CFO-EC-96-03 **TENNESSEE**

Sediment Contaminant Assessment for Shoal Creek, Lawrence County, Tennessee

U.S. Fish and Wildlife Service
Ecological Services
446 Neal Street
Cookeville, Tennessee 38501

December 1996

U.S. FISH and WILDLIFE SERVICE / SOUTHEAST REGION / ATLANTA, GEORGIA

SEDIMENT CONTAMINANT ASSESSMENT FOR SHOAL CREEK, LAWRENCE COUNTY, TENNESSEE

Prepared by

W. Allen Robison, Steven R. Alexander and R. Mark Wilson
U.S. Fish and Wildlife Service
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COMMON AND SCIENTIFIC NAMES

Alabama lamp mussel	Lampsilis virescens
Birdwing pearly mussel	Lemiox rimosus
Boulder darter	Etheostoma wapiti
Cumberland moccasinshell	Medionidus conradicus
Cumberland monkeyface pearly mussel	Quadrula intermedia
Fine-rayed pigtoe mussel	Fusconaia cuneolus
Littlewing pearly mussel	Pegias fabula
Painted creekshell	Villosa taeniata
Pale lilliput pearly mussel	Toxolasma cylindrellus
Shiny pigtoe mussel	Fusconaia cor
Spotfin chub	Cyprinella monacha
Tan riffleshell mussel	Epioblasma florentina walkeri
Wavyrayed lamp mussel	Lampsilis fasciola

ACKNOWLEDGMENTS

Funding for this project was provided by the U.S. Fish and Wildlife Service Environmental Contaminants program (Study ID No. 92-4C04). Analytical support was provided by the Patuxent Analytical Control Facility. Samples were tracked as Catalog No. 4050010. This study was initiated by Mark Wilson prior to his departure for a new position in Albuquerque, New Mexico, in 1992. The authors would like to thank Sandra Silvey for word processing and Dave Pelren for assisting with the habitat evaluation. Lee Barclay, Jerry O'Neal, and Paul Conzelmann provided helpful review comments. Jason Duke prepared the map using a geographic information system (ArcInfo).

EXECUTIVE SUMMARY

Sediment samples were collected from ten locations along Shoal Creek and analyzed for 19 metals and 20 organochlorine compounds. For the organic analyses, hexachlorobenzene was the only chemical detected (0.044 ppm, wet weight). It was found at Shoal Creek Milepoint 32.1 (Site 3).

Barium, beryllium, and manganese concentrations were greatest at Rigsby Hollow (Site 7) located near the Murray-Ohio Superfund Site. Cadmium, lead, molybdenum, selenium, and vanadium were highest at Shoal Creek Milepoint 56 (Site 5), which was located near the Lawrenceburg Water Department intake. Arsenic, boron, iron, magnesium, and strontium concentrations were greatest at Shoal Creek Milepoint 51.7 (Site 10) located about two miles downstream from the former Horseshoe Bend Superfund Site, and also downstream of the new Shoal Creek Dam. Shoal Creek Milepoint 46.1 (Site 4), located at Shoal Creek Road Bridge, had the highest concentrations of aluminum, chromium, copper, mercury, and nickel.

Cadmium (0.20-0.32 ppm) and molybdenum (1.20-1.70 ppm) concentrations were fairly uniform throughout the study area. Mercury (0.012-0.118 ppm) was detected at every site, however, the average concentration upstream of Rigsby Hollow (0.032 ppm) was one-half that for the downstream sites.

Eleven metals (aluminum, arsenic, boron, cadmium, copper, iron, magnesium, manganese, selenium, strontium, and zinc) were lowest at the two sites located furthest downstream (Iron City and Goose Shoals). Maximum concentrations for all 19 metals were found within the 14-mile segment from Shoal Creek Milepoint 56 to Milepoint 42.

Manganese and nickel exceeded Canadian limits of tolerance or severe effect levels at Rigsby Hollow, and also exceeded Canadian lowest effect levels at four and six additional sites, respectively.

