TRACE ELEMENT CONCENTRATIONS IN BED SEDIMENT IN THE MISSISSIPPI EMBAYMENT STUDY UNIT

Michelle L. Wates and Barbara A. Kleiss U.S. Geological Survey Pearl. Mississippi

INTRODUCTION

In 1991. the U.S. Geological Survey (USGS) began the National Water-Quality Assessment (NAWQA) Program to describe current waterquality conditions in a large part of the nation's streams, rivers, and aquifers. The purpose of the NAWQA program is to characterize current waterquality conditions, to observe any changes in water-quality over time, and to improve the understanding of natural and anthropogenic factors that influence water-quality. The study incorporates more than 50 of the nation's largest river basins and aquifer systems; one of these basins is the Mississippi Embayment (MISE) study unit.

In 1995, as a part of the MISE study unit evaluation, the USGS collected bed sediment from 15 sites that (fig.1) represented a variety of land **use** and streams throughout the study unit. More than 85 percent (median value) of the land in the MISE study unit is used for agriculture and includes row crops, grain crops, **pasture/hay**, and other grasses. The remaining land is used for forestry, wetlands, or open water.

The sampling of bed sediment is important because changes in the chemistry of bed sediment can provide insight about the environment surrounding the stream. In addition, it is important to understand the concentrations of potential toxins in sediment that could be available to biotic communities, possibly causing environmental effects.

Bed sediment samples were analyzed to determine the concentrations of 34 trace elements, nine of which were chosen to discuss in this report. These nine, aluminum, arsenic, cadmium, chromium, lead, mercury, nickel, selenium, and zinc, were chosen because, **as** some of EPA's Priority Pollutant's, they are considered a threat to aquatic organisms and human health (Rice 1999). The objectives of this paper are to present trace element data from 15

sites and to compare MISE concentrations to national medians and applicable guidelines.

DATA COLLECTION AND ANALYSIS

At each of the $15\ \text{sampling}\$ sites, $10\$ wet depositional zones likely to have recently deposited, fine-grained sediments were sampled along a 500-meter reach of stream. The ten zones were chosen to represent a variety of depositional areas including left and right bank and center channel as well as varying water depths. In wadeable streams, sediment was collected in the depositional area by using a Teflon spatula. In non-wadeable streams, bottom samples were collected from a bridge or boat by lowering a mechanical sampler, called a Young grab, to the stream bed by a rope. Only the fine surface material scraped from the top 1 centimeter of sample was used. At each site, a sediment sample from the ten zones within the reach was composited. Then the sediment was filtered through a 63-micron mesh, nylon sieve cloth into an acid-rinsed, glass bottle (fig. 2). A bottle filled with native stream water was used to "pressure sieve" the fine material through the sieve. When the sieved sample in the jar reached a depth of 1 centimeter, the bottle was sealed with a Teflonlined lid (Shelton and Capel 1994).

The samples were shipped to the USGS laboratory in Denver, Colorado, for analysis. Trace element concentrations were determined by various analytical methods, such as hydride analysis (HA), graphite furnace atomic absorption (GFAA), inductively coupled plasma atomic emission spectrophotometry (ICP-AES). and cold vapor atomic absorption (CVAA) (Rice 1999).

RESULTS AND DISCUSSION

Bed sediment data collected during the MISE sampling were compared with reported United States medians and Canadian Sediment Quality Guidelines (SQG's) (Rice 1999; Canadian Council of Ministers of the Environment 1999). Although

the U.S. Environmental Protection Agency (USEPA) is conducting extensive sediment analysis programs across the United States, no national guidelines or standards have been established; therefore, the Canadian guidelines are commonly used as standards for comparison. The United States medians were obtained from an extensive report on 541 sites representing 20 other NAQWA study units sampled in 1991 (Rice 1999). The Canadian SQG's recommend a value for a minimum effect level, called an interim sediment quality guideline (ISQG), and a value suggesting a probable effect level (PEL) on stream biota (Canadian Council of Ministers of the Environment 1999).

Trace element concentrations in the MISE study unit were at or below national medians for aluminum, cadmium, lead, mercury, nickel, selenium, and zinc. Similarly, cadmium, lead, mercury, and zinc were below both the suggested ISQG and PEL guidelines. (No Canadian guidelines for aluminum, iron, nickel, or selenium were available for comparison.) Chromium and arsenic, however, exceeded most of the guidelines (table 1).

