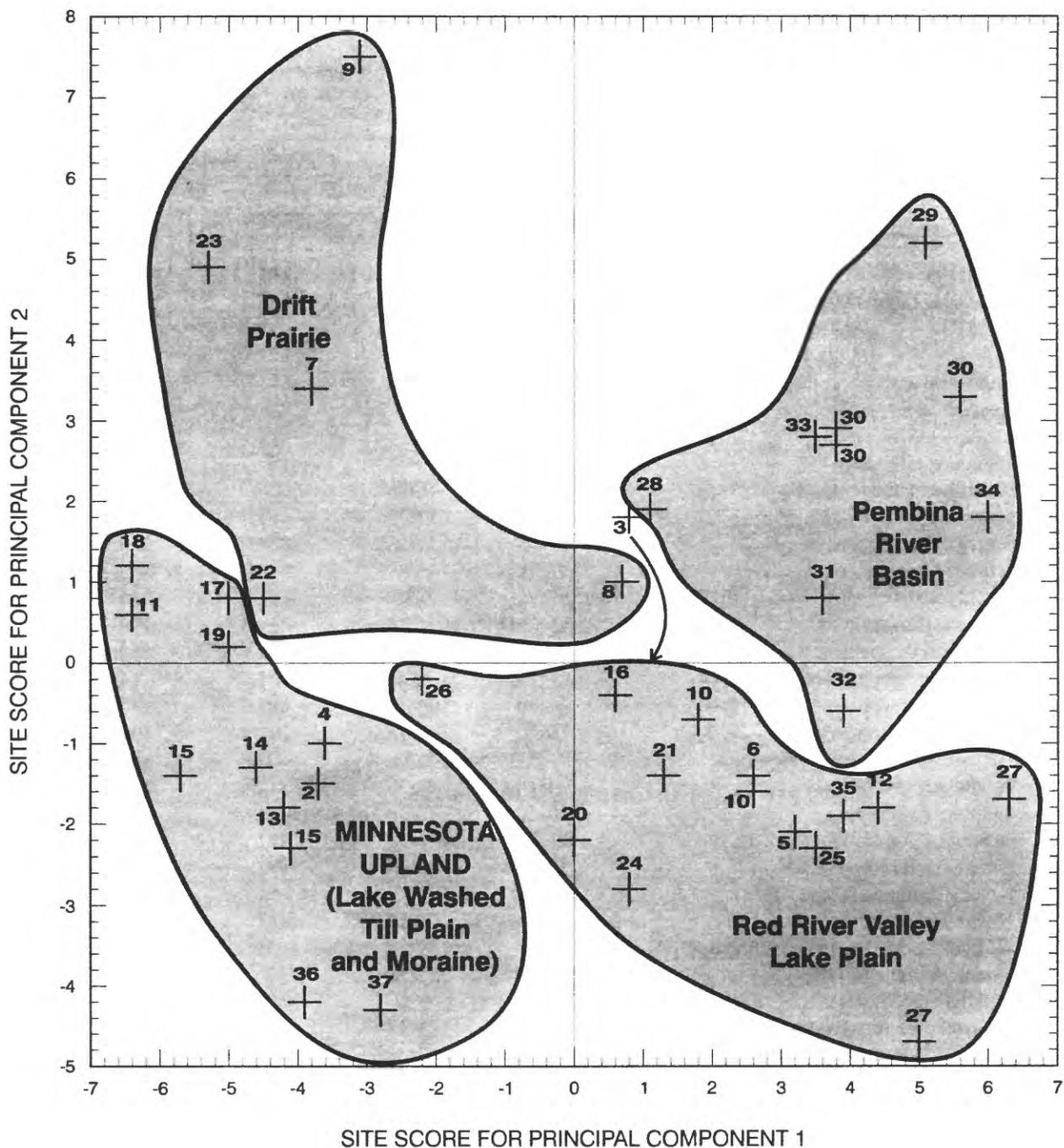


Figure 6. Groupings of sites, based on site scores from principal component analysis of element concentrations in stream-bottom sediments. (Numbers next to plot symbols are site numbers shown in figure 1. Arrow next to site 3 indicates that this site, geographically, is in the Red River Valley Lake Plain.)

Table 6.—Summary of concentrations of organic chemicals in stream-bottom sediments.

[Reporting limits varied due to analytical interferences. The typical reporting limit for polycyclic aromatic hydrocarbons (PAHs) was 50 nanograms per gram. N>RL/N, number of values greater than reporting limit/number of samples analyzed. <RL, less than reporting limit; ng/g, nanograms per gram dry sediment; organochlorines were analyzed in 38 samples; only those detected were shown. Due to analytical interferences, data for *p,p'*-DDD and *p,p'*-DDT were deleted for some samples].