If suitable habitat is present, initial mussel/fish relocations should occur downstream of Milepoint 42. In addition, the following items are recommended for consideration in any future investigations of Shoal Creek: (1) determine contaminant residues in nonlisted mussel species which are co-located with listed species; (2) conduct larval and juvenile mussel toxicity tests using sediment and water from Shoal Creek; (3) measure contaminants in water and sediment in conjunction with toxicity tests; (4) utilize cholinesterase inhibition assays on nonlisted mussel species; (5) analyze sediment samples for polycyclic aromatic hydrocarbons (PAHs); (6) analyze sediment samples for acid volatile sulfide and simultaneously extracted metals; and (7) use benthic invertebrate surveys to help assess relocation areas.

CONTENTS

INTRODUCTION

The U.S. Fish and Wildlife Service (Service) Office in Asheville, North Carolina, and the Cooperative Fisheries Research Unit at Tennessee Technological University (Cookeville, Tennessee) are involved with a joint project to determine streams which are suitable for the translocation of endangered (E) and threatened (T) aquatic species. The goal is to enhance population recovery for several species including: the Alabama lamp mussel (E), birdwing pearly mussel (E), Cumberland monkeyface pearly mussel (E), fine-rayed pigtoe mussel (E), littlewing pearly mussel (E), pale lilliput pearly mussel (E), shiny pigtoe mussel (E), tan riffleshell mussel (E), boulder darter (E), and the spotfin chub (T).

One such project involves Shoal Creek which is located primarily in Lawrence County, Tennessee, and Lauderdale County, Alabama. The Cooperative Fisheries Research Unit is conducting an instream flow analysis, fish and mussel surveys, and a preliminary mussel relocation project. The mussel relocation project involves approximately 4000 individuals, representing 22 species, from the Tennessee River. Glochidial experiments have also been performed with the Cumberland moccasinshell, the wavyrayed lamp mussel, and the painted creekshell. Our contaminant investigation was conducted in support of these cooperative research and recovery efforts to provide data on habitat suitability.

STUDY AREA

In Tennessee, the Elk River-Shoal Creek Basin encompasses 2,715 square miles which includes all, or major portions of, Franklin, Giles, Lawrence, Lincoln, and Moore counties (Denton *et al.* 1994). Shoal Creek originates near New Prospect, Lawrence County, Tennessee, approximately 5 miles east of the City of Lawrenceburg. Beeler Fork and Big Dry Branch confluence at this point to form the headwaters. Shoal Creek flows west to northwest through Lawrenceburg, continues southwesterly for 33.5 miles in Lawrence County, and enters Lauderdale County, Alabama. There it flows south to southwest until it confluences with the Tennessee River (Wilson Lake) at approximately Tennessee River Milepoint 264.5. Major drainages within the watershed include Little Shoal Creek, Crowson Creek, Knob Creek, Chisolm Creek, Factory Creek, Holly Creek and Butler Creek (Figure 1).