Although chromium exceeded the Canadian ISQG recommended value of 37.3 parts per million (ppm) at every site, chromium concentrations exceeded the PEL of 90 ppm at only one site, Tensas River at Tendal, LA (fig. 3). The chromium concentration at that site was 100 ppm. Additionally, the MISE median (65 ppm) exceeded the national median of chromium concentrations, 64 ppm, by only 1.6 percent (fig. 3).

Chromium (Cr) is most commonly found in the environment in the trivalent (+3) and hexavalent (+6) oxidation states. In the +6 state, it is a known carcinogen (causes cancer) and highly toxic to mammals because it easily crosses membranes. However, chromium in the +3 state is considerably less toxic due to its low membrane permeability, and "chromium in biological materials is usually in the +3 form" (Eisler 1986).

Possible natural sources of chromium include the weathering of igneous rock. Industrial sources of chromium include electroplating, coal combustion, and tanneries, among others. Also, "chromium in phosphates used as fertilizers may be an important source of Cr in soil, water, and some foods" (Eisler 1986).

Arsenic concentrations at 2 of the 15 sites did not exceed any of the three standards: the national median (6.3 ppm), the Canadian ISQG (5.9 ppm) or the PEL (17 ppm). Concentrations at 13 of the 15 sites exceeded both the national median and the ISQG but not the PEL. However, arsenic concentrations at the remaining two sites, Cassidy Bayou at Webb, MS (24 ppm), and Little River Ditch No. 1 near Morehouse, MO (17 ppm), exceed the national median, the Canadian ISQG, and the PEL (fig. 4). Arsenic at Cassidy Bayou exceeded the national median by 281 percent and the Canadian PEL by 41 percent. Arsenic at Little River Ditch No. 1 exceeded the national median by 170 percent but equaled the Canadian PEL.

At certain concentrations, arsenic is a carcinogen and is a teratogen (causes fetal deformations, mutations, and fatalities). The more common methods of exposure to arsenic are through "atmospheric emissions...[of] arsenical herbicide sprays" or through eating fish or other stream biota that have been subject to arsenic contamination (Eisler 1988).

Sources of arsenic include natural, industrial, and agricultural. Natural sources of arsenic include igneous rock and are usually associated with gold. Industrial sources of arsenic include mineral smelters and coal-fired power plants. However, according to Eisler (1988), "most arsenic produced domestically is used in the manufacture of agricultural products such as insecticides, herbicides, fungicides . . . " Beginning with the application of lead arsenate in the 1930's, and extending to present day usage of monosodium methylarsonate (MSMA) and disodium methylarsonate (DSMA), arsenic-containing agricultural compounds have been and are being applied to the MISE study unit. During 1990-93, the pesticide MSMA was applied to cotton crops in the United States at an application rate of 6 million pounds of active ingredient per year. During the same period, the pesticide DSMA was applied to cotton crops in the United States at an application rate of 1.25 million pounds of active ingredient per year (Thurman, Zimmerman, Scribner, and Coupe 1998). Some arsenates have a half-life of 16 years (Eisler 1988).

Although pesticides have been applied in the MISE study unit for many decades, there are not enough data available to rule out natural or industrial sources of arsenic and chromium.

