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CONCENTRATIONS OF ARSENIC, CADMIUM, COPPER, LEAD, SELENIUM, AND ZINC IN FISH FROM THE MISSISSIPPI RIVER BASIN, 1995

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Abstract. Fish were collected in late 1995 from 34 National Contaminant Biomonitoring Program (NCBP) stations and 12 National Water Quality Assessment Program (NAWQA) stations in the Mississippi River basin (MRB), and in late 1996 from a reference site in West Virginia. The NCBP sites represented key points (dams, tributaries, etc.) in the largest rivers of the MRB. The NAWQA sites were typically on smaller rivers and were selected to represent dominant land uses in their watersheds. The West Virginia site, which is in an Eastern U.S. watershed adjacent to the MRB, was selected to document elemental concentrations in fish used for other aspects of a larger study and to provide additional contemporaneous data on background elemental concentrations. At each site four samples, each comprising (nominally) 10 adult common carp (*Cyprinus carpio*, 'carp') or black bass (*Micropterus* spp., 'bass') of the same sex, were collected. The whole fish were composited by station, species, and gender for analysis of arsenic (As), lead (Pb), and selenium (Se) by atomic absorption spectroscopy and for cadmium (Cd), copper (Cu), and zinc (Zn) by inductively-coupled plasma emission spectroscopy. Concentrations of most of the elements examined were lower in both carp and bass from the reference site, a small impoundment located in a rural area, than from the NCBP and NAWQA sites on rivers and larger impoundments. In contrast, there were few overall differences between NCBP sites NAWQA sites. The 1995 results generally confirmed the continued weathering and re-distribution of these elemental contaminants in the MRB; concentrations declined or were unchanged from 1984–1986 to 1995 at most NCBP sites, thus continuing two-decade trends. Exceptions were Se at Station 77 (Arkansas R. at John Martin Reservoir, CO), where concentrations have been elevated historically and increased slightly (to 3.8–4.7 μg g^{-1} in bass and carp); and Pb, Cd, and Zn at Station 67 (Allegheny R. at Natrona, PA), where levels of these metals were high in the past and increased from 1986 to 1995.

Keywords: Arkansas River, arsenic, cadmium, copper, irrigation, lead, metals, Mississippi River, Missouri River, monitoring, Ohio River, Red River, selenium, Tennessee River, zinc

1. Introduction

Environmental concentrations of many persistent environmental contaminants have generally declined over the last two decades (Schmitt and Bunck, 1995; Schmitt *et al*., 1999b; Gundersen *et al*., 2000), ostensibly as a result of environmental regu-

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lation. Nevertheless, there is a substantial body of information indicating that concentrations of organochlorine chemicals, mercury (Hg), and other persistent contaminants in fish may remain sufficiently elevated to harm fish and wildlife in some areas, and levels of some may be rising (e.g., Gooch and Matsamura, 1987; Colborn, 1991; Tillitt *et al*., 1992; Farag *et al*., 1994, 1995; Schmitt and Bunck, 1995; Woodward *et al*., 1997; Yeardley *et al*., 1998; Schmitt, 1999, 2002a, b; Schmitt *et al*., 1999b, 2002; Stansley and Roscoe, 1999; Wildhaber *et al*., 2000; Brumbaugh *et al*., 2001). Concentrations of persistent contaminants in fish are therefore measured as integral parts of many environmental monitoring programs (Hirsch *et al*., 1988; Messer *et al*., 1989; Biomonitoring of Environmental Status and Trends Program (BEST), 1996; Schmitt and Dethloff, 2000) and have been recommended as indicators of sustainable economic development (U.S. Council on Environmental Quality, 1997).

This paper summarizes one part of a larger investigation conducted in 1995–1996 that included both chemical and biological indicators (Schmitt, 2002a) and which was designed to assess the exposure of fish in rivers of the Mississippi River Basin (MRB) to environmental contaminants. The paper provides contemporary information on the distribution, concentrations, and ecological risks of arsenic (As), cadmium (Cd), copper (Cu), lead (Pb), selenium (Se), and zinc (Zn) in fish from the MRB, where contaminants in fish had not been evaluated comprehensively since the mid-1980s (Schmitt and Bunck, 1995; Schmitt *et al*., 1999b). The results are compared with previous findings of the National Contaminant Biomonitoring Program (NCBP) and relevant contemporaneous studies, and are evaluated relative to extant information on ecological risk of elemental contaminants in fish. The fish samples collected and analyzed for this study were also analyzed for organochlorine chemical residues and for Hg. Organochlorine findings have been published (Schmitt, 2000b), and those for Hg will be presented in another paper. Raw data for the entire study, as well as 1969–1986 NCBP data, may be obtained at <*http://www.cerc.usgs.gov/data/data.htm*>.

2. Methods and Materials

2.0.1. *Study area and collection sites*

The MRB drains all or parts of 32 states (about 41% of the conterminous U.S.) and parts of two Canadian provinces (Figure 1), and has a human population of more than 72 million. Agricultural development in the MRB is extensive, accounting for >50% of U.S. corn, wheat, soybean, cattle, and hog production (Goolsby, 1996). There is also substantial urban, industrial, and mining activity. Consequently, many programs and studies (e.g., Trefry *et al*., 1985; Garbarino *et al*., 1995; Heiny and Tate, 1997; Schmitt *et al*., 1999b; Horowitz *et al*., 2001) have documented the presence and widespread distribution of elemental contaminants of agricultural, industrial, and mining origin in the Mississippi River and its tributaries as well as

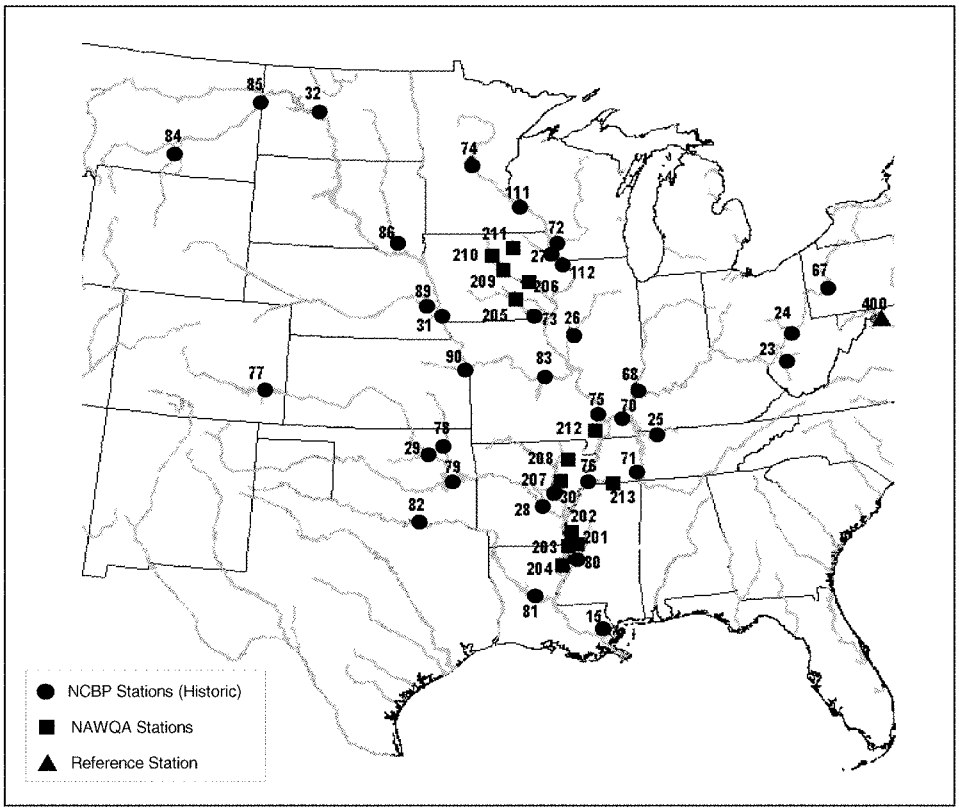

Figure 1. Map of the Mississippi River Basin showing the stations sampled in 1995 (1996 for Station 400). See Table I for station locations.

the export of nutrients and contaminants to the Gulf of Mexico (Trefry *et al*., 1985; Meade, 1995; Rostad, 1997). Information on contaminants in the large rivers of the MRB needed to be updated because substantial quantities of pesticides, nutrients, and other materials were re-distributed within and transported out of the basin by extreme flooding in 1993 and 1995 (Rostad, 1997).

Fish were collected in late 1995 from 34 NCBP stations in the MRB (Figure 1, Table I). At these sites, which represent key points (i.e., confluences of major tributaries, dams) on some of the largest U.S. rivers, concentrations of accumulative contaminants in fish were monitored from 1967 through 1986 (Schmitt and Bunck, 1995; Schmitt *et al*., 1999b). Fish were also collected in 1995 at 12 National Water Quality Assessment Program (NAWQA) sites – nine in the Mississippi Embayment (MSE) Study Unit (Mallory, 1994) and four in the Eastern Iowa Basins (EIB) Study Unit (Kalkhoff *et al*., 1994; Figure 1, Table I). The NAWQA sites are typically situated on lower-order rives and streams than the NCBP sites, and they were selected to represent prevalent land-use patterns in their respective basins. In late 1996, samples were collected from the water supply reservoirs of the USGS

Leetown Science Center in Kearneysville, WV (Table I). This site is located in the upper Potomac River watershed, which is adjacent to the easternmost drainages of the MRB (Figure 1). The site was sampled primarily because it was the source of the fish used to develop some of the biological methods used in the larger study (Schmitt and Dethloff, 2000; Schmitt, 2002a); their contaminant content had not been previously determined. Because all the NCBP and NAWQA sites in the MRB are contaminated to some degree, the West Virginia site was also believed to provide additional information on contemporary background concentrations. Additional contemporaneous data for elemental contaminants in carp were available from two sources: a NAWQA investigation conducted in the Red River of the North (RRN) basin (Brigham *et al*., 1998; Goldstein *et al.*, 1996; Goldstein and DeWeese, 1999); and a recent study of metals in fish from waters contaminated by Pb smelters that included the Mississippi River at Herculaneum, MO (Schmitt *et al*., 2002). The U.S. parts of the RRN basin lie completely within the North-Central MRB and, like adjacent parts of the MRB, much of the RRN watershed is devoted to agriculture and is sparsely populated; however, the population centers of the RRN basin support little industry and there is no mining (Brigham *et al*., 1998). In contrast, the Herculaneum smelter has operated since 1864 and the Mississippi River near the site is heavily contaminated (Schmitt *et al*., 2002). Herculaneum is 160 km upstream from NCBP Station 75 (Mississippi R. at Cape Girardeau, MO; Table I).

2.1. Target species and sampling strategy

This study was designed to retain comparability with historic NCBP data (Schmitt *et al*., 1999b) and other investigations based on composite samples of whole fish while also accommodating the biological measurements incorporated into the larger study (Schmitt and Dethloff, 2000), many of which are gender-specific and require live or freshly killed individual fish. Common carp (*Cyprinus carpio*, hereafter 'carp') and black bass (*Micropterus* sp., 'bass') were targeted for collection. These taxa were selected because they are widely distributed and were prevalent in past NCBP and NAWQA collections in the MRB (Crawford and Luoma, 1993; Heiny and Tate, 1997; Schmitt *et al*., 1999b) and because the biological endpoints measured in other components of the larger study (Schmitt, 2002a) had been most thoroughly tested in them. The collection target at NCBP sites and the reference site was 10 (each) adult male and female of each taxon – 40 fish per site. Both carp and bass were sought at only one NAWQA site; carp were targeted exclusively at 10, and only largemouth bass (*M. salmoides*) were sought at one. Collectors were instructed to obtain adult carp and bass of a size representative of those believed to be present based on extant information, and to avoid extremely large or small fish. Alternate species were permitted if carp or bass were not available.