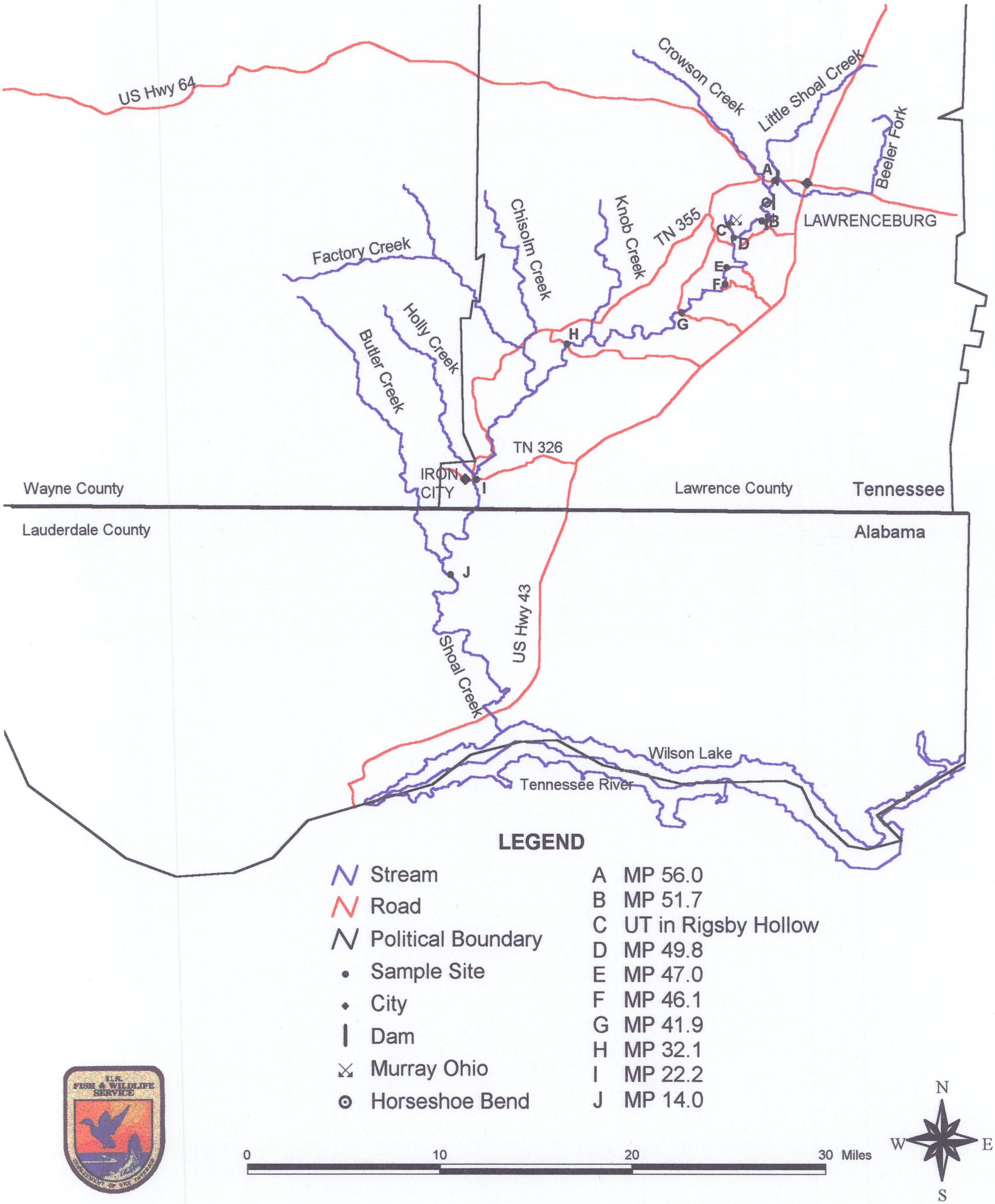
Both Lawrence County and Lauderdale Counties lie within the Western Highland Rim Physiographic Province of Tennessee. This area is characterized predominantly by rolling topography which is crossed by numerous streams. Although there are level areas in the vicinity of Lawrenceburg (Lawrence County) and Hohenwald (Lewis County), there are extensive areas in Giles, Lawrence, and Wayne Counties, where elevations exceed 1000 feet (Miller 1974). This basin lies within an area described by Omernik (1987) as the Interior Plateau and is currently considered by the Service to be part of the Lower Tennessee-Cumberland Ecosystem (FWS 1994, 1995). Primary land uses within the watershed include agriculture, forestry, and some industry near Lawrenceburg, Loretto, and Iron City.

Domestic water withdrawals and recreational, municipal and industrial discharges are located within the watershed. The major water withdrawal is the City of Lawrenceburg Water Department at Shoal Creek Milepoint (MP) 55.9. The following permitted discharges to Shoal Creek are located within Lawrence County, Tennessee:

City of Lawrenceburg Sewage Treatment Plant - MP 55.5
Murray Ohio Co. Outfall 002 - MP 56.2
Murray Ohio Co. Outfall 001 - MP 55.4
UCAR Carbon Co. Outfall - MP 51.9
City of Loretto Sewage Treatment Plant - MP 38.0

The following two permitted discharges to Shoal Creek are located within Lauderdale County, Alabama: Marina Mar, Inc., and Emerald Beach Marina, Inc. These two discharges are located close to the Wilson Lake portion of the Tennessee River and are downstream from the study area.

Figure 1. Shoal Creek Drainage Basin



The Tennessee Department of Environment and Conservation (TDEC 1990) identified a section of Shoal Creek as partially supporting designated uses. This was based on water quality monitoring data collected during 1988-1989 at Shoal Creek MP 32.2. Nitrates were of primary concern because they exceeded the State water quality standard in more than 25% of the samples collected. Previous rapid bioassessment surveys by Holland (1988) indicated that the West Fork of Shoal Creek fully supported designated uses (TDEC 1990).