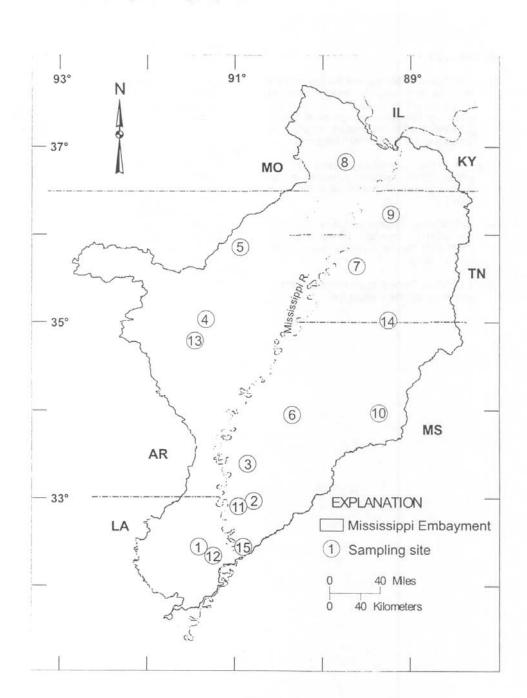
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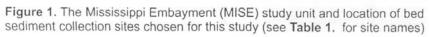
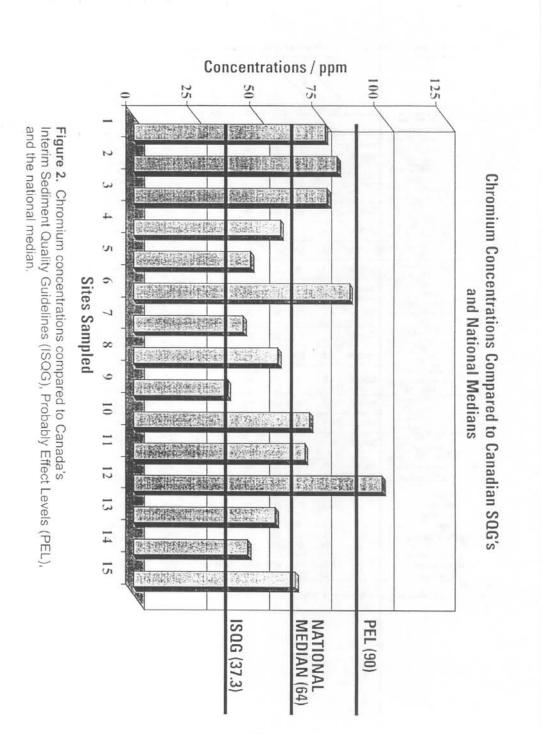
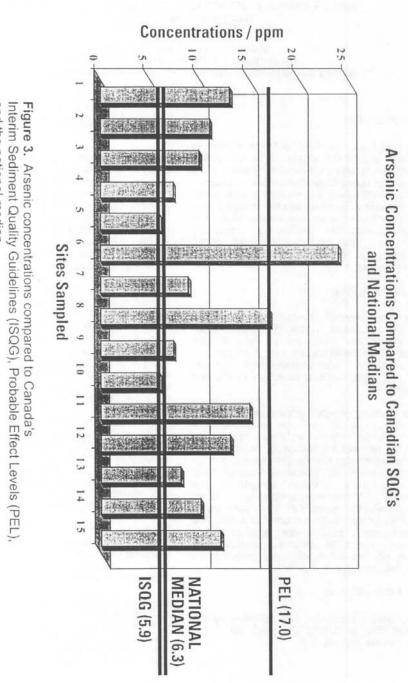


Table 1. Trace elements in bed sediments of the Mississippi Embayment Study Unit [parts per million (ppm). Canadian Interim Sediment Quality Guidline (ISOG). Canadian Probable Effect Level (PEL)]