| Analyte                                                                      | Reporting limit range, in ng/g | N>RL/N | Concentrations  |                  |
|------------------------------------------------------------------------------|--------------------------------|--------|-----------------|------------------|
|                                                                              |                                |        | Median, in ng/g | Maximum, in ng/g |
| Organochlorines:                                                             |                                |        |                 |                  |
| <i>p,p'</i> -DDD                                                             | 1-1                            | 4/30   | <RL             | 8.9              |
| <i>p,p'</i> -DDE                                                             | 1-2                            | 9/38   | <RL             | 16               |
| <i>p,p'</i> -DDT                                                             | 2-2                            | 3/30   | <RL             | 23               |
| PAHs (molecular formula in parentheses):                                     |                                |        |                 |                  |
| acenaphthene (C <sub>12</sub> H <sub>10</sub> )                              | 10-500                         | 9/38   | <RL             | 47               |
| acenaphthylene (C <sub>12</sub> H <sub>8</sub> )                             | 5-500                          | 10/38  | <RL             | 48               |
| anthracene (C <sub>14</sub> H <sub>10</sub> )                                | 5-500                          | 19/38  | 19              | 120              |
| benz[ <i>a</i> ]anthracene (C <sub>18</sub> H <sub>12</sub> )                | 5-500                          | 16/38  | RL              | 320              |
| benzo[ <i>a</i> ]pyrene (C <sub>20</sub> H <sub>12</sub> )                   | 50-500                         | 17/38  | <RL             | 300              |
| benzo[ <i>k</i> ]fluoranthene (C <sub>20</sub> H <sub>12</sub> )             | 5-50                           | 24/38  | 32              | 250              |
| benzo[ <i>b</i> ]fluoranthene (C <sub>20</sub> H <sub>12</sub> )             | 5-50                           | 23/38  | 37              | 360              |
| benzo[ <i>g,h,i</i> ]perylene (C <sub>22</sub> H <sub>12</sub> )             | 20-500                         | 6/38   | <RL             | 220              |
| chrysene (C <sub>18</sub> H <sub>12</sub> )                                  | 50-500                         | 21/38  | 22              | 790              |
| dibenz[ <i>a,h</i> ]anthracene (C <sub>22</sub> H <sub>14</sub> )            | 20-500                         | 5/38   | <RL             | 150              |
| 1,2-dimethylnaphthalene (C <sub>12</sub> H <sub>12</sub> )                   | 10-500                         | 5/38   | <RL             | 14               |
| 1,6-dimethylnaphthalene (C <sub>12</sub> H <sub>12</sub> )                   | 10-50                          | 9/38   | <RL             | 40               |
| 2,6-dimethylnaphthalene (C <sub>12</sub> H <sub>12</sub> )                   | 10-50                          | 19/38  | 10              | 100              |
| 2-ethylnaphthalene (C <sub>12</sub> H <sub>12</sub> )                        | 10-500                         | 8/38   | <RL             | 30               |
| fluoranthene (C <sub>16</sub> H <sub>10</sub> )                              | 50                             | 37/38  | 37.5            | 1,000            |
| fluorene (C <sub>13</sub> H <sub>10</sub> )                                  | 10-50                          | 16/38  | <RL             | 71               |
| indeno[1,2,3- <i>c,d</i> ]pyrene (C <sub>22</sub> H <sub>12</sub> )          | 20-500                         | 16/38  | <RL             | 280              |
| 2-methylanthracene (C <sub>15</sub> H <sub>12</sub> )                        | 10-50                          | 10/38  | <RL             | 75               |
| 1-methylfluorene (C <sub>14</sub> H <sub>12</sub> )                          | 10-500                         | 6/38   | <RL             | 43               |
| 1-methylphenanthrene (C <sub>15</sub> H <sub>12</sub> )                      | 10-50                          | 12/38  | <RL             | 85               |
| 4H-cyclopenta[ <i>d,e,f</i> ]phenanthrene (C <sub>15</sub> H <sub>10</sub> ) | 20-500                         | 10/38  | <RL             | 100              |
| 1-methylpyrene (C <sub>17</sub> H <sub>12</sub> )                            | 10-500                         | 12/38  | RL              | 98               |
| naphthalene (C <sub>10</sub> H <sub>8</sub> )                                | 5-500                          | 4/38   | <RL             | 38               |
| phenanthrene (C <sub>14</sub> H <sub>10</sub> )                              | 5-500                          | 21/38  | 14.5            | 410              |
| pyrene (C <sub>16</sub> H <sub>10</sub> )                                    | 50-500                         | 33/38  | 40              | 650              |
| 2,3,6-trimethylnaphthalene (C <sub>13</sub> H <sub>14</sub> )                | 10-500                         | 6/38   | <RL             | 47               |
| Heterocyclic compounds and PAH derivatives:                                  |                                |        |                 |                  |
| acridine                                                                     | 10-500                         | 3/38   | <RL             | 58               |
| anthraquinone                                                                | 20-500                         | 16/38  | 28              | 470              |
| benzo[ <i>c</i> ]cinnoline                                                   | 10-500                         | 0/38   | <RL             | <RL              |
| 2,2'-biquinoline                                                             | 20-500                         | 2/38   | <RL             | 37               |
| carbazole                                                                    | 10-500                         | 18/38  | <RL             | 100              |
| 2-chloronaphthalene                                                          | 10-500                         | 0/38   | <RL             | <RL              |
| dibenzothiophene                                                             | 5-500                          | 11/38  | <RL             | 55               |
| isoquinoline                                                                 | 10-500                         | 1/38   | <RL             | 37               |
| phenanthridine                                                               | 10-500                         | 2/38   | <RL             | 52               |
| quinoline                                                                    | 10-500                         | 1/38   | <RL             | 19               |

Table 6.—Summary of concentrations of organic chemicals in stream-bottom sediments—continued.

| Analyte                                                                                               | Reporting<br>limit range,<br>in ng/g | N>RL/N | Concentrations     |                     |
|-------------------------------------------------------------------------------------------------------|--------------------------------------|--------|--------------------|---------------------|
|                                                                                                       |                                      |        | Median,<br>in ng/g | Maximum,<br>in ng/g |
| Monoaromatic compounds, including nitrated, chlorinated, and phenolic compounds and phthalate esters: |                                      |        |                    |                     |
| C <sub>8</sub> -alkylphenol                                                                           | 10-500                               | 0/38   | <RL                | <RL                 |
| azobenzene                                                                                            | 20-500                               | 0/38   | <RL                | <RL                 |
| bis(2-ethylhexyl)phthalate                                                                            | 10-50                                | 35/38  | 66.5               | 520                 |
| butylbenzylphthalate                                                                                  | 10-50                                | 32/38  | 48                 | 110                 |
| di- <i>n</i> -butylphthalate                                                                          | 10-10                                | 37/38  | 55                 | 100                 |
| 4-chloro-3-methylphenol                                                                               | 30-500                               | 1/38   | <RL                | 11                  |
| 2-chlorophenol                                                                                        | 10-500                               | 0/38   | <RL                | <RL                 |
| <i>p</i> -cresol                                                                                      | 50-50                                | 26/38  | 23                 | 1,200               |
| 1,2-dichlorobenzene                                                                                   | 10-500                               | 0/38   | <RL                | <RL                 |
| 1,3-dichlorobenzene                                                                                   | 10-500                               | 0/38   | <RL                | <RL                 |
| 1,4-dichlorobenzene                                                                                   | 5-500                                | 0/38   | <RL                | <RL                 |
| diethylphthalate                                                                                      | 10-50                                | 31/38  | 17                 | 51                  |
| dimethylphthalate                                                                                     | 5-500                                | 2/38   | <RL                | 120                 |
| di- <i>n</i> -octylphthalate                                                                          | 20-500                               | 8/38   | <RL                | 140                 |
| 2,4-dinitrotoluene                                                                                    | 20-500                               | 0/38   | <RL                | <RL                 |
| 2,6-dinitrotoluene                                                                                    | 50-5000                              | 0/38   | <RL                | <RL                 |
| nitrobenzene                                                                                          | 10-500                               | 0/38   | <RL                | <RL                 |
| pentachloroanisole                                                                                    | 5-500                                | 0/38   | <RL                | <RL                 |
| pentachloronitrobenzene                                                                               | 30-500                               | 0/38   | <RL                | <RL                 |
| phenol                                                                                                | 5-50                                 | 30/38  | 13                 | 73                  |
| 1,2,4-trichlorobenzene                                                                                | 10-500                               | 0/38   | <RL                | <RL                 |
| 3,5-xyleneol                                                                                          | 20-500                               | 2/38   | <RL                | 50                  |
| Other base-neutral-acid extractable organic compounds:                                                |                                      |        |                    |                     |
| 4-bromophenyl phenyl ether                                                                            | 10-500                               | 0/38   | <RL                | <RL                 |
| 4-chlorophenyl phenyl ether                                                                           | 10-500                               | 0/38   | <RL                | <RL                 |
| isophorone                                                                                            | 10-500                               | 0/38   | <RL                | <RL                 |
| bis(2-chloroethoxy) ether                                                                             | 10-500                               | 0/38   | <RL                | <RL                 |
| N-nitrosodi- <i>n</i> -propylamine                                                                    | 10-500                               | 0/38   | <RL                | <RL                 |
| N-nitrosodiphenylamine                                                                                | 10-500                               | 1/38   | <RL                | 40                  |

or different dominant sources of PAHs associated with low versus high concentrations.