TABLE I

Locations of National Contaminant Biomonitoring Program (NCBP) and National Water Quality Assessment Program (NAWQA) stations in the Mississippi River basin sampled in 1995, and of the reference site sampled in 1996

Program, sub-basin (NCBP) or Study Unit (NAWQA), and station number	River	Nearest city or feature	Latitude, longitude
NCBP			
Arkansas-Red R. (ARR)			
29	Arkansas	Keystone Res., OK	36°07′54.0″N, 96°20′47.0″W
77	Arkansas	John Martin Res., OK	38°03′55.0″N, 102°56′02.0″W
78	Verdigris	Oolagah, OK	36°31′16.0″N, 95°33′37.0″W
79	Canadian	Eufaula, OK	35°16′43.0″N, 95°34′39.0″W
82	Red	Lake Texoma, TX/OK	33°52′08.0″N, 96°47′04.0″W
Lower Missouri R. (LMO)			
31	Missouri	Nebraska City, NE	40°40′15.9″N, 95°49′44.6″W
83	Missouri	Hermann, MO	38°42′24.1″N, 91°26′17.5″W
86	James	Olivet, SD	43°13′45.0″N, 97°41′05.0″W
89	Platte	Louisville, NE	40°59′33.1″N, 96°12′30.9″W
90	Kansas	Bonner Springs, KS	39°02′47.0″N, 94°47′05.0″W
Upper Missouri R. (UMO)			
32	Missouri	Garrison Dam, ND	47°28′27.3″N, 101°26′15.5″W
84	Big Horn	Hardin, MT	45°52′12.2″N, 107°34′34.0″W
85	Yellowstone	Sidney, NE	47°34′46.8″N, 104°13′10.7″W
Lower Mississippi R. (LMS)			
15	Mississippi	Luling, LA	29°59′53.2″N, 90°25′31.1″W
28	Arkansas	Pine Bluff, AR	34°16′27.0″N, 94°57′12.0″W
30	White	Devall's Bluff, AR	34°47′01.0″N, 91°26′28.0″W
75	Mississippi	Cape Girardeau, MO	37°18′36.0″N, 89°31′01.2″W
76	Mississippi	Memphis, TN	38°08′30.3″N, 90°03′36.6″W
80	Yazoo	Redwood, MS	32°24′36.0″N, 90°55′27.0″W
81	Red	Alexandria, LA	31°20′48.0″N, 92°27′37.0″W
Upper Mississippi R. (UMS)			
26	Illinois	Beardstown, IL	40°07′50.6″N, 90°20′45.6″W
27	Mississippi	Guttenburg, IA	42°43′37.2″N, 91°01′30.0″W
72	Wisconsin	Woodman, WI	43°05′42.0″N, 90°48′57.6″W

TABLE I
(continued)

Program, sub-basin (NCBP) or Study Unit (NAWQA), and station number	River	Nearest city or feature	Latitude, longitude
Upper Mississippi R. (UMS) *(continued)*			
73	Des Moines	Keosauqua, IA	40°44′52.8″N, 91°59′38.4″W
74	Mississippi	Little Falls, MN	45°58′48.0″N, 94°22′00.0″W
111	Mississippi	Lake City, MN	44°22′49.8″N, 92°07′33.0″W
112	Mississippi	Dubuque, IA	42°26′27.6″N, 90°35′06.0″W
Ohio R. (OHR)			
23	Kanawha	Winfield, WV	38°29′06.0″N, 81°48′57.6″W
24	Ohio	Marietta, OH	39°24′36.8″N, 81°26′26.3″W
25	Cumberland	Clarksville, OH	36°32′28.6″N, 87°22′04.7″W
67	Allegheny	Natrona, PA	40°39′54.0″N, 79°41′24.0″W
68	Wabash	New Harmony, IN	38°11′58.4″N, 87°58′36.0″W
70	Ohio	Metropolis, IL	37°07′40.8″N, 88°39′25.2″W
71	Tennessee	Savannah, TN	35°12′52.0″N, 88°18′36.0″W
NAWQA			
Eastern Iowa Basins (EIB)			
205	S. Skunk	Oskaloosa, IA	41°21′19.0″N, 92°39′31.0″W
206	Iowa	Morengo, IA	41°50′23.0″N, 92°11′54.0″W
209[a]	S. Fork Iowa	New Providence, IA	42°19′26.0″N, 93°10′10.0″W
210	Iowa	Rowan, IA	42°45′36.0″N, 93°37′23.0″W
211	Cedar	St. Charles City, IA	43°03′45.0″N, 92°40′23.0″W
Mississippi Embayment (MSE)			
201	Big Sunflower	Anguilla, MS	32°58′18.0″N, 90°46′40.0″W
202	Bogue Phalia	Leland, MS	33°24′22.0″N, 90°50′26.0″W
203	Steele Bayou	Rolling Fork, MS	32°54′71.0″N, 90°57′10.0″W
204	Tensas	Tendal, LA	32°25′56.0″N, 91°21′57.0″W
207	Cache	Cotton Plant, AR	35°02′32.0″N, 91°19′12.0″W
208	Cache	Egypt, AR	35°51′23.0″N, 90°56′15.0″W
212	Little R. Ditch	Moorehouse, MO	36°50′03.0″N, 89°43′48.0″W
213	Wolf	LaGrange, TN	35°01′57.0″N, 89°14′48.0″W
Reference site (REF)			
400	Leetown Reservoir	Kearneysville, WV	39°21′02.2″N, 77°55′32.7″W

[a] Samples from Station 209 were lost in transit.

2.2. Field procedures

Fish were captured by electrofishing and held alive until they were processed (generally <4 hr) as described by Schmitt *et al.* (1999a). In short, each fish was measured, weighed, and placed on the dull side of a clean sheet of aluminum foil. The abdominal cavity was dissected open and gender was determined by gonadal observation. Samples of blood, liver, kidney, scales, and spleen were obtained for other analyses (Schmitt and Dethloff, 2000) after which all remaining tissues were returned to the carcass. The carcass was then wrapped in the foil on which it was processed, labeled, and chilled. Carcass samples comprised whole fish minus approximately 5 mL of blood, 5–8 1-cm^3 pieces of liver, five 1-cm^3 gonad pieces, the entire spleen, 5–10 scales, and a 1-cm^3 piece of both the posterior and anterior kidneys. The total mass of tissues not included in the carcass analyses represented <1% of the original mass of each fish. Between samples all contact surfaces and instruments were thoroughly cleaned with tap water and rinsed with de-ionized water and acetone. When all sampling at a station was completed, fish were frozen (–20 °C) and shipped in dry ice to the analytical laboratory, where they were kept frozen until prepared for analysis. Scale samples from each fish were returned to the laboratory for age determination.

2.3. Laboratory analyses

Sample processing and elemental contaminant analyses were performed by contract laboratories under the supervision of the U.S. Fish and Wildlife Service (FWS)-Patuxent Analytical Control Facility (PACF) in Laurel, MD, which maintained quality assurance (Q/A) oversight. For compatibility with other aspects of the larger study (Schmitt, 2002a) and previous studies in the MRB (e.g., Schmitt *et al.*, 1999b), samples from each station were composited by species and gender. Individual fish were partly thawed and band-sawed into pieces. All the pieces of all the fish in the sample were then ground together three times with a commercial meat grinder. A 100 g sub-sample was retained and re-frozen for elemental contaminants and moisture analysis. Additional aliquots were prepared for Q/A and for analyses not reported here (Schmitt, 2002a, b). All equipment was disassembled, washed in hot soapy water, and rinsed with water, acetone, and petroleum ether between samples.

For analyses of elemental contaminants and moisture content, the 100-g aliquots of ground fish were freeze-dried and ground to 100-mesh with a cutter-hammer mill, which was rinsed thoroughly with HNO_3 between samples. Moisture content was determined by weight loss during lyophilization. Freeze-dried fish (0.25–0.50-g) was digested in 5 mL of HNO_3 (Baker Instra-Analyzed) heated in a microwave oven (3 min @ 120 W, 3 min @ 300 W, 15 min @ 450 W), then diluted to 50 mL with ultrapure water. Concentrations of total As, Pb, and Se in the digestates were determined by graphite-furnace atomic absorption (AA) spectroscopy. Concentrations of total Cd, Cu, and Zn, along with additional elements not reported here,

TABLE II
Results of quality assurance analyses[a] for six elements

Quality assurance component	Element					
	As	Cd	Cu	Pb	Se	Zn
Duplicate sample analyses						
Mean difference (%)	19.3	9.4	4.8	14.0	6.04	3.7
SD	23.4	4.8	3.6	10.5	3.8	2.9
n[b]	3	5	9	8	9	9
Reference material, NRC DOLT-2 (Dogfish liver)						
Certified concentration (μg g^{-1}, dw)	16.60	20.80	25.80	0.22	6.06	85.8
95% CLM	1.10	0.50	1.10	0.02	0.49	2.5
Mean concentration (μg g^{-1}, dw)	15.83	21.34	26.24	0.22	5.68	89.2
SD	1.09	0.48	0.62	0.15	0.21	2.9
Mean recovery (%)	95.3	102.5	101.7	98.7	93.7	103.9
SD (%)	6.5	2.3	2.4	67.3	3.48	3.4
n	9	9	9	9	9	9
Fortified samples						
Mean recovery (%)	97.7	107.1	104.8	103.7	98.4	105.5
SD	11.0	3.8	2.6	1.9	3.0	14.6
n	9	9	9	9	9	9

[a] All blanks < LOD.
[b] Pairs (of 9) in which both analyses were > LOD.

were determined by inductively coupled plasma emission spectroscopy (ICPES) without pre-concentration using a Leeman ES200 simultaneous spectrometer. Q/A measures included analyses of blanks, fortified samples, duplicates, and standard reference materials (Table II). LODs were computed individually for each analyte in each sample, but were nominally 0.15 μg g^{-1} dry-weight (dw) for Cd; 0.7 μg g^{-1} for As, Cu, and Se, 2.5 μg g^{-1} for Zn; and 3 μg g^{-1} for Pb (Table III). These values, as well as the analytical results, were converted to wet-weight (ww) concentrations (Table III) for statistical analysis and reporting and for comparisons with other studies.

Scale samples from each fish were cleaned, dried, and either mounted between glass microscope slides or pressed in acetate. They were read with the aid of either a

TABLE III

Occurrence (percentages of samples and stations, including the reference site), limits of detection (LOD), and maximum concentrations of analytes in composite carcass samples

Analyte	Samples	Stations	LOD range	Maximum 1995 concentrations			
	(% of 163)	(% of 47)	(μg g^{-1})[a]	Conc. (μg g^{-1})	Station	Sex	Species
Arsenic	28	48	0.11–0.51	0.56	78	M	Largemouth bass
Cadmium	49	91	0.02–0.10	0.51	67	M	Carp
Copper	100	100	0.11–0.51	3.8	15	F	White bass
Lead	87	100	0.01–0.04	0.69	111	M	Carp
Selenium	100	99	0.11–0.51	4.7	77	M	Carp
Zinc	100	100	0.23–1.66	150	79	M	Carp

[a] Wet-weight concentrations estimated from dry-weight values and moisture content.

dissecting microscope or scale projector, and age was estimated (yr) as the number of completed annuli (Jearld, 1993).