Denton *et al.* (1994) identified an 0.8 mile segment of Shoal Creek (Waterbody No. TN 06030005082) as partially supporting designated uses. Pathogens, organic enrichment, low dissolved oxygen, ammonia, and metals were noted as causes of impacts. Industrial and municipal point source discharges were considered to be sources of the impacts observed.

One CERCLA (Superfund) site and one former site are located adjacent to Shoal Creek. They are the Murray-Ohio Site at MP 49.8 and the Horseshoe Bend Site at MP 53.7 (Figure 1). Remediation of the Murray Ohio Site is currently in the design phase. The Horseshoe Bend Site was vacated from the National Priorities List as a result of a petition and the threat of a legal challenge by the potentially responsible parties (personal communication, Patricia Fremont, USEPA). Our ten sampling areas (Figure 1, Table 1) were selected primarily to help determine whether pollutants from known sources were impacting Shoal Creek. Our main concerns were with accumulation of contaminants within the sediments and potential adverse effects on mussel and fish species.

Table 1. Sampling Site Locations and Site Numbers

Lawrenceburg Water Department (#5)	Lawrence County	MP 56.0
Downstream of New Shoal Creek Dam (#10)	Lawrence County	MP 51.7
Unnamed Tributary in Rigsby Hollow (#7) (Murray Ohio Superfund Site)	Lawrence County	-----
Confluence of UT and Shoal Creek (#8)	Lawrence County	MP 49.8
Nelson Road (#6)	Lawrence County	MP 47.0
Shoal Creek Road Bridge (#4)	Lawrence County	MP 46.1
Long Branch Road Bridge (#9)	Lawrence County	MP 41.9
Busby Road (#3)	Lawrence County	MP 32.1
Iron City, TN (#2)	Lawrence County	MP 22.2
Goose Shoals Bridge (#1)	Lauderdale County	MP 14.0

METHODS

Duplicate sediment samples were collected during June 1992 by extracting a sediment plug with a 4-foot length of PVC pipe. The pipe was inverted to remove excess water and the sediment sample removed and weighed. The sample was then transferred to a chemically precleaned container and stored on ice for transport to the Cookeville Field Office. All samples were then refrigerated and held until shipment to the analytical laboratory (Hazelton Environmental Services, Inc., of Madison, Wisconsin) in April 1993.

One set of samples was analyzed for 20 organochlorine compounds by gas chromatography. The other sample set was analyzed for 19 metals by inductively coupled plasma spectroscopy, arsenic and selenium by graphite furnace, and mercury by cold vapor atomic absorption. Moisture determinations were made on all 40 samples. Specific extraction, digestion, and analytical methods are summarized in Appendix I.

Descriptive summary statistics, data transformations and statistical analyses were done following techniques described in Snedecor and Cochran (1980) and Steel and Torrie (1960). QuattroPro for Windows was used to calculate summary statistics, perform logarithmic transformations and plot normal and exponentially-fitted data graphs. Analytical results reported as below detection levels were set equal to the detection level for calculation purposes only.

Habitat evaluations based on the Rapid Bioassessment Protocols developed by USEPA (1989) were performed at each site in May 1995. The following parameters were included: instream cover, epifaunal substrate, embeddedness, channel alteration, sediment deposition, frequency of riffles, channel flow, bank vegetative protection, bank stability and riparian vegetative zone width.

Quality Assurance/Quality Control

Analytical quality control procedures utilized by the contract laboratory were verified by the Patuxent National Wildlife Research Center in Laurel, Maryland. None of the 20 organochlorine chemicals analyzed were detected in the procedural blank sample, or during the duplicate analysis of sediments collected at MP 47.0 (Site 6). Recoveries for spiked sample analyses of sediments from Site 6 ranged from 50% for trans-nonachlor to 125.71% for o,p'-DDT. Recovery for hexachlorobenzene was 75.71%. Results for duplicate analysis of sediment moisture content were 30.5% and 26.7%, which yielded a relative percent difference of 13.29. The detection limit was 0.01 μg/g for all organochlorine chemicals except PCBs and toxaphene, which ranged from 0.097 to 0.103 μg/g.