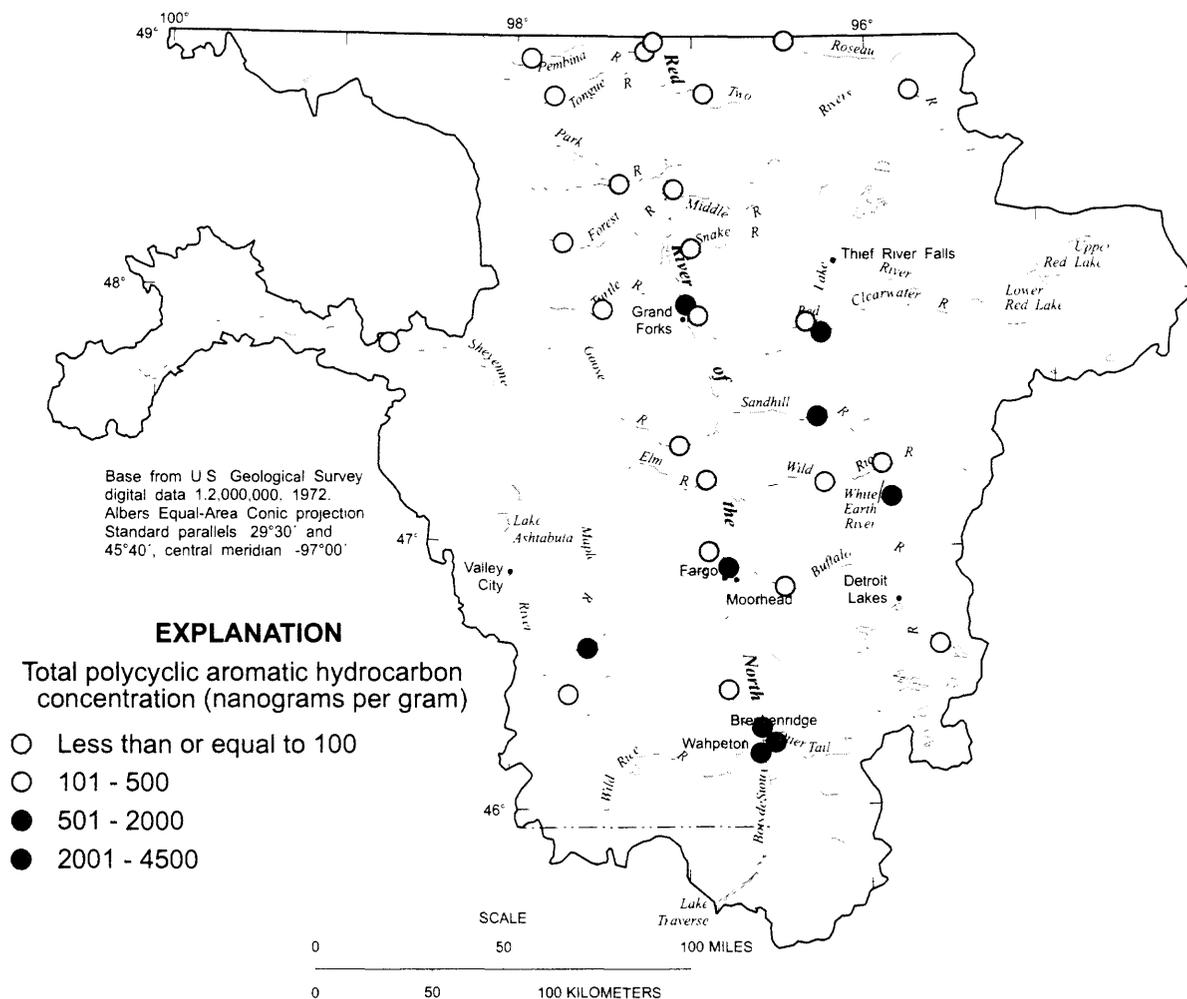
There are several sources of PAHs to the aquatic environment, which vary in importance depending on proximity to a water body. Wakeham and others (1980) have noted that deposition and/or runoff of petroleum products, combustion by-products (primarily fossil-fuel combustion; natural fires are also a source), and dust from roads (including PAHs from tire dust, automobile exhaust, and asphalt) all contribute to the PAH load. Fossil-fuel combustion has been identified as a dominant source of PAHs to aquatic environments that lack major point-source inputs of hydrocarbons. Many PAHs, including those frequently detected in this study, have been found to be enriched over the past century by

about 10 to 100 times in sediment cores from lakes (Wakeham and others, 1980) and rivers (Hites and others, 1980).

PAH concentrations tended to be higher in Red River Basin stream-bottom sediments than those in the western United States, but lower than those in northeastern United States (Tom Lopes, U.S. Geological Survey, written commun., 1996).

### Trace Elements in Fish Livers

The national NAWQA protocol for fish tissue analysis states that livers are the target organ for trace-element determinations (Crawford and Luoma, 1993). One drawback to this approach is in assessing human health

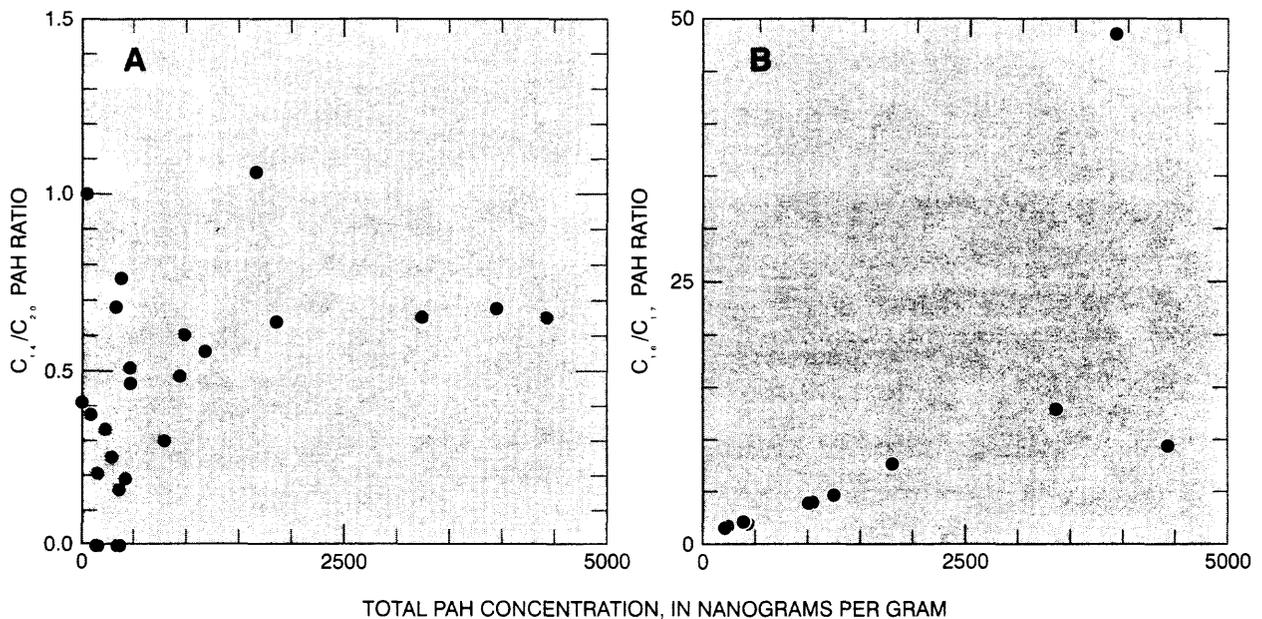


**Figure 7. Distribution of total polycyclic aromatic hydrocarbon (PAH) concentrations in stream-bottom sediments. (Notes: Data less than reporting limits were set equal to zero. Two samples, from different years, were collected at each of four sites; the mean concentration for each site was used for map symbol.)**