2.4. Data set composition and statistical analyses

2.4.1. *Species Composition*

A total of 163 composite samples from 47 stations (including the reference site), which together represented 1308 fish, were analyzed; samples from one NAWQA site were lost in transit. Of the samples analyzed, 89 (55%) from 45 stations (96%) were carp and 58 samples (36%) from 30 stations (64%) were bass – largemouth, smallmouth (*Micropterus dolomieui*), and spotted (*M. punctulatus*). Most of these were largemouth bass, which were obtained from 23 stations. Exclusively smallmouth bass were obtained at four stations (67, 72, 74, and 111), and only spotted bass were collected at Station 23. Two samples each of both largemouth and spotted bass from one station (25) were analyzed, and the bass samples from one station (83) comprised both largemouth and spotted bass. The remaining 16 samples (10%) comprised white sucker (*Catostomus commersoni*; two samples from one station), white bass (*Morone chrysops*; four samples, two stations), sauger (*Stizostedion canadense*; three samples, two stations), brown trout (*Salmo trutta*; two samples, one station), goldeye (*Hiodon alosoides*; two samples, one station), smallmouth buffalo (*Ictiobus bubalus*; two samples, one station), and northern pike (*Esox lucius*, one sample, one station). At most NCBP stations there was at least one species common to both the 1995 and 1986 collections (Schmitt *et al.*, 1999b) for the examination of within-taxon temporal trends. For Station 90 (Kansas R.), where fish were not collected in 1986, 1995 data were compared to results from 1984 (Schmitt and Brumbaugh, 1990).

2.4.2. *Fish Size and Age*

Concentrations of certain contaminants in fish increase with fish size, and these relationships as well as the concentrations vary among taxa (Goldstein *et al*., 1996; Goldstein and DeWeese, 1999; Schmitt *et al*., 1999b; Brumbaugh *et al*., 2002; Wiener *et al*., 2002). Accordingly, length, weight and age data of bass and carp were examined for extremes in variation and overall consistency across stations (Schmitt, 2002a). Most largemouth bass were 200–500 mm long, weighed 200–1500 g, and were 2–6 yr old. As is typical for these species, smallmouth and spotted bass were smaller than largemouth bass from some sites; however, most were similar in size to largemouth bass. The spotted and largemouth bass from Station 25 were nearly identical in size and age. Carp were more variable in length and weight than bass; most were 300–750 mm long, weighed 500–5000 g, and were 2–6 yr old. However, four carp were >1000 mm, 10 weighed 300–500 g, and eight were 5000–7500 g. Carp and bass from the reference site were slightly smaller and younger than those from most MRB stations but similar in size to fish from several of the closest NCBP stations sampled (Stations 23 and 67). Overall, the sizes of the bass and carp analyzed were relatively consistent considering the wide geographic range and diversity of water body sizes and ecological conditions represented by the stations sampled. The size range of the bass comprised by the composite samples was smaller than those in the composite samples analyzed by Brumbaugh *et al*., (2002), and all bass in the composites were larger than the 180 mm total length mininum specified by Yeardley *et al*. (1998). A detailed analysis of the fish size and age information is presented elsewhere (Schmitt, 2002b).

2.4.3. *Statistical Analyses*

A value of one-half the LOD was substituted for censored values (i.e., < LOD) in all computations, a procedure that introduces relatively little bias (U.S. Environmental Protection Agency (U.S. EPA), 2000). Preliminary analyses using Levene's test indicated that $\log_{10}$-transformed elemental concentrations reasonably approximated normality. Further analyses (ANOVA) indicated that for the elements reported here, differences between male and female carp and bass were not statistically significant ($p > 0.05$), and the samples representing male and female carp and bass from each station were treated as replicates in subsequent analyses. Within-taxon temporal and geographic comparisons were made where possible because elemental contaminant concentrations vary widely among fish taxa (Lowe *et al*., 1985; Schmitt *et al*., 1999b). For statistical testing of geographic trends, stations were aggregated by sub-basin and program (NCBP vs. NAWQA – Table I) for geographic analysis. The MSE and EIB Study Units are wholly contained within the Lower Mississippi River (LMS) and Upper Mississippi River (UMS) sub-basins, respectively (Figure 1, Table I). Therefore, comparisons of these sub-basins represent regional contrasts of the large-river stations against those on lower-order rivers and streams, the latter selected based upon prevailing land-use patterns in their watersheds (Hirsch *et al*., 1988). Log-transformed concentrations of Cd, Cu,

Pb, Se, and Zn in carp and bass and of Cd in carp were tested with a one-way ANOVA in which 'station' was treated as a fixed effect. Differences among sub-basins and programs were tested as planned contrasts using single degree-of-freedom F-tests. These analyses were not performed for As in either taxon or for Cd in bass because large percentages of the concentrations were censored; geographic and temporal comparisons for these elements were restricted to visual analyses. Temporal changes in concentrations of Pb, Se, Zn, and Cu at individual NCBP stations were also tested by analyzing the log-transformed elemental concentrations in the 141 station-year-species combinations (total $N = 242$) in the combined-year data set as a one-way ANOVA. Fisher's protected LSD was then used to contrast the 36 pairs of station-year-species means for each element that represented 1995 vs. 1986 concentrations (1984 for Station 90) in the same species at a site. A significance level of $\alpha = 0.05$ was used in all statistical tests unless otherwise indicated.

3. Results and Discussion

3.1. Lead

Environmental releases of Pb in North America have been greatly reduced over the last two decades through controls on industrial discharges and the elimination of Pb from motor fuels. Nevertheless, substantial quantities are still emitted by mining, smelting, and other activities and there is atmospheric transport from other parts of the world. In addition, much Pb remains in the environment from past emissions and uses (e.g., Schmitt *et al.*, 2002). Not surprisingly, Pb was detected (>0.006–>0.032 μg g^{-1}) in 87% of the samples and in at least one sample from all stations sampled (Table II). At the West Virginia reference site, Pb was detected at low concentrations (0.09–0.12 μg g^{-1}) in both carp samples but not in either sample of largemouth bass (<0.03 μg g^{-1}; Figure 2). Concentrations were slightly greater in largemouth bass (0.03–0.07 μg g^{-1}) than in spotted bass (0.03 μg g^{-1}) from Station 25 (Cumberland R.), the only station from which both species were analyzed. The greatest Pb concentration (0.69 μg g^{-1}) was in carp from Station 111 (Mississippi R. at Lake City, MN; Table III); concentrations in the other samples from this site were low (<0.04–0.10 μg g^{-1}), however (Figure 2). Pb concentrations were also relatively high (>0.2 μg g^{-1} in one or both samples) in carp from NCBP Stations 67 (Allegheny R.), 85 (James R.), 24 (Ohio R.), 25 (Tennnesee R.), 28 (Arkansas R.), 78 (Verdigris R.), 79 (Canadian R.), 73 (Des Moines R.), and at NAWQA Station 204 (Tensas R.); in smallmouth buffalo from Station 23 (Kanawha R.); and in largemouth bass from Stations 28 and 70 (Ohio R. at Metropolis, IL; Figure 2). Concentrations of Pb in carp from most sites in the MRB (Figure 2), including those in rural areas, were greater than the mean for whole carp from the RRN reported by Goldstein and DeWeese (1999), which was 0.14 μg g^{-1} dw (about 0.04 μg g^{-1} ww using the 70% moisture content for

RRN carp reported by Brigham *et al.* (1998)). The RRN values were similar to concentrations in carp from the West Virginia reference site, however (Figure 2). All 1995 Pb concentrations from the MRB, as well as those from the RRN and the reference site, were low compared to the 1.2–4.4 μg g^{-1} reported for similar-sized carp and other fishes collected in 1992 from the Mississippi River at Herculaneum, MO by Schmitt *et al.* (2002).

Concentrations of Pb in MRB carp (2% censored; i.e., < LOD) differed significantly among stations and sub-basins, but not programs, and no group of stations differed significantly from the reference site (Table IV). Among sub-basins, greatest concentrations were in the Ohio River (OHR) sub-basin and lowest were in the Lower Missouri River (LMO) and Lower Mississippi River (LMS) sub-basins and in the MSE Study Unit. The LMS and MSE did not differ significantly, nor did the EIB Study Unit differ from the Upper Mississippi River (UMS) sub-basin (Table IV). In bass (24% censored), Pb concentrations also differed significantly among stations and sub-basin, with greatest levels occurring in the OHR and LMO sub-basins and lowest in the Arkansas-Red River (ARR) sub-basin and MSE Study Unit; the latter differed significantly (Table IV). Several sub-basins also differed significantly (greater) from the reference site (Table IV). Overall, concentrations of Pb in bass from the NCBP stations were significantly greater than levels at the NAWQA sites ($n = 2$), but neither group differed significantly from the reference site (Table IV).

Greatest Pb concentrations (individual samples, station means, or both) in 1986 (Schmitt *et al.*, 1999b) occurred at several sites in the MRB where levels remained comparatively high in 1995: Stations 78 (Verdigris R.), 79 (Canadian R.), 89 (Platte R.), and 73 (Des Moines R.). In 1986, concentrations were also elevated at Station 69 (Ohio R. at Cincinnati, OH), which was not sampled in 1995, and at Stations 76 (Mississippi R. at Memphis, TN) and 83 (Missouri R. at Hermann, MO; Schmitt *et al.*, 1999b). Relative to 1986 (1984 for Station 90), Pb concentrations decreased significantly at many of these NCBP stations where levels were historically elevated, especially in carp (Table V). In contrast, mean concentrations in carp about doubled from 0.24 g g^{-1} in 1986 to 0.45 g g^{-1} in 1995 at Station 67, where the 1995 Pb maximum occurred (Table III), but this change was not statistically significant (Table V). Although concentrations of Pb were generally lower in bass than in carp (Figure 2, Table V), concentrations in bass nevertheless increased significantly at Stations 67, 30 (White R.), 27 (Mississippi R. at Guttenburg, IA), and 72 (Wisconsin R.; Table V).

Although Pb is readily incorporated by fish into bones, scales, and certain organs (e.g., Farag *et al.*, 1994), it does not biomagnify (Settle and Patterson, 1980). Consequently, there appears to be little risk to piscivorous wildlife from Pb in fish (Henny *et al.*, 1994). Effects on heme synthesis in fish have been detected at carcass concentrations exceeding about 1.0 μg g^{-1}, depending also on Zn burden (Schmitt *et al.*, 1984, 1993). In laboratory studies other effects have been associated with higher whole-body concentrations (Jarvinen and Ankley, 1999).