Results indicated very good agreement between the duplicate metal analyses on sediments collected at Site 10 (Appendix II, Table II-A). Relative percent differences ranged from 1.4 for nickel (Ni) to 19.2 for lead (Pb). Recovery results varied from 72.6% for selenium (Se) to 122.7% for Pb (Table II-B). Analysis of a certified reference material resulted in recoveries from 82.4% for Se to 140.2% for iron (Fe) (Table II-C). None of the 19 metals analyzed were detected in the procedural blank sample tested along with the sediments. Detection limits for the 19 metals analyzed ranged from 0.010 ppm (dry weight) for mercury (Hg) to 2.50 ppm for aluminum (Al) and Fe (Table II-D).

RESULTS

Habitat Assessments

Instream cover (i.e., snags, submerged logs, undercut streambanks) exhibited slight variability with a 30-50% mix of stable habitat present. Epifaunal substrate, which was defined as well-developed riffles with a length extending two times the width of the stream and as wide as the stream with an abundance of cobble, was prevalent in moderate gradient areas. Embeddedness was fairly constant and averaged 25-50% coarse material (gravel, cobble and boulders) surrounded by fine sediment.

With the exception of occasional gravel removal near bridge abutments, dredging, channelization, or other channel alterations were essentially absent. Although there was some evidence indicating recent deposition of courser materials near islands and point bars, no significant sedimentation from erosion or poor agricultural practices was observed. The patterns which were observed are subject to periodic change based on the dynamics of the fine and coarse particles in the stream bed, the frequency of high flow events, and the occurrence of natural stream obstructions.

Significant distances between riffle/run complexes were observed. As the stream gradient declined, pool areas were more prevalent. Channel flow was generally considered to be optimal with water reaching both banks and a minimal amount of channel substrate exposed. Natural flow is altered by the presence of a weir at MP 55.9, and by dams located at MP 54.1 and MP 51.6. Minimal areas of bank scour and failure were observed, and the average width of the riparian zones was estimated at 36-54 feet with a predominance of native vegetation.

Chemical Analyses

Nineteen metals and 20 organochlorine compounds (Table 2) were analyzed in sediments collected at nine locations along Shoal Creek. Sediment from the unnamed tributary in Rigsby Hollow, Lawrence County, Tennessee, was also collected because of the industrial effluents received by the stream, and because of the proximity of this stream to the Murray-Ohio Superfund Site. Of the 20 organochlorine compounds analyzed, only hexachlorobenzene (HCB) was detected (0.044 ppm, wet weight). It was found in the sediments from Shoal Creek MP 32.1 (Site #3) near Busby Road in Lawrence County, Tennessee. The 19 other organochlorine analytes were below detection limits in all samples.

Table 2. Contaminants analyzed for the Shoal Creek project.

Organic	Metals
BHC (beta-; delta-; gamma-; isomers)	Aluminum (Al)
Chlordane (alpha-; gamma-; isomers)	Arsenic (As)
DDD (o,p'-; p,p'- isomers)	Boron (B)
DDE (o,p'-; p,p'- isomers)	Barium (Ba)
DDT (o,p'-; p,p'- isomers)	Beryllium (Be)
Dieldrin	Cadmium (Cd)
Endrin	Chromium (Cr)
Hexachlorobenzene (HCB)	Copper (Cu)
Heptachlor epoxide	Iron (Fe)
Nonachlor (cis-; trans-isomers)	Mercury (Hg)
Oxychlordane	Magnesium (Mg)
Polychlorinated biphenyls (PCBs)	Manganese (Mn)
Toxaphene	Molybdenum (Mo)
	Nickel (Ni)
	Lead (Pb)
	Selenium (Se)
	Strontium (Sr)
	Vanadium (V)
	Zinc (Zn)

Metals results are reported and discussed on dry weight basis (Table 3, Figures 2-6). Wet weight results are provided in Appendix III for comparison. The highest concentrations of the following five metals were found at Shoal Creek MP 56.0 (Site 5): cadmium (Cd), Pb, molybdenum (Mo), Se, and vanadium (V). At Shoal Creek MP 51.7, two miles downstream from the former Horseshoe Bend Superfund Site, the greatest concentrations of arsenic (As), boron (B), Fe, magnesium (Mg), and strontium (Sr) were observed. This site was also downstream from the new Shoal Creek Dam. Barium (Ba), beryllium (Be), and manganese (Mn) were highest at Rigsby Hollow (Site 7). Five metals, Al, chromium (Cr), copper (Cu), Hg, and Ni, were highest at the Shoal Creek Road Bridge site (MP 46.1). Thus, the three most upstream sites accounted for about 68% of the highest concentrations, and four sites accounted for 95%. Maximum concentrations for all 19 metals were found within the 14-mile stream segment from MP 56 to MP 42. In contrast, the concentrations for 11 metals (58%) were lowest at the two sites furthest downstream (Iron City and Goose Shoals).