risk. Fish livers are not typically consumed by humans, and thus may be a poor indicator of potential human health issues. We examined composite fish liver samples in 1992 from common carp (*Cyprinus carpio*), white suckers (*Catostomus commersoni*), and creek chubs (*Semotilus atromaculatus*) (table 7). In 1994, eight composite carp and two composite channel catfish samples were analyzed for mercury in livers, muscle (fillet) tissue, and whole bodies (Goldstein and others, 1996). We also examined trace elements in the 1994 whole-body composite samples, but not in the other tissues. Thus, we can indirectly compare element concentrations in carp livers and whole bodies, although the tissue samples were from different fish during different years.

Data from all three species are summarized in table 7 and figure 9. Cu, Fe, Mn, and Zn are essential elements for metabolism (Gough and others, 1979), although they can be toxic at high concentrations. Cu, Fe, and Zn were detected at high concentrations (tens to hundreds of micrograms per gram) (fig. 9). Manganese was present at several micrograms per gram in nearly all fish. Concentrations of these four elements are probably normal, and are in the range as those reported for fish elsewhere (see, for example, Cowx, 1982).

Some trace elements, such as As, Cd, Cr, Pb, Hg, Se, and Ag, are nonessential elements (not essential for metabolism), and can exhibit adverse biological effects at fairly low concentrations. Some elements bioaccumulate or biomagnify through the food chain



**Figure 8. Ratios of selected light to heavy polycyclic aromatic hydrocarbon (PAH) concentrations versus total PAH concentrations in stream-bottom sediments. A - 14-carbon/20-carbon PAHs; B - 16-carbon/17-carbon PAHs.**

(Chapman and others, 1996). Elements that bioaccumulate tend to reach a relatively constant concentration across the various trophic levels of aquatic biota, whereas elements that biomagnify tend to have increasing concentrations with increasing trophic levels. Mercury biomagnifies in food chains (see, for example, Rask and others, 1994), often reaching levels of concern in large gamefish in many waters of the United States and Canada.

Mercury levels in fish livers were fairly low, with a concentration range of 0.03-0.6  $\mu\text{g/g}$  dry weight (0.0066-0.13  $\mu\text{g/g}$  wet weight). Goldstein and others (1996) noted that when fish-mercury concentrations are below about 0.5-1  $\mu\text{g/g}$  wet weight, the concentrations in fish livers are usually less than whole-body or fillet (muscle) concentrations of the same fish. At concentrations greater than about 1  $\mu\text{g/g}$  wet weight, livers contain higher levels of mercury than muscle or whole-fish tissues. [Note: the mercury data in table 7 are dry-tissue concentrations. Water accounts for about 70 percent of the wet-tissue mass for whole fish and about 78 percent of the wet-tissue mass for fish livers; therefore, wet-weight concentrations are about 30 percent of the reported dry-weight concentrations for whole-fish and 22 percent for fish livers.]

Cadmium concentrations in carp livers tended to increase with fish size (weight, length) and generally were higher at downstream locations on the Red River (table 7A). Larger fish generally were sampled at the downstream sites, so it was not possible to determine whether cadmium concentrations are influenced more by sampling location or fish size (see following section). Concentration ranges were similar for manganese (3.3-8.1  $\mu\text{g/g}$ ) and cadmium (1.1-13  $\mu\text{g/g}$ ) in carp livers, although the concentrations of these two elements did not correlate. Cadmium was not detected in white sucker or creek chub liver tissues; however neither species was collected from the mainstem of the Red River, and few samples of these species were collected.

### Trace Elements in Whole-Fish Samples

Table 7C and figure 9 summarize trace element concentrations, determined by the NWQL, in whole-fish composite samples. Mercury concentrations ranged from 0.21-0.59  $\mu\text{g/g}$  dry weight (0.068-0.17  $\mu\text{g/g}$  wet weight) in common carp, and 0.25-0.37  $\mu\text{g/g}$  dry weight (0.079-0.10  $\mu\text{g/g}$  wet weight) in channel catfish. Mercury data for the same whole-fish composite samples, analyzed by another laboratory, were somewhat higher than data from the NWQL (0.14-0.22  $\mu\text{g/g}$  wet weight for carp; 0.11  $\mu\text{g/g}$  wet weight for catfish) (Goldstein and others, 1996).

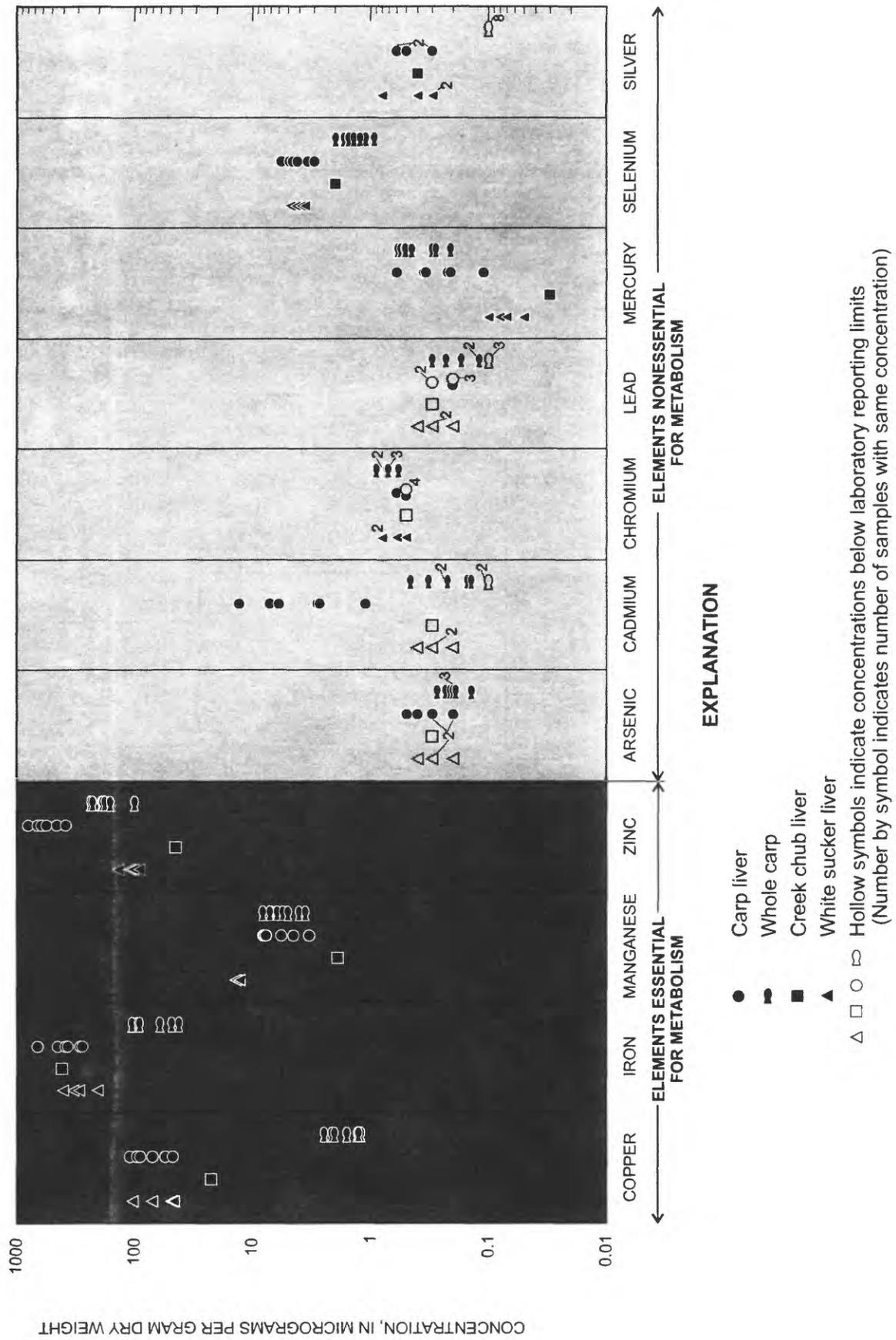
Table 7.—Selected fish-sample data: location, common name, mean weight and length, and concentrations of selected chemical constituents in composite fish samples.