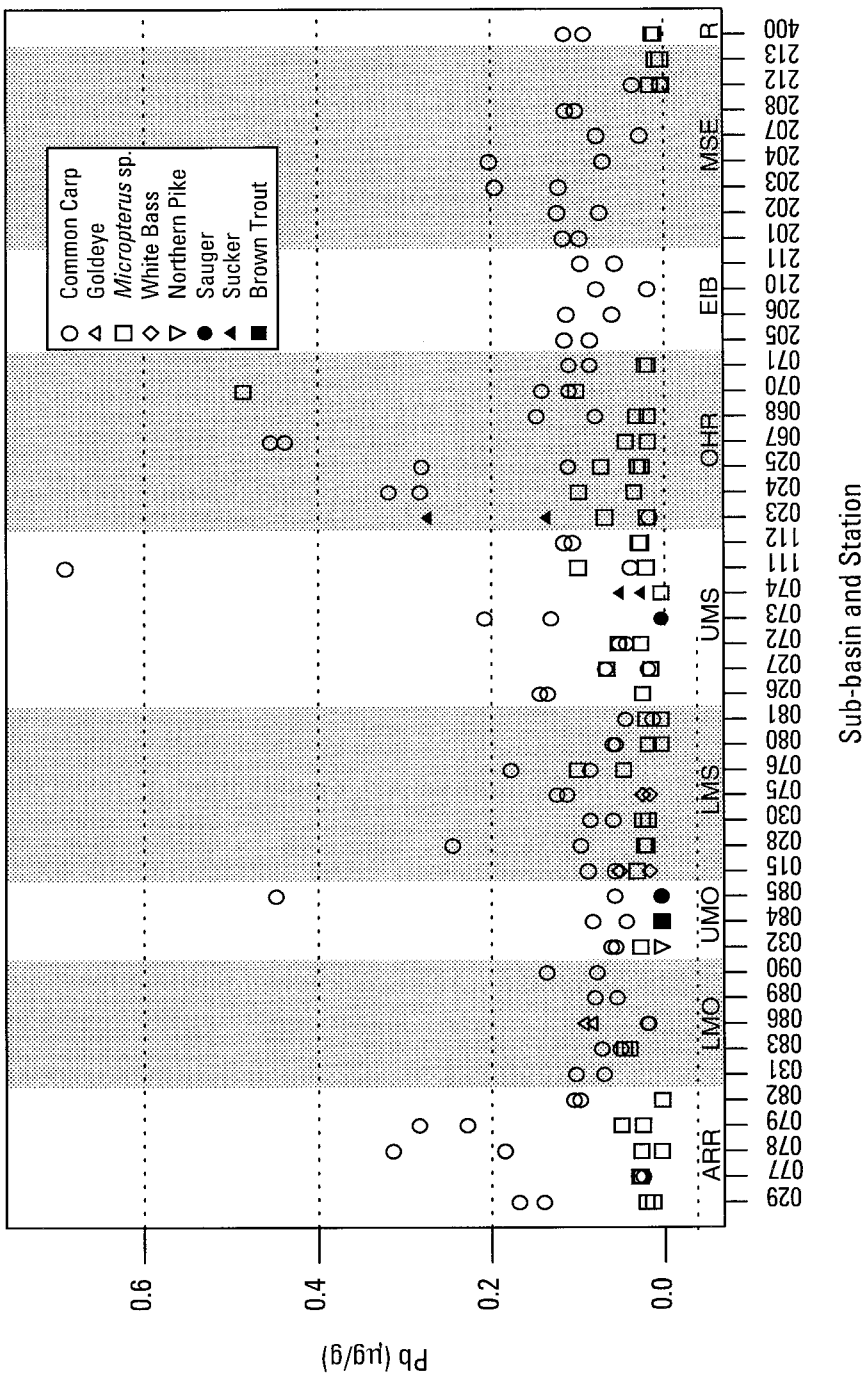

Figure 2. Concentrations of Pb ($\mu g\ g^{-1}$, ww) in composite samples of whole fish, by sub-basin, station, and taxon. See Table I for station locations.

TABLE IV

Least-squares geometric mean concentrations of Pb, Se, Cu, Zn, and Cd in bass and carp (Cd in carp only, see text for explanation) collected from the MRB in 1995. Shown are means for sub-basins, programs, and the reference site, as identified in Table I. Also shown are ANOVA results as F-values (** $p < 0.01$; ns, $p > 0.05$) for among-station differences. Within columns (elements), sub-basin, program, and reference site means containing the same subscript do not differ significantly ($p > 0.05$)[a]

Taxon and sub-basin (no. stations)	Program	Element				
		Pb	Se	Cu	Zn	Cd
Bass						
ARR (5)	NCBP	0.01_{abc}	0.75_{ab}	0.49_{b}	17.75_{a}	–
LMO (1)	NCBP	0.04_{a}	0.59_{b}	0.56_{ab}	19.29_{a}	–
LMS (6)	NCBP	0.02_{ab}	0.36_{a}	0.52_{cd}	18.05_{a}	–
MSE (2)	NAWQA	0.01_{c}	0.39_{c}	0.57_{ab}	20.57_{a}	–
OHR (7)	NCBP	0.04_{a}	0.40_{c}	0.51_{b}	21.56_{a}	–
UMO (1)	NCBP	0.03_{ab}	0.98_{a}	0.72_{a}	21.22_{a}	–
UMS (6)	NCBP	0.02_{ab}	0.40_{c}	0.50_{b}	18.70_{a}	–
REF (1)	REF	0.01_{ABbc}	0.28_{Aa}	0.48_{Ad}	17.44_{Aa}	–
NCBP mean (28)	NCBP	0.03_{B}	0.54_{B}	0.54_{A}	19.37_{A}	–
NAWQA mean (2)	NAWQA	0.01_{A}	0.39_{C}	0.57_{A}	20.57_{A}	–
ANOVA F (df = 28, 29)	–	3.52**	21.49**	0.68ns	1.42ns	–
Carp						
ARR (5)	NCBP	0.12_{ab}	0.98_{a}	1.04_{a}	80.84_{abc}	0.09_{ab}
LMO (5)	NCBP	0.06_{c}	0.70_{bc}	1.15_{a}	62.50_{d}	0.07_{bc}
LMS (7)	NCBP	0.08_{bc}	0.55_{cd}	1.05_{a}	63.32_{d}	0.05_{cd}
MSE (7)	NAWQA	0.07_{bc}	0.76_{b}	1.14_{a}	74.87_{bcd}	0.06_{bc}
OHR (7)	NCBP	0.13_{a}	0.51_{d}	1.05_{a}	60.79_{cd}	0.11_{a}
UMO (3)	NCBP	0.08_{abc}	0.82_{ab}	1.12_{a}	86.72_{ab}	0.07_{bc}
UMS (6)	NCBP	0.10_{abc}	0.57_{cd}	1.07_{a}	93.07_{a}	0.05_{cd}
EIB (4)	NAWQA	0.07_{bc}	0.67_{bcd}	1.02_{a}	74.94_{bcd}	0.04_{d}
REF (1)	REF	0.10_{Aabc}	0.13_{Ae}	0.98_{Aa}	40.64_{Ae}	0.01_{Ae}
NCBP mean (33)	NCBP	0.09_{A}	0.67_{B}	1.08_{A}	73.44_{AB}	0.07_{B}
NAWQA mean (11)	NCBP	0.07_{A}	0.71_{B}	1.08_{A}	74.91_{B}	0.05_{B}
ANOVA F (df = 44, 44)	–	3.00**	8.02**	1.38ns	4.01*	8.92**

[a] As determined by non-orthogonal, single degree-of-freedom (df) F-tests.

TABLE V

Geometric mean concentrations (μg g^{-1}, wet weight) of Pb, Se, Zn, and Cu in 1986 (1984 for Station 90) for taxa common to both collections at the indicated stations (as identified in Table I). For each element, pairs of means containing the same subscript do not differ significantly ($p > 0.05$, Fischer's protected LSD). Also shown are overall ANOVA F-values

Sub-basin and station	Taxon	Element and collection year							
		Pb		Se		Zn		Cu	
		1986	1995	1986	1995	1986	1995	1986	1995
ARR									
29	Common carp	0.20_a	0.15_a	0.43_a	0.50_a	55.2_a	67.8_a	0.72_a	0.93_a
77	Common carp	0.05_a	0.03_a	3.34_a	4.19_a	71.9_a	83.9_a	0.72_a	0.98_a
78	Common carp	0.53_a	0.24_a	0.52_a	1.30_b	63.4_a	85.6_a	1.00_a	1.14_a
79	Common carp	0.43_a	0.25_a	0.39_a	0.53_b	53.4_a	106.8_b	0.58_a	1.22_b
82	Common carp	0.14_a	0.10_a	0.52_a	0.61_a	59.6_a	66.4_a	0.88_a	0.98_a
LMO									
31	Common carp	0.10_a	0.09_a	1.01_a	0.77_a	62.8_a	66.7_a	0.87_a	1.15_a
86	Common carp	0.09_a	0.02_b	0.45_a	0.42_a	69.6_a	71.1_a	0.90_a	0.97_a
	Mooneye	0.24_a	0.09_a	0.88_a	0.91_a	20.6_a	30.8_b	0.63_a	0.45_a
90	Common carp	0.11_a	0.10_a	0.60_a	0.84_b	49.8_a	65.6_a	0.86_a	1.22_a
UMO									
32	Common carp	0.22_a	0.06_b	0.68_a	0.67_a	76.2_a	78.3_a	1.27_a	1.18_a
84	Brown trout	0.07_a	0.01_b	1.52_a	1.32_a	26.0_a	25.0_a	2.40_a	0.60_b
85	Common carp	0.07_a	0.16_a	0.66_a	0.57_a	66.8_a	65.3_a	0.58_a	0.90_a
	Sauger	0.39_a	0.01_b	0.54_a	0.75_a	13.5_a	21.8_b	4.71_a	0.48_b
LMS									
15	White bass	0.03_a	0.03_a	0.76_a	0.94_a	15.1_a	17.8_a	4.95_a	3.44_a
30	*Micropterus*[a]	0.01_a	0.02_b	0.41_a	0.41_a	14.1_a	22.8_b	0.33_a	0.51_a
75	Common carp	0.20_a	0.12_a	0.81_a	0.53_b	63.2_a	54.6_a	0.80_a	0.88_a
UMS									
26	Common carp	0.12_a	0.14_a	0.66_a	0.48_b	66.5_a	99.5_b	0.79_a	1.12_a
27	*Micropterus*[a]	0.01_a	0.03_b	0.46_a	0.52_a	15.0_a	19.2_a	0.63_a	0.46_a
	Common carp	0.08_a	0.04_a	0.51_a	0.54_a	66.2_a	90.4_a	0.80_a	1.03_a
72	*Micropterus*[a]	0.01_a	0.04_b	0.30_a	0.24_a	13.0_a	19.8_b	0.59_a	0.48_a
	Common carp	0.21_a	0.05_b	0.35_a	0.46_a	58.8_a	79.3_a	2.37_a	0.97_b

TABLE V
(continued)

Sub-basin and station	Taxon	Element and collection year							
		Pb		Se		Zn		Cu	
		1986	1995	1986	1995	1986	1995	1986	1995
UMS *(continued)*									
73	Common carp	0.12_a	0.17_a	0.73_a	0.85_a	58.3_a	93.8_b	0.85_a	1.26_a
74	White sucker	0.07_a	0.04_a	0.20_a	0.13_b	15.1_a	24.3_b	3.55_a	1.22_b
111	Common carp	0.29_a	0.17_a	0.59_a	0.58_a	91.4_a	102.0_a	1.05_a	1.11_a
112	Common carp	0.08_a	0.11_a	0.39_a	0.56_b	57.9_a	95.3_b	0.69_a	0.93_a
OHR									
23	*Micropterus*[a]	0.07_a	0.04_a	0.35_a	0.38_a	14.0_a	24.3_b	0.22_a	0.58_b
24	Common carp	0.25_a	0.30_a	0.53_a	0.67_a	73.1_a	81.9_a	0.62_a	1.46_b
25	*Micropterus*[a]	0.06_a	0.04_a	0.35_a	0.30_a	16.2_a	22.4_a	0.37_a	0.48_a
	Common carp	0.33_a	0.18_a	0.46_a	0.43_a	67.9_a	74.0_a	0.75_a	1.15_a
67	Micropterus[a]	0.01_a	0.03_b	0.38_a	0.45_a	14.6_a	23.3_b	1.28_a	0.52_b
	Common carp	0.24_a	0.45_a	0.50_a	0.55_a	72.0_a	87.3_a	0.68_a	1.56_b
68	Common carp	0.18_a	0.11_a	0.46_a	0.62_a	62.2_a	60.8_a	1.22_a	1.00_a
70	*Micropterus*[a]	0.07_a	0.22_a	0.37_a	0.43_a	13.0_a	20.4_b	1.46_a	0.50_b
	Common carp	0.12_a	0.13_a	0.36_a	0.58_b	59.3_a	75.1_a	0.98_a	0.93_a
ANOVA F[b]		7.41		17.19		28.94		8.14	

[a] Largemouth, smallmouth, or spotted bass.
[b] Degrees-of-freedom = 140, 101; all $p < 0.01$.