| | | | 35 51 5 55 55 55 55 55 55 55 55 55 55 55 | | | | | | | | | anur | |
|--------------------------------|---|---------|--|-------|----------|----------|------|-------|----------|-------|------------|-------|--------|
| | | | Percent | ppm | 2 C3 | ppm | ppm | ppm | ppm | ppm | ppm | ppm | . ppm |
| U.S. Median Concentrations* | | 6.4 | 6.3 | 0.4 | 64 | 27 | 3.5 | 27 | 0.06 | 27 | 0.7 | 110 | |
| | Canadian ISQG** | | 10 - 10 | 5.9 | + 0.6 | 37.3 | 35.7 | | 35 | 0.2 | 1 | | 123 |
| | Canadian PEL** | | her ha | 17 | 3.5 | 90 | 197 | | 91.3 | 0.5 | Q | | 385 |
| EF. NO. | SITE NAME | SITE ID | 352 M. | | 82.42 | | 1.00 | | in state | | 841 8 | | 94.4 |
| 1 | Bayou Macon near Delhi, LA | 7370000 | 7.8 | 13 | 0.39 | 77 | . 30 | 4 | 21 | | 32 | | 1120 |
| 2 | Big Sunflower River near Anguilla, MS | 7288700 | 8.2. | 11 | 0.5 | 82 | 33 | 3.9 | 23 | 0.07 | 34 | 0.8 | 130 |
| 3 | Bogue Phalia near Leland, MS | 7288650 | 7.4 | 9.9 | 0.4 | 78 | 30 | 3.5 | 14 | 0.03 | 31 | 0.8 | 110 |
| 4 | Cache River near Cotton Plant, AR | 7077555 | 6.3 | 7.3 | 0.2 | 59 | 15 | 3 | 20 | 0.06 | 26 | 0.9 | 92 |
| 5 | Cache River at Egypt. AR | 7077380 | 15.4 | 5.9 | 0.2 | 47 | 14 | 2.3 | 17. | 0.04 | 20 | 0.6 | °67 |
| 6 | Cassidy Bayou at Webb, MS | 7280900 | 8.7 | 24 | 0.4 | 87 | 41 | 4.2 | 21 | 0.06 | 40 | 0.6 | 140 |
| 7 | Hatchie River at Rialto, TN | 7030050 | 5 | 8.8 | 0.1 | 44 | 13 | 2.5 | 15 | 0.03 | 22 | 0.2 | 57 |
| 8 | Little River Ditch No. 1 near Morehouse, MO | 7043500 | 6.2 | 17 | 0.3 | 58 | 19 | 3.5 | 19 | 0.05 | - 30 | 0.3 | 93 |
| 9 | Obion River at Hwy 51 near Obion, TN | 7023800 | 4.6 | 7.3 | 0.2 | 38 | 12 | 2 | 14 | 0.03 | 5-17 | 0.3 | 52 |
| 10 | Skuna River at Bruce, MS | 7283000 | 5.9 | 5.9 | 0.1 | 71 | 11 | 3 | 19. | 0.03 | 25 | 0.3 | 68 |
| 11 | Steele Bayou East Prong near Rolling Fork, MS | 7288870 | 6.8 | 15 | 0.5 | 69 | 22 | 3.3 | .25 | 0.04 | 27 | 0.7 | 97 |
| 12 | Tensas River at Tendal, LA | 7369500 | 9.1 | 13 | 0.6 | 100 | 40 | 4.5 | 17 | 0.05 | .38 | 1 | 140 |
| 13 | White River at Devalls Bluff, AR | 7077000 | 5.1 | 8 | 0.4 | 57 | 17 | 2.4 | ,251 | 0.03 | 129 | 0.6 | 85. |
| 14 | Woll River at Lagrange, TN | 7030392 | 4.7 | 10 | 0.1 | 46 | 12 | 27 | 14 | 0.03 | .19 | 0.3 | 50 |
| 15 | Yazoo River below Steele Bayou near Long Lake, MS | 7288955 | 6.7 | 12 | 0.3 | 65 | 18 | 3.2 | 16 16 | 0.03 | 30 5 xy | 0.5 | 91 |
| Average Minimum | | 6.53, | 11.21 | 0.31 | 65.20 | 21.80 | 3.20 | 18.67 | 0.04 | 28.00 | 0.56 | 92.80 | |
| Maximum | | 4.6 | 5.9 | 0,1 | 38 | 11 | 2 | 6143 | 0.03 | 517 | 0.2 | 50 | |
| Maximum Median | | .9.1 | 24 10 | 0.6 | 100 | 41 | 4.5 | 25 | 0.07 | 40 | 1 | 140 | |
| Number of Detects | | . 15 | 10 | 0.3 | 65 15 | 18 15 | 3.2 | 15: | 0.035 | 29 | 0.6 | 92 | |
| Percent Detects | | 100 | 15 | 100 | 100 | 100 | 100 | 100 | 15 | 100 | 100 | 100 | |
| 25th percentile | | 5.25 | 7.65 | 0.20 | 52.00 | 13.50 | 2.60 | 15.50 | 0.03 | 23.50 | 0.30 | 67.50 | |
| 50th percentile | | 6.30 | 10.00 | | 65.00 | 18.00 | 3.20 | 19.00 | 0.04 | 29.00 | 0.60 | 92.00 | |
| | 5th percentile | | 7.60 | 13.00 | | 77.50 | | 3.70 | 21.00 | 0.05 | 31.50 | 0.78 | 115.00 |

*Rice 1999 **Canadian Council of Ministers of the Environment 1999





and the national median.