[Map numbers refer to figure 1. All samples except the 1994 organochlorines were analyzed by the U.S. Ecological Survey National Water Quality Laboratory. 1994 organochlorines samples were analyzed by the Mississippi State Chemical Laboratory. <: less than; µg/g, micrograms per gram; ng/g, nanograms per gram; PCBs, polychlorinated biphenyls; total chlordane, sum of *trans*-nonachlor and *cis*- and *trans*-chlordane; total DDT, sum of *p,p'*- and *o,p'*- isomers of DDT and its metabolites DDD and DDE.]

| Map number                                                                                   | Site name                                   | Species (common name) | Mean weight, in grams | Mean length, in centimeters | Mercury, in µg/g    | Cadmium, in µg/g         |                    |
|----------------------------------------------------------------------------------------------|---------------------------------------------|-----------------------|-----------------------|-----------------------------|---------------------|--------------------------|--------------------|
| A. Selected trace elements in fish livers, 1992 samples. Concentrations in µg/g, dry tissue. |                                             |                       |                       |                             |                     |                          |                    |
| 38                                                                                           | Otter Tail River near Detroit Lakes, Minn.  | Creek chub            | 45                    | 15.9                        | 0.03                | <0.3                     |                    |
| 38                                                                                           | Otter Tail River near Detroit Lakes, Minn.  | White sucker          | 93                    | 20.5                        | .07                 | <.4                      |                    |
| 2                                                                                            | Otter Tail River at Breckenridge, Minn.     | Common carp           | 1,176                 | 44.5                        | .35                 | 2.8                      |                    |
| 2                                                                                            | Otter Tail River at Breckenridge, Minn.     | Common carp           | 1,143                 | 44.1                        | .34                 | 2.7                      |                    |
| 3                                                                                            | Bois de Sioux River near Wahpeton, N. Dak.  | Common carp           | 1,419                 | 49.3                        | .22                 | 6.0                      |                    |
| 4                                                                                            | Red River of the North at Wahpeton, N. Dak. | Common carp           | 1,668                 | 51.1                        | .60                 | 7.1                      |                    |
| 39                                                                                           | Sheyenne River at Valley City, N. Dak.      | White sucker          | 290                   | 28.3                        | .10                 | <.3                      |                    |
| 11                                                                                           | Buffalo River near Glyndon, Minn.           | Common carp           | 801                   | 36.3                        | .11                 | 1.1                      |                    |
| 23                                                                                           | Forest River near Fordville, N. Dak.        | White sucker          | 150                   | 23.6                        | .05                 | <.2                      |                    |
| 23                                                                                           | Forest River near Fordville, N. Dak.        | White sucker          | 172                   | 24.4                        | .08                 | <.3                      |                    |
| 40                                                                                           | Red River of the North at Drayton, N. Dak.  | Common carp           | 1,771                 | 51.0                        | .21                 | 13.0                     |                    |
| Total                                                                                        |                                             |                       |                       |                             |                     |                          |                    |
| Map number                                                                                   | Site name                                   | Species (common name) | Mean weight, in grams | Mean length, in centimeters | Total PCBs, in ng/g | Total chlordane, in ng/g | Total DDT, in ng/g |
| B. Selected organochlorines in whole fish, 1992 samples. Concentrations in ng/g, wet tissue. |                                             |                       |                       |                             |                     |                          |                    |
| 38                                                                                           | Otter Tail River near Detroit Lakes, Minn.  | White sucker          | 56                    | 17.6                        | <50                 | <5                       | <5                 |
| 2                                                                                            | Otter Tail River at Breckenridge, Minn.     | Common carp           | 763                   | 38.8                        | <50                 | <5                       | 12                 |
| 2                                                                                            | Otter Tail River at Breckenridge, Minn.     | Common carp           | 828                   | 39.1                        | <50                 | <5                       | 16                 |
| 3                                                                                            | Bois de Sioux River near Wahpeton, N. Dak.  | Common carp           | 935                   | 41.2                        | 50                  | <5                       | 44                 |
| 4                                                                                            | Red River Of The North at Wahpeton, N. Dak. | Common carp           | 1,020                 | 41.9                        | 66                  | 86                       | 57                 |
| 39                                                                                           | Sheyenne River at Valley City, N. Dak.      | White sucker          | 122                   | 21.0                        | 67                  | <5                       | 44                 |
| 11                                                                                           | Buffalo River near Glyndon, Minn.           | Common carp           | 298                   | 26.7                        | <50                 | <5                       | 71                 |
| 13                                                                                           | White Earth River near Waubun, Minn.        | White sucker          | 70                    | 18.5                        | <50                 | <5                       | <5                 |
| 16                                                                                           | Goose River at Hillshoro, N. Dak.           | White sucker          | 135                   | 22.7                        | <50                 | <5                       | 17                 |
| 23                                                                                           | Forest River near Fordville, N. Dak.        | Creek chub            | 45                    | 16.0                        | <50                 | <5                       | <5                 |
| 23                                                                                           | Forest River near Fordville, N. Dak.        | White sucker          | 95                    | 20.1                        | <50                 | <5                       | 5                  |
| 40                                                                                           | Red River of the North at Drayton, N. Dak.  | Common carp           | 685                   | 39.0                        | 70                  | <5                       | 63                 |
| 36                                                                                           | South Fork Roseau River near Malung, Minn.  | White sucker          | 64                    | 17.6                        | <50                 | <5                       | <5                 |