The greatest 1995 concentrations (ca. 0.5–0.7 μg g^{-1}) were therefore about half the concentrations associated with impaired heme synthesis in fish. Higher-level effects specifically associated with Pb at environmental concentrations have not been reported in fish; however, in combination with other elemental contaminants and environmental factors, effects on individual fish and fish populations have been documented (Farag *et al*., 1994, 1995; Woodward *et al*., 1997; Wildhaber *et al*., 2000).

3.2. Cadmium

Cadmium is present in many common materials and is released to the environment from mining, smelting, and a variety of other sources and activities. In 1995, Cd was detected (ca. 0.05 μg g^{-1}) in 49% of the samples from 91% of the stations sampled (Table III). Concentrations ranged from <0.05 μg g^{-1} to about 0.5 μg g^{-1}, the latter in carp from Station 67 (Allegheny R.; Table III, Figure 3). Concen-

trations were uniformly low (<0.03 μg g^{-1}) in all samples from the reference site. In contrast, comparatively high concentrations of Cd (>0.15 μg g^{-1}), as individual samples, station means, or both, were detected at NCBP Stations 24 (Ohio R. at Marietta, OH), 25 (Cumberland R.), 90 (Kansas R.), 78 (Verdigris R.), 73 (Des Moines R.), and 30 (White R.). At all of these sites except Station 30, where one relatively high value occurred in largemouth bass, the highest concentrations were in carp (Figure 3). Cd concentrations at Stations 67, 78, and 24 have been among the greatest in previous NCBP collections (May and McKinney, 1981; Lowe *et al*., 1985; Schmitt and Brumbaugh, 1990; Schmitt *et al*., 1999b). Station 78 has a long history of contamination by metals from the Tri-State Mining District of Missouri, Oklahoma, and Kansas, where Zn and other metals were mined for many years and where there are abandoned mines and ore-processing facilities (May and McKinney, 1981; Pita and Hyne, 1975; Wildhaber *et al*., 2000). Goldstein and DeWeese (1999) reported that concentrations of Cd in carp collected in 1994 from the RRN averaged 0.22 μg g^{-1} dw (about 0.07 μg g^{-1} ww), a level exceeded at most MRB sites but which was greater than all samples from the reference site (Figure 3).

Schmitt *et al*. (1999b) noted that Cd concentrations tended to be greater in carp than in other taxa, a trend that held through 1995 (Figure 3). Concentrations of Cd in carp differed significantly among stations and sub-basins, but not between the NAWQA and NCBP sites. Concentrations were significantly greater at NCBP and NAWQA sites than at the reference site (Table IV), where levels were < LOD in both samples (Figure 3). Greatest mean concentrations of Cd in carp occurred in the OHR and ARR sub-basins, and neither NAWQA Study Unit (MSE, EIB) differed significantly from its respective sub-basin (LMS, UMS; Table IV). Concentrations of Cd in bass (95% censored) were not analyzed statistically.

Relative to previous collections, concentrations of Cd in carp increased at Stations 67 and 90 (1984) and decreased at Stations 32 (Missouri R. at Garrison Dam, ND) and 79 (Canadian R.). Concentrations also increased in largemouth bass at Station 30 (White R.), white bass at Stations 15 and 25, and in other taxa at stations in the Upper Missouri River (UMO) sub-basin—goldeye at Station 86 (James R.), sauger at Station 85 (Yellowstone R.), and brown trout at Station 84 (Big Horn R.). Carp were collected at Stations 85 and 86 in both 1986 and 1995, but Cd concentrations were low in all samples (Figure 3).

Whole-organism Cd concentrations of 2 μg g^{-1} are indicative of contamination, levels of 5 μg g^{-1} are considered hazardous to the organism, and dietary levels of 13–15 μg g^{-1} represent a hazard to higher trophic levels (Eisler, 1985; Jarvinen and Ankley, 1999). Even the greatest 1995 concentrations were well below the lowest of these toxicity thresholds.

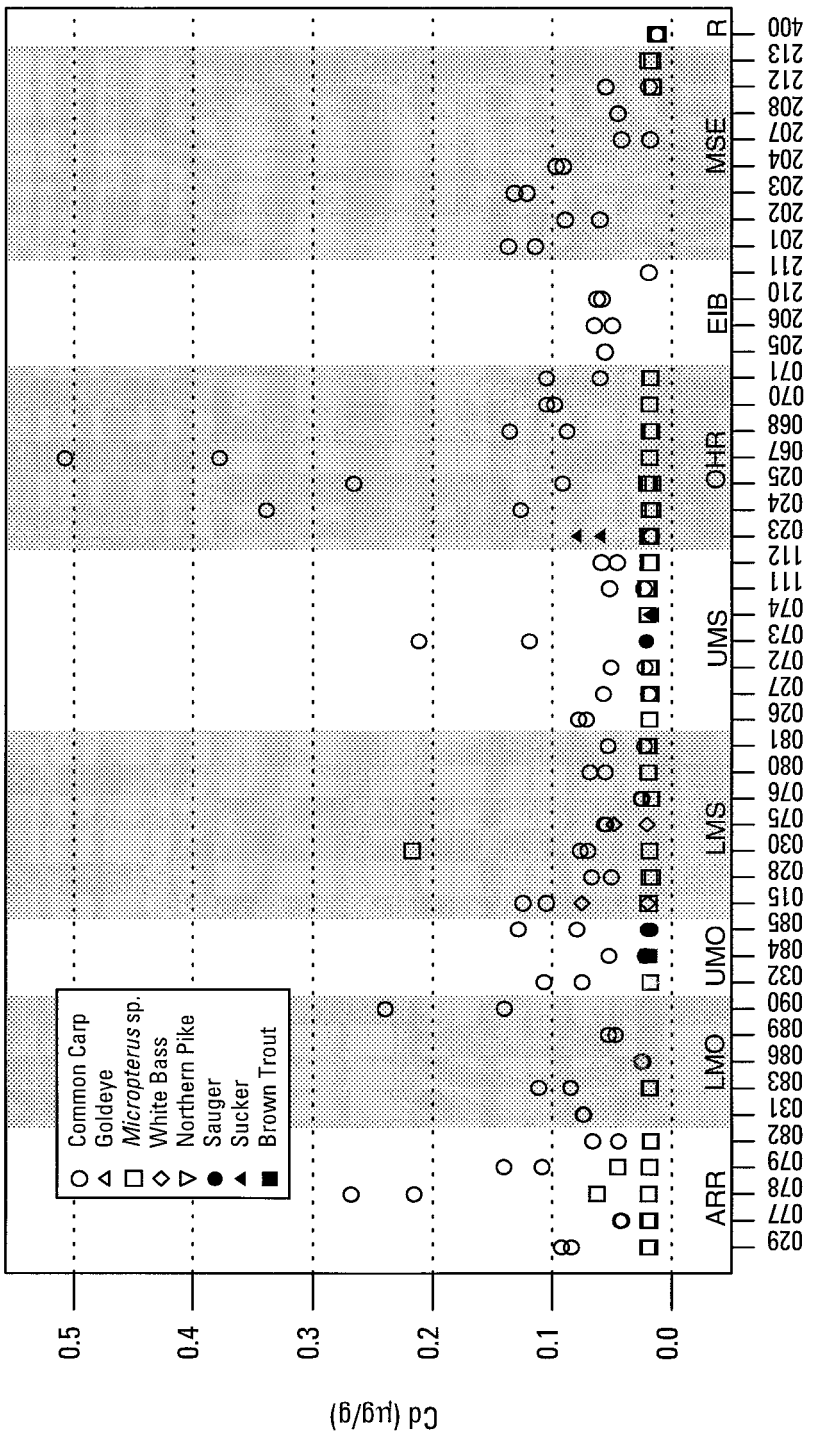

Figure 3. Concentrations of Cd ($\mu g\ g^{-1}$, ww) in composite samples of whole fish, by sub-basin, station and taxon. See Table I for station locations.

3.3. SELENIUM

Selenium is released to the environment from the combustion of fossil fuels and can be leached from arid, seleniferous soils by irrigation (Lemly, 1996). In 1995, Se was detected (>0.02 μg g^{-1}) in all but two samples (white sucker from Station 74, carp from Station 400; Figure 5). Except for Station 77 (Arkansas R. at John Martin Reservoir, CO), concentrations were relatively low; they ranged from barely detectable (ca. 0.20 μg g^{-1}) to 1.40 μg g^{-1} (Figure 4). In contrast, concentrations were 3.5–4.7 μg g^{-1} in all samples (carp and largemouth bass) from Station 77 (Figure 4, Table III). Nationally, the maximum 1986 concentration (3.4 μg g^{-1}) was also in carp from Station 77 (Schmitt *et al.*, 1999b). In 1995, Se concentrations exceeded 1.0 μg g^{-1} in samples from only two other stations: NCBP Station 84 (Big Horn R.), where concentrations were 1.0–1.4 μg g^{-1} in all samples (carp and brown trout); and NCBP Station 78 (Verdigris R.), where concentrations were about 1.2 μg g^{-1} in both 1995 samples of carp but were lower (0.7 μg g^{-1}) in largemouth bass (Figure 4). Concentrations at Station 84 were also comparatively high in 1986 (Table V; Schmitt *et al.*, 1999b). Concentrations at the West Virginia reference site were 0.27–0.30 μg g^{-1} in largemouth bass and <0.12–0.29 μg g^{-1} in carp (Figure 4), the latter only slightly lower than the 1.18 μg g^{-1} dw (about 0.35 μg g^{-1} ww) mean for whole carp collected from the RRN in 1994 (Goldstein and DeWeese, 1999). Both are similar to concentrations in fish from many rural MRB sites (Figure 4).