Molybdenum (Mo) concentrations averaged 1.42 ppm and were fairly uniform (1.20-1.70 ppm) throughout the study area (Figure 6), as were concentrations of Cd (0.20-0.32). Concentrations of Be were all below 1.0 ppm, except at Rigsby Hollow (1.27 ppm). Although Hg concentrations varied from 0.012 to 0.118 ppm, the average concentration upstream from Rigsby Hollow was one-half (0.032 ppm) of that for the downstream sites. While Pb was highest at the Lawrenceburg Water Department intake (MP 56.0), it was also above the mean for all Shoal Creek mainstem sites (15.66 ppm) at the Shoal Creek Road Bridge (MP 46.1).

On average, concentrations of Cr and Pb at the Shoal Creek mainstem sites were only slightly higher than the results observed at the Rigsby Hollow tributary site. Conversely, B, Ba, and Mn concentrations at Rigsby Hollow ranged from two to six times higher than the respective averages for the nine mainstem sites. Values for Al, Fe, Mg, Se, V, and Zn were slightly higher at Rigsby Hollow when compared to mainstem site averages. Average concentrations of As, Cu, Ni, and Sr at the mainstem sites were essentially equal to those measured at the Rigsby Hollow site. Although both linear and exponential regression plots for most metals in Shoal Creek sediments indicated a decrease in concentration with distance downstream from Lawrenceburg, only exponential plots are shown in Figures 7-11. Although Ba exhibited a slight increase (Figure 9), Cd, Cr, Hg, and Mo were fairly uniform (Figures 9, 11).

Table 3. Metals Results (ppm, dry weight) for Shoal Creek Sediment Samples.

MP	56.0	51.7	Rigsby Hollow	49.8	47.0	46.1	41.9	32.1	22.2	14.0	Average	Geometric Mean
Al	18435	17011	19261	18778	17109	19306	18855	9387	14917	5929	15525	14616
As	5.81	15.55	5.44	5.25	2.14	4.43	2.89	2.50	2.10	2.24	4.77	3.77
Ba	70.09	26.61	151.72	79.43	95.72	122.78	125.00	69.70	99.59	51.09	82.22	75.23
Be	0.56	0.96	1.27	0.69	0.58	0.71	0.77	0.63	0.87	0.72	0.72	0.71
B	4.71	19.81	10.77	10.37	4.69	5.29	7.75	4.64	3.01	2.45	6.97	5.70
Cd	0.32	0.31	0.31	0.28	0.22	0.21	0.20	0.24	0.20	0.21	0.24	0.24
Cr	47.30	14.70	24.01	35.62	18.73	90.42	31.84	20.70	15.33	28.55	33.69	28.42
Cu	11.43	10.98	9.21	13.76	6.99	20.97	7.58	6.59	6.98	3.20	9.83	8.69
Fe	16504	28190	21768	18033	10531	15278	13282	11937	10055	16393	15578	14857
Pb	44.35	10.55	9.76	12.52	10.44	20.00	11.26	7.04	11.15	13.61	15.66	13.48
Mg	1007	5808	2230	1355	771	1031	1135	679	802	400	1443	1050
Mn	235	394	2493	1057	426	940	486	232	120	514	489	402
Hg	0.052	0.012	0.050	0.063	0.090	0.118	0.046	0.038	0.061	0.030	0.057	0.048
Mo	1.70	1.20	1.28	1.46	1.44	1.38	1.36	1.60	1.34	1.35	1.43	1.42
Ni	17.57	17.01	37.86	56.18	11.73	126.25	27.79	20.86	16.71	16.12	34.47	25.05
Se	1.22	1.03	1.19	0.92	0.90	1.04	1.16	0.58	0.80	0.25	0.88	0.81
Sr	14.24	32.08	13.07	10.37	8.17	11.71	15.08	11.42	10.35	4.90	13.15	11.65
V	68.17	34.75	66.75	62.74	53.83	56.81	58.80	33.44	46.27	35.38	50.02	48.42
Zn	66.61	49.45	58.84	88.08	34.07	82.64	46.93	41.39	35.91	34.02	53.23	49.96
% Moisture	42.5	17.70	24.20	32.90	32.20	28.0	28.4	39.6	27.6	26.8	30.0	-----