Table 7.—Selected fish-sample data: location, common name, mean weight and length, and concentrations of selected chemical constituents in composite fish samples—Continued.

| Map number                                                                                                                                                                                  | Site name                                      | Species (common name) | Mean weight, in grams | Mean length, in centimeters | Mercury, in µg/g | Cadmium, in µg/g | Total PCB's in ng/g | Total chlordane, in ng/g | Total DDT, in ng/g |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------|-----------------------|-----------------------|-----------------------------|------------------|------------------|---------------------|--------------------------|--------------------|
| C. Selected trace elements and organochlorines in whole-fish composites, 1994 samples. Trace element concentrations in µg/g, dry tissue; organochlorine concentrations in ng/g, wet tissue. |                                                |                       |                       |                             |                  |                  |                     |                          |                    |
| 4                                                                                                                                                                                           | Red River of the North at Wahpeton, N. Dak.    | Common carp           | 1,372                 | 46.5                        | 0.56             | <0.1             | 55                  | 11                       | 207                |
| 4                                                                                                                                                                                           | Red River of the North at Wahpeton, N. Dak.    | Common carp           | 1,820                 | 51.8                        | .45              | <.1              | <50                 | <10                      | 13                 |
| 6                                                                                                                                                                                           | Red River of the North below Fargo, N. Dak.    | Common carp           | 1,906                 | 55.0                        | .28              | .15              | 320                 | <10                      | 20                 |
| 6                                                                                                                                                                                           | Red River of the North below Fargo, N. Dak.    | Common carp           | 972                   | 41.2                        | .21              | .14              | <50                 | <10                      | 82                 |
| 6                                                                                                                                                                                           | Red River of the North below Fargo, N. Dak.    | Channel catfish       | 528                   | 40.5                        | .25              | <.1              | 100                 | <10                      | 127                |
| 6                                                                                                                                                                                           | Red River of the North below Fargo, N. Dak.    | Channel catfish       | 245                   | 33.1                        | .37              | .16              | 63                  | <10                      | 87                 |
| 21                                                                                                                                                                                          | Red River of the North at Grand Forks, N. Dak. | Common carp           | 1,203                 | 44.9                        | .30              | .22              | 170                 | 22                       | 217                |
| 21                                                                                                                                                                                          | Red River of the North at Grand Forks, N. Dak. | Common carp           | 1,762                 | 51.8                        | .59              | .46              | 62                  | <10                      | 85                 |
| 40                                                                                                                                                                                          | Red River of the North at Drayton, N. Dak.     | Common carp           | 1,993                 | 54.2                        | .52              | .32              | 64                  | <10                      | 139                |
| 40                                                                                                                                                                                          | Red River of the North at Drayton, N. Dak.     | Common carp           | 1,215                 | 45.6                        | .51              | .22              | 200                 | <10                      | 100                |



**Figure 9. Selected trace element concentrations in fish tissue samples. (Fish liver samples from 1992, whole carp samples from 1994.)**

Cadmium concentrations were higher in whole-carp samples collected from the downstream locations (Red River at Grand Forks, N. Dak. and at Drayton, N. Dak.), compared with similar-sized fish from upstream sites (Red River at Wahpeton, N. Dak. and at Fargo, N. Dak.). This provides evidence that location in the basin partially determines cadmium burdens in fish, and possibly indicates the general location of cadmium contamination in the basin.

## Organochlorines in Whole-Fish Samples

Fish tissue analyses yielded more organochlorine compounds, often at higher concentrations, than stream-bed sediment analyses. Thus, fish are more sensitive than stream-bed sediments as indicators of organochlorine contamination.

Samples collected in 1992 showed low, but detectable levels of organochlorines in fish tissue (table 7B). Generally, more organochlorine compounds were detected, and at higher levels, in common carp than in white suckers, although there are few white sucker samples to make this comparison. In common carp, *cis*- and *trans*-chlordane; *trans*-nonachlor; the DDT metabolites *o,p'*-DDD, *p,p'*-DDD, and *p,p'*-DDE; and PCBs were all detected, with *p,p'*-DDE being the most abundant compound. In white suckers, PCBs were detected in one sample and *p,p'*-DDE was detected in three samples. No organochlorines were detected in the one creek chub sample. Carp were collected primarily from the mainstem of the Red River. White suckers and creek chubs were collected from tributaries, with creek chubs coming from sites farthest from the mainstem of the Red River.

Eight composite whole-carp and two composite whole-channel catfish samples, all from the Red River, were analyzed for organochlorines in 1994 by the Mississippi State Chemical Laboratory. A similar suite of organochlorines found in the 1992 samples also was detected (table 7C). DDT metabolite and PCB concentrations tended to be somewhat higher than those determined by the NWQL, which may in part be due to the higher analytical recoveries associated with the Mississippi State Chemical Laboratory's analyses. The DDT metabolite *p,p'*-DDE was detected in every sample, at concentrations ranging from 13 to 150 ng/g. PCBs and *p,p'*-DDD were detected in nearly every sample. Also detected were *trans*-nonachlor, toxaphene, *cis*-chlordane (reported as *alpha* chlordane), dieldrin, *o,p'*-DDD, and *p,p'*-DDT. Total DDT concentrations (the sum of both isomers of DDT, DDE, and DDD) ranged from 13 ng/g in carp from Wahpeton to 217 ng/g in carp from Grand Forks. Total DDT concentrations

were lowest at the most upstream location (Wahpeton), highest in the middle reaches of the Red River (near Fargo and Grand Forks), and at intermediate levels at the most downstream site.

Brigham (1994) noted a long-term decrease in levels of DDT and metabolites in carp, using data from the U.S. Fish and Wildlife Service (Red River at Noyes, Minn., 1978-86 data) and from this study (Red River at Drayton, N. Dak., 1992 data). The decrease is consistent with DDT being banned for use in the United States and Canada since the early 1970's.

Geographic comparison of contaminants in fish is somewhat hampered by differences in fish distribution. At the large river sites on the Red River and at tributary sites close to the mainstem of the Red River, carp were most abundant. Farther away from the main stem of the Red River in the larger tributaries, white suckers were more abundant and carp were absent. Creek chubs were collected from the smaller tributaries. While contaminant levels are higher in fish from the mainstem of the Red River, this in part reflects differences in the species, sizes, and ages of fish sampled. The carp collected were larger (table 7), and older (probably at least five years old based on age analyses of scales from a subset of fish) than the other fish sampled. Therefore, carp would have had more time to accumulate contaminants.

## Implications for Resource Quality

Stream-bottom sediments and fish tissues accumulate hydrophobic contaminants over time, thereby serving as long-term indicators of the quality of aquatic resources. Although numerous potentially toxic trace elements were detected in sediments and fish in this study, the levels of these chemicals do not indicate acute contamination. This section briefly compares selected criteria or standards to concentrations of these chemicals in sediments and fish tissues of the Red River Basin.