There were no censored values for Se in bass, and only one value was < LOD in carp. Se concentrations in both carp and bass differed significantly among stations and sub-basins in both carp and bass, but differed among programs only in bass (Table IV). NCBP sub-basins with the greatest concentrations (ARR, UMO, and LMO) differed significantly from all others and from the reference site, and concentrations at the reference site were significantly lower than in all sub-basins (Table IV). Concentrations in both NAWQA Study Units (MSE and EIB) were significantly greater than in their respective NCBP sub-basin (UMS and LMS; Table IV). Overall, Se concentrations in carp did not differ significantly between NCBP and NAWQA stations, but both averaged much greater than the reference site (Table IV). In bass, geographic trends were similar; however, concentrations in the MSE Study Unit (two stations) were significantly, but not substantially, different from those in LMS bass, but were lower than the NCBP sites as a group (Table IV).

Concentrations of Se in carp increased significantly from 1986 to 1995 at Stations 70 (Ohio R. at Metropolis, IL), 78 (Verdigris R.), 79 (Canadian R.), 90 (Kansas R.), and 112 (Mississippi R. at Dubuque, IA) while decreasing at Stations 26 (Illinois R.), and 75 (Mississippi R. at Cape Girardeau, MO; Table V). Concentrations also decreased in white sucker from Station 74 (Mississippi R. at Little Falls, MN), but there were no significant changes in bass (Table V). As noted previously, the relatively high concentrations of Se in brown trout from Station 84

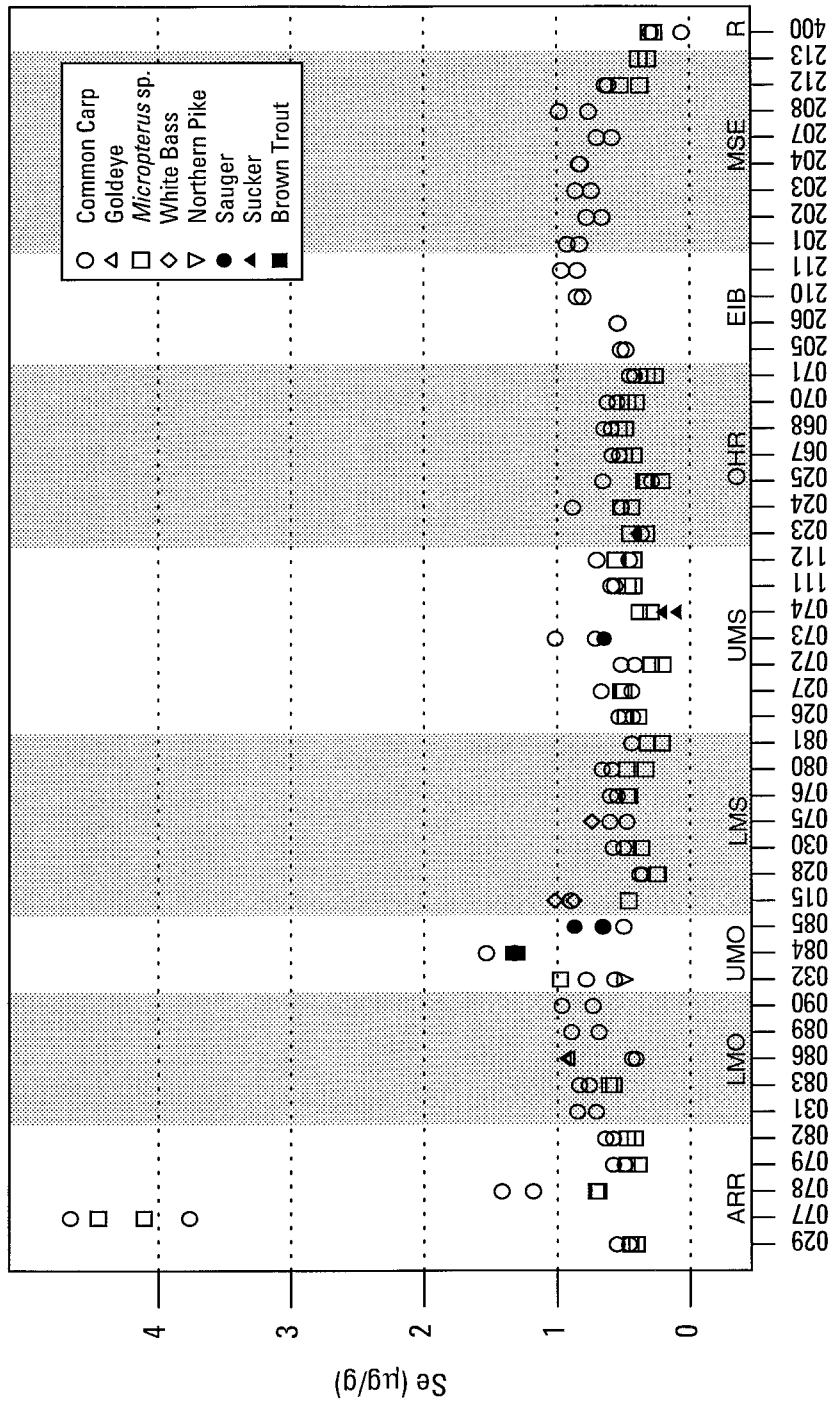

Figure 4. Concentrations of Se ($\mu g\ g^{-1}$, ww) in composite samples of whole fish, by sub-basin, station and taxon. See Table I for station locations.

remained unchanged from 1986 to 1995 (Table V). In contrast, Se concentrations in carp at Station 77 increased by 25% from 1986 to 1995. Although this change was not statistically significant, it should be noted that concentrations at this site have been increasing since the 1970s (May and McKinney, 1981; Lowe *et al.*, 1985; Schmitt and Brumbaugh, 1990; Schmitt *et al.*, 1999b). Nationally, the geometric mean concentration of Se in fish (all NCBP stations) declined slightly from 1978–1981 to 1984 (Schmitt and Brumbaugh, 1990), but increased slightly from 1984 to 1986 (Schmitt *et al.*, 1999).

The bioaccumulation of Se can become problematic for fish and wildlife when arid, seleniferous soils are leached by irrigation, as it has in parts of the western U.S. (Lemly, 1996). Se bioaccumulation to harmful levels has also been noted in cooling reservoirs associated with coal-fired power plants (Baumann and Gillespie, 1986). According to Lemly (1996), the whole-fish threshold for Se toxicity (to the fish) is about 4 μg g^{-1} dry weight (0.8 μg g^{-1} ww), and for the protection of piscivorous wildlife it is about 3 μg g^{-1} dry weight (0.6 μg g^{-1} ww). The carp from Stations 77, 78, and 84 exceeded both values in 1995. So also did the largemouth bass from Station 77 and one sample of carp from each of NCBP Stations 32 (Missouri R. at Garrison Dam, MT), 89 (Platte R.), 90 (Kansas R.), and 85 (Yellowstone R.); and NAWQA Stations 201 (Big Sunflower R.), 211 (Cedar R.), and 208 (Cache R.). Both samples of carp from NCBP Stations 15 (Mississippi R. at Luling, LA) and 86 (James R.) exceeded 0.6 μg g^{-1} (Figure 4).

3.4. Arsenic

Elevated environmental concentrations of As typically originate as byproducts of metallurgical processes, from the combustion of fossil fuels, and from the use of arsenical pesticides and defoliants. In 1995, concentrations of As were > LOD (0.2–0.3 μg g^{-1}) in only 28% of the samples from 48% of the stations sampled (Table III). Greatest concentrations (0.30–0.52 μg g^{-1} in one or more samples) were found at NCBP Stations 78 (Verdigris R.), 79 (Canadian R.), 29 (Arkansas R. at Keystone Reservoir, OK), 15 (Mississippi R. at Luling, LA), 80 (Yazoo R.), 26 (Illinois R.), 76 (Mississippi R. at Memphis), and 75 (Mississippi R. at Cape Girardeau, MO; Table III, Figure 5). Except for one carp sample from Station 76, these greatest values all occurred in largemouth bass (Figure 5). At Station 25 (Cumberland R.), where two species of bass were collected, concentrations were about the same in both: 0.22–0.29 μg g^{-1} in largemouth bass, <0.21–0.29 μg g^{-1} in spotted bass (Figure 5). In addition to Station 76, concentrations were also comparatively high (>0.2 μg g^{-1}) in at least one carp sample from Stations 29 and 77 (Arkansas R. at John Martin Reservoir, CO), 80 (Yazoo R.), 24 (Ohio R. at Marietta, OH), and 71 (Tennessee R.). Arsenic concentrations in carp collected from the RRN in 1994 averaged 1.18 μg g^{-1} dw (about 0.35 μg g^{-1} ww; Goldstein and DeWeese, 1999), which is greater than all but the highest concentrations in

MRB carp (Figure 5). Conversely, As concentrations were < LOD (ca. 0.12 μg g^{-1}) in all samples from all NAWQA sites in the MRB and from the reference site.

Concentrations of As in NCBP fish have historically been greatest at stations outside the MRB (i.e., in the Colorado River basin and the Great Lakes – Schmitt and Brumbaugh, 1990; Schmitt *et al*., 1999b). One possible reason is the tendency of As to accumulate in the planktivorous fishes (corregonine salmonids, clupeids, etc.) collected in these regions, which were not targeted in 1995. The lone exception was Station 69 (Ohio R. at Cincinnati, OH), which was not sampled in 1995. Temporal trends for As were not tested statistically due to the large number of censored values. Nevertheless, concentrations in carp and bass were lower in 1995 than in 1986 at Station 70 (Ohio R. at Metropolis, IL) but increased in other species at Stations 74 (Mississippi R. at Little Falls, MN), 84 (Big Horn R.), and 85 (Yellowstone R.; data not shown).

Because As tends to accumulate in planktivorous species (and also sculpins, *Cottus* spp.) to a greater degree than in other fishes (Hunter *et al*., 1981; Schmitt and Brumbaugh, 1990; Wagemann *et al*., 1978) and can be further accumulated by piscivores (Hunter *et al*., 1981), the occurrence of planktivorous fishes at some sites and the dynamics of the ecosystems in which they occur may confound trends for As. The comparatively high concentrations of As in largemouth bass in the southern parts of the MRB, especially in the storage impoundments and the river systems containing them, may therefore be as much or more a function of the occurrence of planktivorous clupeids (i.e., *Dorosoma* spp.) as a reflection of environmental concentrations. In addition, large amounts of arsenical herbicides and defoliants are used in cotton farming and in other applications in the MRB, and As is released along with Se, Hg, and other elements during the combustion of coal. Large amounts are also released during the smelting of metals. Coal-fired power plants are distributed throughout the MRB, and there are numerous active and inactive smelters (Schmitt *et al*., 2002). Collectively, these facts may explain the occurrence of comparatively high concentrations of As in fish from some parts of the MRB and the RRN.

Arsenic concentrations in freshwater fish (ca. 0.5–1 μg g^{-1}) are low relative to naturally occurring levels in marine fishes and invertebrates, and are typically less than levels associated with adverse impacts in laboratory studies (Jarvinen and Ankley, 1999). Concentrations in the 1995 MRB samples (<0.6 μg g^{-1}) are probably not a hazard to either the fish or to higher trophic level organisms that might consume them (U.S. EPA, 1984; Eisler, 1994). In addition, As is largely accumulated by fish as organoarsenicals, which are less toxic than inorganic forms (Maeda, 1994; Law, 1996).