### Sediments

Median and maximum concentrations of some chemical constituents in Red River Basin stream-bottom sediments are in the range of concentrations that may adversely affect aquatic biota (table 8). We used two sets of sediment-quality guidelines for this comparison. From available sediment-contaminant toxicity literature, Long and Morgan (1991) determined 10th- and 50th-percentile (median) sediment-contaminant concentrations that were found to cause adverse biological effects. These were termed "effects range low" (ER-L) and "effects range median" (ER-M)

concentrations. The studies that were reviewed to arrive at these values vary in number and methodology; thus Long and Morgan assigned subjective levels of confidence (low, medium, or high) to their effects-range values for each contaminant. Their ER-L and ER-M values are given in table 8 for comparison to contaminant concentrations observed in stream-bottom sediments of the Red River Basin.

The other guidelines, also developed from available toxicity literature, are the draft Canadian Interim Sediment Quality Guidelines (Evaluation and Interpretation Branch, Environment Canada, written commun., Sept. 1995; and Canadian Council of Ministers of the Environment, 1995). These guidelines define the threshold effect level (TEL) as "the concentration below which adverse effects are expected to occur rarely," and the probable effect level as "the level [concentration] above which adverse effects are predicted to occur frequently." Occasional adverse effects are expected at concentrations between the PEL and the TEL.

Trace-element concentrations were generally low compared to those thought to adversely affect biota (table 8). Maximum concentrations of chromium, nickel, and zinc exceeded ER-L values of Long and Morgan (1991). About half of the nickel concentrations exceeded the ER-L value for nickel, and the maximum nickel concentration exceeded its ER-M value. In addition to these elements, several other trace elements had maximum and in some cases median concentrations that exceeded the Canadian TEL and PEL values (table 8). However, as discussed earlier, chromium and nickel appear to be of natural origin, associated with aluminosilicate minerals. Furthermore, concentrations of all these elements were determined following strong-acid digestion, which does not necessarily indicate bioavailable concentrations. The fraction of metals (chemicals) sorbed to mineral surfaces is more readily available to biota, whereas strong-acid digestion techniques determine both this labile fraction and the more recalcitrant fraction incorporated in the mineral matrix. The current guidelines are for total concentrations, although bioavailability, which may differ among different sediment types and grain sizes, is acknowledged as an important consideration (Canadian Council of Ministers of the Environment, 1995).

Maximum concentrations of DDT, DDE, and DDD exceed their ER-L values, and are of similar magnitude to their ER-M values (table 8). The ER-M concentration for total DDT is 350 ng/g, which is more than ten times the highest ER-M concentration of the individual compounds. This apparent discrepancy possibly results

from differences in observed effects in the various studies summarized by Long and Morgan (1991); they reported low confidence in the ER-M values for the individual DDT compounds, but medium confidence for total DDT.

Maximum concentrations of DDD and DDE also exceeded the Canadian PEL values, indicating the potential for toxicity associated with these compounds. The Canadian PEL for total DDT was 4,450 ng/g, again much higher than those of the individual compounds. In a separate analysis that focused on toxicity of DDT and its principal metabolites, MacDonald (1994) reported a sediment effect concentration (SEC, which may be interpreted similarly to the above ER-M or PEL values) of 31 ng/g for DDT (*o,p'* and *p,p'* isomers), which is slightly higher than the maximum *p,p'*-DDT concentration observed in this study. DDE (SEC=5,580 ng/g), DDD (SEC=1,170 ng/g), and total DDT (sum of both isomers of DDT, DDE, and DDD; SEC=7,120 ng/g) were found to be less toxic than indicated by the ER-M or PEL values cited earlier.

Maximum concentrations of eight PAHs exceeded their ER-L values. No PAH concentrations exceeded their ER-M values (table 8) in sediment samples from this study.

### Fish Tissues

The Minnesota Department of Health (1996) has an advisory for consumption of fish from the Red River, based both on mercury and PCBs. The North Dakota Department of Health (1995) has also issued a fish-consumption advisory, based on mercury. The Minnesota mercury guidelines are increasingly restrictive at higher concentrations (Minnesota Department of Health, 1996). The Federal Food and Drug Administration has an action level of 1 µg/g wet weight for mercury in edible fish tissues.

The Minnesota and North Dakota fish-consumption advisories are mainly focused on popular, predatory gamefish such as walleye (*Stizostedion vitreum*), northern pike (*Esox lucius*), and channel catfish (*Ictalurus punctatus*). The Minnesota Department of Natural Resources (1994) reported mercury concentrations in excess of 0.5 µg/g wet weight from several game fish from the Red River Basin. Large

Table 8.—Comparison of selected chemical constituents in stream-bottom sediments with concentrations thought to adversely affect aquatic biota (from Long and Morgan, 1991; and interim Canadian Sediment Quality Guidelines, see text).

[Boldface indicates constituents where maximum (and median, for nickel) concentrations exceeded Long and Morgan's effects range-low (ER-L) values.  $\mu\text{g/g}$ , micrograms per gram;  $\text{ng/g}$ , nanograms per gram; ER-L, effects range-low; ER-M, effects range-median; TEL, threshold effect level; PEL, probable effect level; <RL, less than reporting limit; NA, not available; --, no guideline exists.]

| Constituent                         | Sediment-quality guideline |              |                       |       |                     |                   |
|-------------------------------------|----------------------------|--------------|-----------------------|-------|---------------------|-------------------|
|                                     | Concentration              |              | Long and Morgan, 1991 |       | Canadian freshwater |                   |
|                                     | Median                     | Maximum      | ER-L                  | ER-M  | TEL                 | PEL               |
| Trace elements, in $\mu\text{g/g}$  |                            |              |                       |       |                     |                   |
| Antimony                            | 0.9                        | 2            | 2                     | 25    | --                  | --                |
| Arsenic                             | 7.9                        | 22           | 33                    | 85    | 5.90                | 17.0              |
| Cadmium                             | .6                         | 2.8          | 5                     | 9     | .596                | 3.53              |
| <b>Chromium</b>                     | 65                         | <b>95</b>    | 80                    | 145   | 37.3                | 90.0              |
| Copper                              | 22                         | 36           | 70                    | 390   | 35.7                | 197               |
| Lead                                | 13                         | 26           | 35                    | 110   | 35.0                | 91.3              |
| Mercury                             | .03                        | .13          | .15                   | 1.3   | .174                | .486              |
| <b>Nickel</b>                       | <b>30</b>                  | <b>56</b>    | 30                    | 50    | 18.0                | 35.9              |
| Silver                              | .2                         | .4           | 1                     | 2.2   | --                  | --                |
| <b>Zinc</b>                         | 90                         | <b>140</b>   | 120                   | 270   | 123                 | 315               |
| Organic chemicals, in $\text{ng/g}$ |                            |              |                       |       |                     |                   |
| <i>p,p'</i> -DDD                    | <RL                        | <b>8.9</b>   | 2                     | 20    | 3.54                | 8.51              |
| <i>p,p'</i> -DDE                    | <RL                        | <b>16</b>    | 2                     | 15    | 1.42                | 6.75              |
| <i>p,p'</i> -DDT                    | <RL                        | <b>23</b>    | 1                     | 7     | <sup>1</sup> 6.71   | <sup>1</sup> 88.9 |
| Acenaphthene                        | <RL                        | 47           | 150                   | 650   | <sup>1</sup> 46.9   | <sup>1</sup> 245  |
| <b>Anthracene</b>                   | 9.5                        | <b>120</b>   | 85                    | 960   | <sup>1</sup> 74.8   | <sup>1</sup> 693  |
| <b>Benz[a]anthracene</b>            | 35                         | <b>320</b>   | 230                   | 1,600 | 31.7                | 385               |
| Benzo[a]pyrene                      | <RL                        | 300          | 400                   | 2,500 | 31.9                | 782               |
| <b>Chrysene</b>                     | 22                         | <b>790</b>   | 400                   | 2,800 | 57.1                | 862               |
| <b>Dibenz[a,h]anthracene</b>        | <RL                        | <b>150</b>   | 60                    | 260   | <sup>1</sup> 6.22   | <sup>1</sup> 135  |
| <b>Fluoranthene</b>                 | 37.5                       | <b>1,000</b> | 600                   | 3,600 | 111                 | 2,355             |
| <b>Fluorene</b>                     | <RL                        | <b>71</b>    | 35                    | 640   | <sup>1</sup> 21.2   | <sup>1</sup> 144  |
| Naphthalene                         | <RL                        | 38           | 340                   | 2,100 | <sup>1</sup> 34.6   | <sup>1</sup> 391  |
| <b>Phenanthrene</b>                 | 14.5                       | <b>410</b>   | 225                   | 1,390 | 41.9                | 515               |
| <b>Pyrene</b>                       | 40                         | <b>650</b>   | 350                   | 2,200 | 53.0                | 875               |