3.5. Zinc and copper

The ICPES elemental scan yielded data for some analytes of marginal environmental significance. Although all can be toxic to fish under certain conditions,

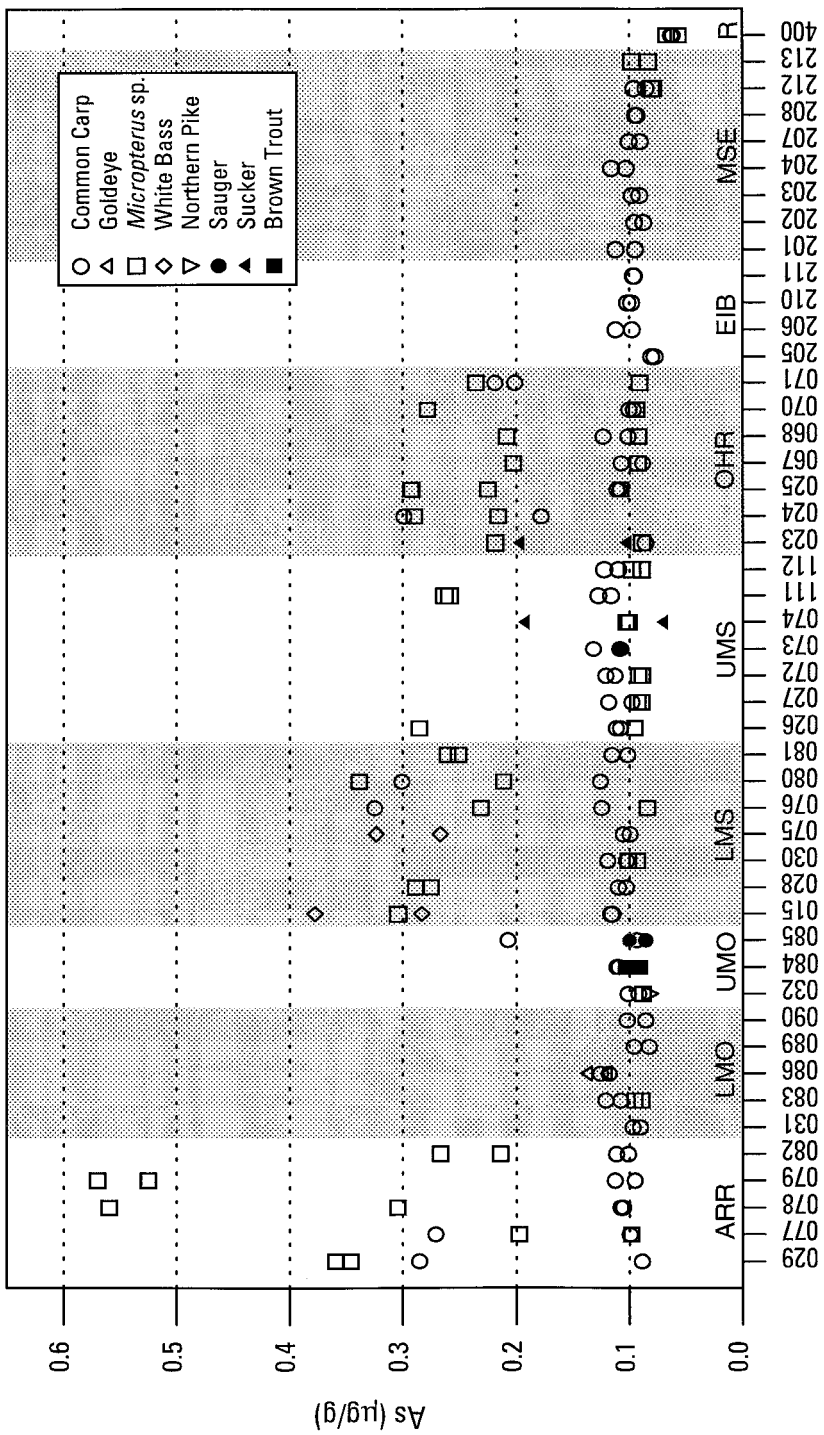

Figure 5. Concentrations of As ($\mu g\, g^{-1}$, ww) in composite samples of whole fish, by sub-basin, station and taxon. See Table I for station locations.

many (including Cu and Zn) are also essential trace elements that do not normally accumulate in environmentally exposed fish to concentrations that represent a threat to higher-level organisms, even in heavily contaminated areas (Schmitt *et al*., 1993; 2002). Many elements accumulate preferentially in specific organs and tissues (e.g., May and McKinney, 1977; Harrison and Klaverkamp, 1990; Farag *et al*., 1995; Goldstein *et al*., 1996; Goldstein and DeWeese, 1999; Taylor *et al*., 2000) such as liver (Zn, Cu, etc.), kidney (Cd), bone (Pb), gill (Cu), or muscle (Hg). The accumulation of these elements also differs greatly among taxa; for example, carp seem to accumulate Zn to a greater extent than other fishes (Lowe *et al*., 1985; Schmitt and Brumbaugh, 1990, Schmitt *et al*., 1999b), and white perch (*Morone americana*) accumulate Cu in their livers in a condition analogous to Wilson's disease in humans (Bunton *et al*., 1987). Data for the elements not reported here can be obtained at <*http://www.cerc.usgs.gov/data/data.htm*>.

3.5.1. *Zinc*

Zinc is an essential element that is released to the environment from mining, smelting, and a variety of other activities and sources (May and McKinney, 1977; Schmitt *et al*., 2002). In 1995, Zn was detected in all samples (Table III). Concentrations in carp ranged from 16.7 μg g^{-1} to 150.0 μg g^{-1}. Greatest concentrations in carp (>90 μg g^{-1}) occurred at NCBP Stations 79 (Canadian R.) and 84 (Big Horn R.); at two OHR stations – 67 (Allegheny R.) and 24 (Ohio R. at Marietta, OH); and at five UMR stations – 26 (Illinois R.), 112 (Mississippi R. at Dubuque, IA), 27 (Mississippi R. at Guttenburg, IA), 73 (Des Moines R.), and 111 (Mississippi R. at Lake City, MN); and at one NAWQA site in the EIB Study Unit – Station 210 (Iowa R.; Figure 6). The lowest was at Station 23 (Kanawha R.). At the reference site, Zn concentrations in carp were also low (37.3–44.3 μg g^{-1}) in both samples (Figure 6). Concentrations in carp collected from the RRN in 1994 by Goldstein and DeWeese (1999) were higher; they averaged 216 μg g^{-1} dw (about 64.8 μg g^{-1} ww), a concentration typical of most MRB stations (Figure 6). In contrast to Pb, concentrations of Zn in carp were greater at many MRB sites than in those collected in 1992 from the Mississippi River near the smelter at Herculanuem, MO by Schmitt *et al*. (2002). In taxa other than carp, Zn concentrations ranged from 13.7 μg g^{-1} in smallmouth bass from Station 74 (Mississippi R. at Little Falls, MN) to 41.6 μg g^{-1} in goldeye from Station 86 (James R.; Table III, Figure 6). Relative to carp, Zn concentrations in bass were uniformly low; although one sample of largemouth bass from Station 79 (Canadian R.) contained 37.3 μg g^{-1}, all others were between 13.0 and 30.0 μg g^{-1} (Figure 6). Concentrations were slightly greater in spotted bass (23.9–25.6 μg g^{-1}) than in largemouth bass (19.9–20.4 μg g^{-1}) from Station 25.

Concentrations of Zn in carp differed significantly among stations and sub-basins, but not among programs (Table IV). Levels were generally greatest in the UMS, UMO, and ARR sub-basins and lowest in the OHR, LMO, and LMS sub-

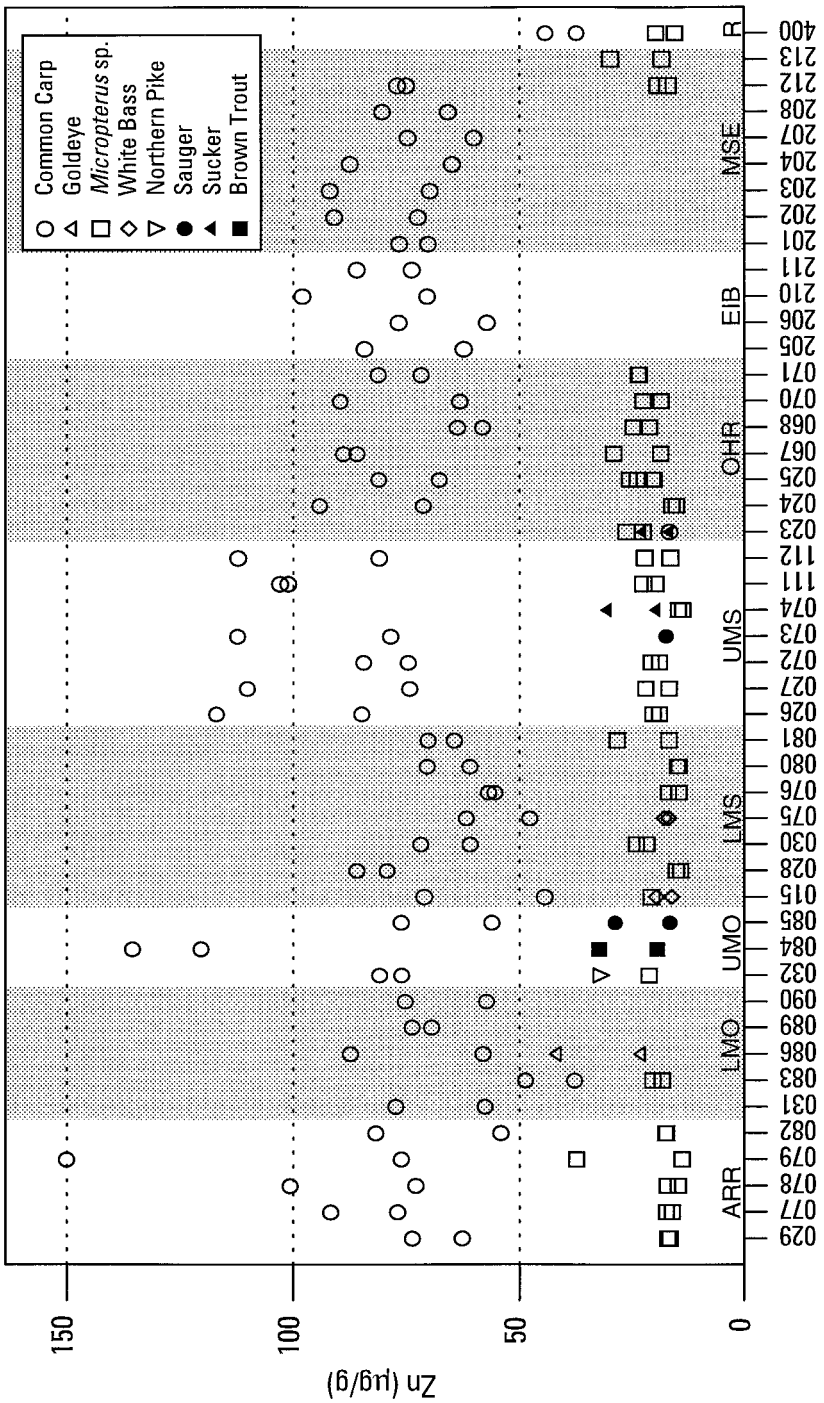

Figure 6. Concentrations of Zn ($\mu g\ g^{-1}$, ww) in composite samples of whole fish, by sub-basin, station and taxon. See Table I for station locations.

basins (Table IV). Concentrations of Zn in bass did not differ significantly among stations, sub-basins, or programs (Table IV).

Concentrations of Zn in carp increased significantly from 1986 to 1995 at Stations 26 (Illinois R.), 73 (Des Moines R.), 79 (Canadian R.), and 112 (Mississippi R. at Dubuque, IA); in bass at Stations 30 (White R.), 72 (Wisconsin R.), 23 (Kanawha R.), 67 (Allegheny R.), and 70 (Ohio R. at Metropolis, IL). Increases were also significant in white sucker at Station 74 (Mississippi R. at Little Falls, MN), sauger at Station 85 (Yellowstone R.), and mooneye at Station 86 (James R.; Table V). Concentrations of Zn in carp from many MRB sites exceeded levels associated with adverse effects in other taxa in laboratory studies (Jarvinen and Ankeley, 1999).

3.5.2. *Copper*

Like Zn, Cu is an essential element that occurs naturally and is also released from a variety of sources. Consequently, Cu was detected by ICPES in all samples (Table III). In contrast to Zn, however, there were fewer clearly evident trends in the 1995 results for Cu. Concentrations ranged from 0.35 to 3.84 μg g^{-1} and were greatest in white bass from NCBP Station 15 (Mississippi R. at Luling, LA; Table III, Figure 7). Concentrations were also higher than most (>1.5 μg g^{-1}) in white bass from Station 75 (Mississippi R. at Cape Girardeau, MO), and in carp from Stations 30 (White R.), 89 (Platte R.), 67 (Allegheny R.) and 24 (Ohio R. at Marietta, OH; Figure 7). Copper concentrations at the reference site were about 1.0 μg g^{-1} in carp; in largemouth bass they were 0.35–0.66 μg g^{-1} (Figure 7). At Station 25, concentrations were slightly greater in spotted bass (0.52–0.67 μg g^{-1}) than in largemouth bass (0.43–0.52 μg g^{-1}). Goldstein and DeWeese (1999) reported that Cu averaged 3.02 μg g^{-1} dw (about 0.9 μg g^{-1} ww) in carp collected from the RRN in 1994, which is slightly lower than most of the 1995 MRB values but about the same as those in carp from the reference site (Figure 7). Although high compared to other species, the 1995 concentrations in white bass from Station 15 were nevertheless about 10-fold lower than those typical of the congeneric white perch (*Morone Americana*) from Atlantic coastal rivers and estuaries (Bunton *et al*., 1987; Schmitt and Brumbaugh, 1990).

Concentrations of Cu in bass differed significantly, but the differences were small; and differences among stations and programs were not statistically significant (Table IV). Concentrations were generally lowest at the reference site and in the ARR, UMS LMS, and OHR sub-basins, and levels in the MSE Study Unit were significantly greater than in the LMS sub-basin (Table IV). In contrast to bass, no geographic differences in carp were statistically significant (Table IV).

Relative to 1986, Cu concentrations increased significantly in carp at Station 79 (Canadian R.), 24 (Ohio R. at Marietta, OH), and 67 (Allegheny R.), and in bass at Station 23 (Kanawha R.). Concentrations decreased in carp at Station 72 (Wisconsin R.), bass at Stations 67 and 70 (Ohio R. at Metropolis, IL), white sucker at Station 74 (Mississippi R. at Little Falls, MN), brown trout at Station 84 (Big Horn

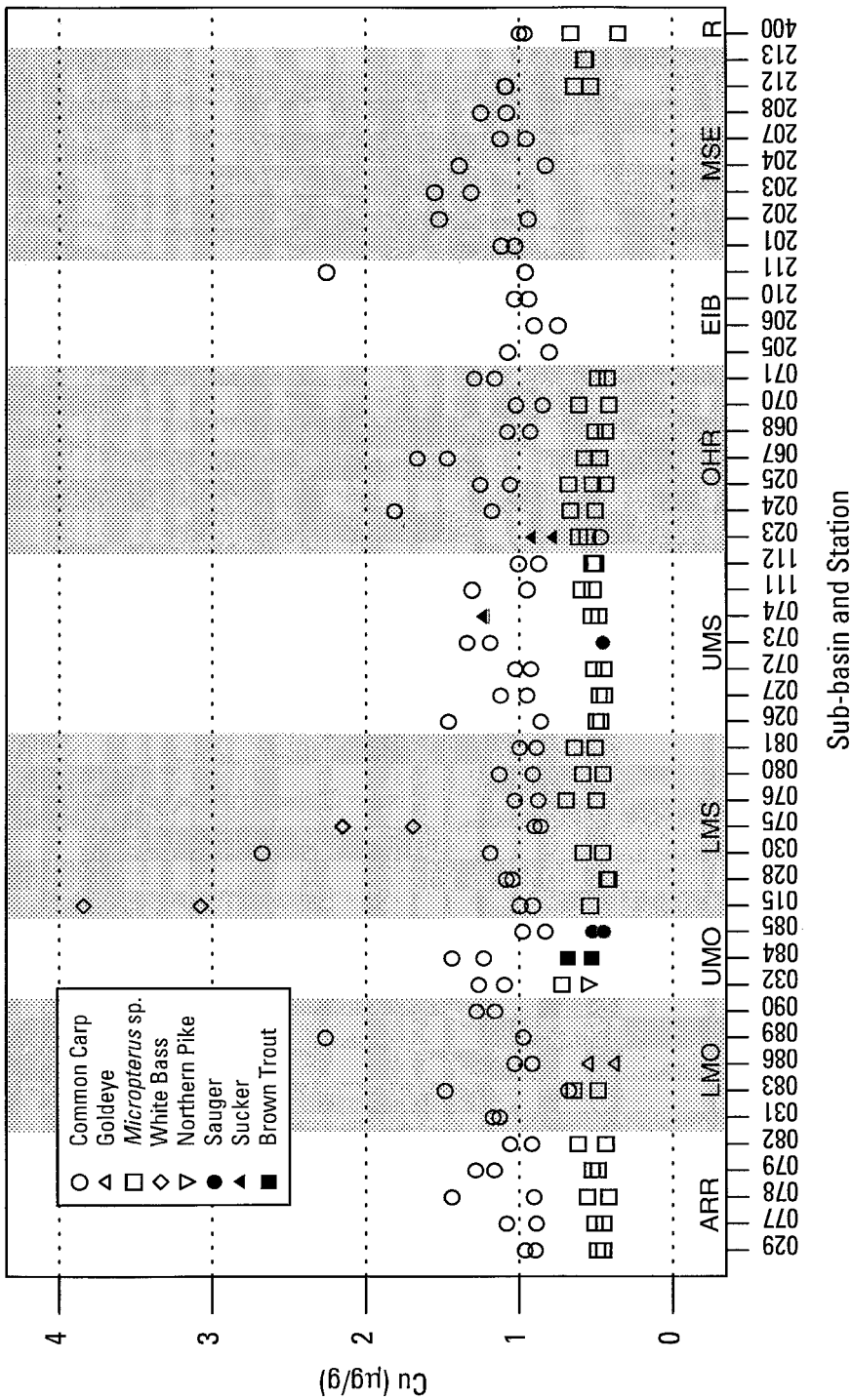

Figure 7. Concentrations of Cu ($\mu g\ g^{-1}$, ww) in composite samples of whole fish, by sub-basin, station and taxon. See Table I for station locations.

R.), and sauger at Station 85 (Yellowstone R.; Table V). On a dry-weight basis, the 1995 Cu concentrations in the two samples of brown trout from Station 84 (1.83–2.52 μg g^{-1}) were within the range of values reported for this species collected from reference sites in Montana, but were 2- to 3-fold lower than concentrations associated with adverse effects on brown trout health and physiology in fish from mining-contaminated sites (Farag *et al.*, 1995).

4. Summary and Conclusions

Several trends were evident from the results of this study. First, concentrations of most of the elements examined were lower in both carp and bass from the West Virginia reference site than from the rivers and larger impoundments in the MRB. Although the fish from the reference site were slightly smaller and younger than those from some sites in the MRB, the concentration differences were greater than would be expected based solely on fish size. Instead, these differences probably reflect a relative lack of pollution sources relative to the MRB rivers, which are all contaminated to some degree by agricultural, municipal, and industrial activities, and ecosystem differences between the sites. In addition, concentrations of all the elements reported here except Pb and Cu were lower in carp from the reference site than in those from the RRN (Brigham *et al.*, 1998; Goldstein and DeWeese, 1999). Although there are many possible explanations for this finding, a potentially important one is the location of the RRN basin (North-Central U.S.) compared to the Potomac River basin (Eastern U.S.) with respect to atmospheric sources of Pb and other elemental contaminants. In contrast, concentrations of As were greater in carp from the RRN than from most sites in the MRB and were much greater than at the reference site, which suggests agricultural, municipal, or natural sources, singly or in combination.

Overall, there were few differences between NCBP sites, which are typically situated on large rivers and their impoundments, and the NAWQA sites, which generally represent lower-order rivers and streams. It should be noted, however, that the degree to which the results (i.e., temporal and geographic differences or not) documented here may have been influenced by fish size and age was not determined. The accumulation of Hg with increasing age and body size in predatory fish has been well documented (Wiener *et al.*, 2002) and may also occur for As and Se; however, such relationships have been explored to a far lesser degree for these and other elemental contaminants than for Hg.

Of the elemental contaminants in fish reported here, only Se occurred at potentially problematic concentrations relative to current values for evaluating risk to fish and wildlife. Concentrations of Se were comparatively high (ca. 5 μg g^{-1}) in all samples from Station 77 (Arkansas R. at John Martin Reservoir, CO), where levels have been high in the past. Although 25% higher than when last sampled in 1986, the increase at Station 77 was not statistically significant ($p > 0.05$).

Nevertheless, Se concentrations at this site have been increasing for two decades. The Upper Arkansas River basin contains seleniferous rocks and soils that have been leached by irrigation. Slightly elevated Se concentrations were also present in fish from several sites in the UMO sub-basin, where there are also seleniferous rocks and soils and irrigated agriculture.

Differences among taxa were highly evident. Concentrations of Cd and Zn tended to be greatest in carp than in all other species analyzed. Nevertheless, Cd concentrations in carp were comparatively high (>0.2 μg g^{-1}) only at one site in each of the ARR, LMO, LMS, and UMS sub-basins, and at two stations in the OHR sub-basin. Zn concentrations were more variable, and few trends were evident. Pb concentrations were also greatest in carp, but were generally low compared to fish from heavily contaminated sites (cf. Schmitt *et al.*, 2002); levels were <0.2 μg g^{-1} at all stations except one each in the MSE Study Unit and the LMO, UMO, and LMS sub-basins; two in the UMS and ARR sub-basins; and five stations in the OHR sub-basin. At one of the latter (Station 67, Allegheny River at Natrona, PA), concentrations of Pb, Cd, and Zn increased from 1986 to 1995. Concentrations of As were greatest in bass from sites in the ARR sub-basin, and may be at least partly related to the structure of the reservoir ecosystems represented by those sites. Cu concentrations were greatest in white bass and carp, but there were no temporal or geographic trends. At the one site at which largemouth bass and spotted bass of similar size were analyzed, differences in the concentrations of the elements reported here were small.

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