<sup>1</sup> No freshwater guideline exists; reported value is a marine sediment guideline.

channel catfish (> 3 kg) from the Red River had mercury concentrations that exceed the federal standard of 1.0  $\mu\text{g/g}$ . The largest catfish analyzed was 4.4 kg (9.6 pounds), and had a mercury concentration of 1.8  $\mu\text{g/g}$ . In contrast, the smaller fish from our study had lower mercury levels. Also, Goldstein and others (1996) reported that carp (mean weight = 1.52 kg) and channel catfish (mean weight = 0.39 kg) had relatively low levels of mercury in muscle tissue (mean = 0.31 and 0.18  $\mu\text{g/g}$  wet weight, respectively).

This study confirmed that PCBs are present at levels of concern in Red River fish. The Minnesota Department of Health (1996) has guidelines for PCBs in edible fish tissues, which state that people should limit consumption to one meal per week if the total PCB concentration is from 25-100  $\text{ng/g}$ ; one meal per month at levels of 110-470  $\text{ng/g}$ , and no consumption if the concentration exceeds 470  $\text{ng/g}$ . Whole-carp samples from this study had PCB concentrations from <50 to 320  $\text{ng/g}$ . Larger carp from the Red River generally had

higher PCB concentrations than smaller fish from the tributaries. Channel catfish had moderate PCB levels (63 to 100 ng/g).

No state health advisories have been issued for DDT in fish tissues. The USEPA established that a fish-tissue DDT concentration of 31.6 ng/g poses an excess cancer risk of one in a million. They further established a screening value of 300 ng/g (one in one hundred thousand risk level) for DDT in edible fish tissues (these criteria are explained by Nowell and Resek, 1994). Total DDT levels in carp from this study ranged from 12 to 217 ng/g. Thus no samples exceeded the more widely used screening level established by the USEPA, although several exceeded the one in one million risk level.

This study did not focus on edible portions of fish (fillets), or on the largest (and presumably most contaminated) fish in the Red River Basin. Goldstein and others (1996) have shown that mercury is at higher concentrations in muscle (fillet) tissue than in whole carp or channel catfish of the Red River, probably because low-mercury tissues, such as bones, tend to dilute the higher levels present in muscle tissue. They also showed that at relatively low mercury levels (less than about 0.5-1.0 µg/g, wet-weight basis), mercury is higher in muscle (fillet) tissue than in liver tissue. Organochlorines tend to accumulate in fatty tissues. The level of organochlorines in the edible portion of fish depends, in part, on how the fish is cleaned and prepared (Minnesota Department of Health, 1996).

Larger fish tend to have higher levels of hydrophobic contaminants. However, few data are available for contaminants in large gamefish in the basin. Most fish that have been analyzed for contaminants in the Red River Basin are much smaller than the larger fish present in the river. Walleye up to 6.4 kg (14 pounds), northern pike up to 11.4 kg (25 pounds), channel catfish up to 15.5 kg (34 pounds), and carp up to 11.4 kg (25 pounds) have been caught in the Red River (Mike Larson, Minnesota Department of Natural Resources, Baudette, Minn., written commun., 1996).

## Summary

Stream-bottom sediment and fish-tissue samples from the Red River of the North Basin were analyzed for a large suite of chemical elements and organic chemicals as part of the U.S. Geological Survey's NAWQA program. Although the potentially toxic chemicals measured in this study generally were at low levels compared to more contaminated areas of the Nation,

some contaminants may be of concern because of their possible effects on aquatic biota and human health.

Many trace elements, including those that are toxic at high concentrations, were detected in Red River Basin stream-bottom sediments. Many of these elements appear to be at natural levels, associated with aluminosilicate minerals rather than anthropogenic sources. Maximum stream-bed sediment concentrations of chromium, nickel, and zinc were in the range of concentrations that may adversely affect aquatic organisms, although these metals were probably at natural levels. Cadmium, lead, and mercury, may be present at elevated concentrations in some sediment samples, although levels of these elements do not indicate acute contamination. Mercury, the element of greatest health concern in the region, was detected at low concentrations in 38 of 43 samples (<0.02-0.13 µg/g).

The insecticide DDT and its metabolites were the only organochlorines detected in stream sediments. Concentrations of these compounds were typically near or below laboratory reporting limits, but were significantly higher in samples from streams in the Red River Valley Lake Plain, a highly agricultural area with the greatest population density in the basin, compared to upland areas. This pattern probably reflects greater historical DDT usage in the lake plain. The most frequently detected organochlorine in sediments was the DDT metabolite *p,p'*-DDE, (9 of 38 samples; <1-16 ng/g).

PAHs were detected in stream sediments throughout the Red River Basin, at higher levels than in the western United States, but at lower levels than in the northeastern United States.

This study confirms previous findings of mercury and organochlorines in fish tissues in the Red River Basin. Mercury was detected in all of the fish samples, at concentrations of 0.03-0.6 µg/g dry weight (about 0.0066-0.13 µg/g wet weight) in fish livers, and 0.21-0.59 µg/g dry weight (about 0.068-0.17 µg/g wet weight) in whole fish samples; these levels are below restrictive fish-consumption advisories, and always well below the Federal (Food and Drug Administration) action level of 1 µg/g wet weight. Data from other studies show higher mercury levels in large, predatory gamefish in the Red River Basin. Several organochlorines were detected in fish. These include DDT and its metabolites, PCBs, and chlordane. Total DDT (the sum of DDT and its metabolites) concentrations ranged from <5-217 nanograms per gram, and at least one component of total DDT was

detected in 19 of 23 fish samples. Fish appear to be more sensitive than stream-bed sediments as indicators of organochlorine contamination in the Red River Basin. The levels of these contaminants may be of concern to people who eat the fish regularly.

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