Fig. 2. Metals in Shoal Cr. Sediments
(Al, Fe)

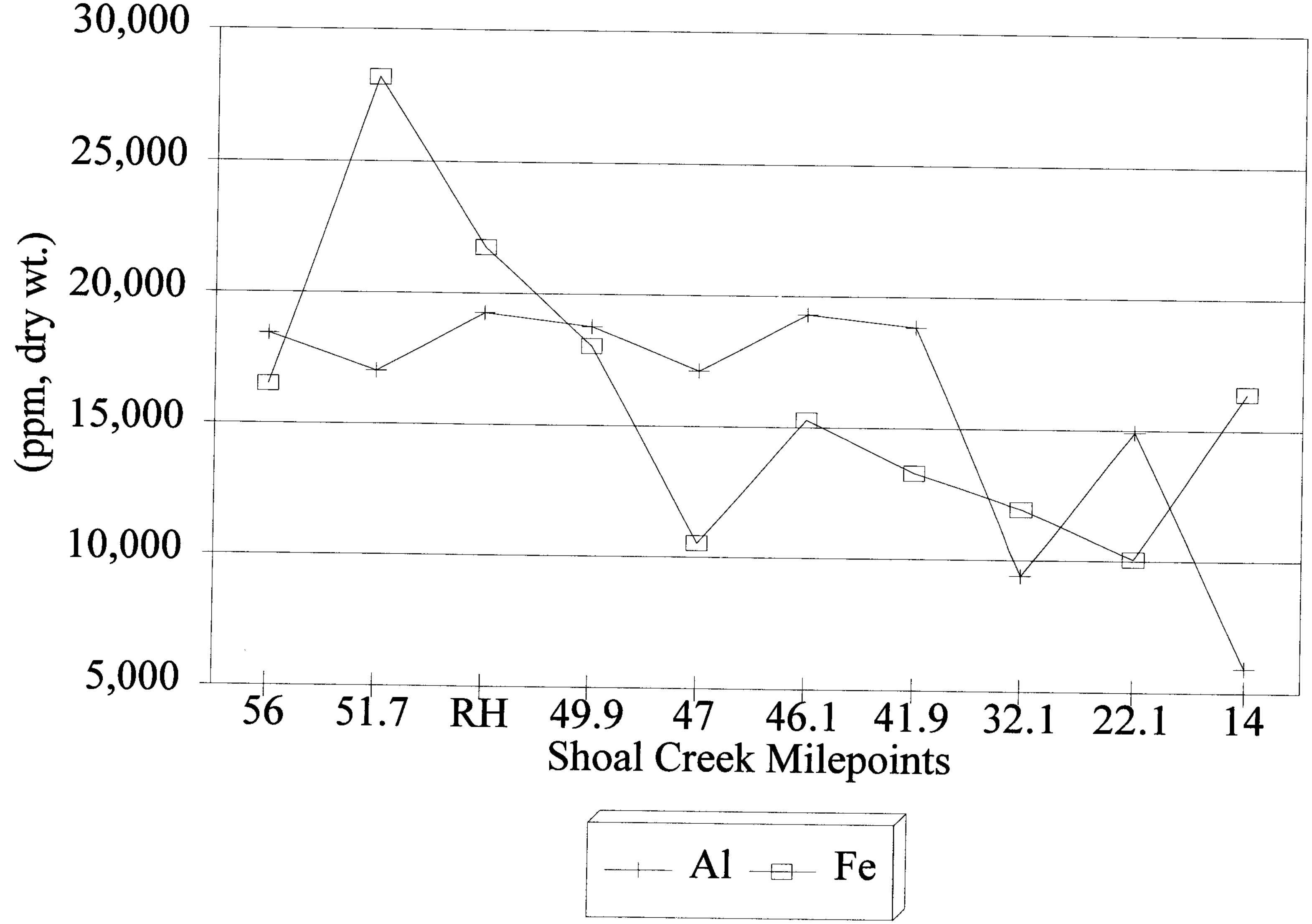


Fig. 3. Metals in Shoal Cr. Sediments
(Mg, Mn)

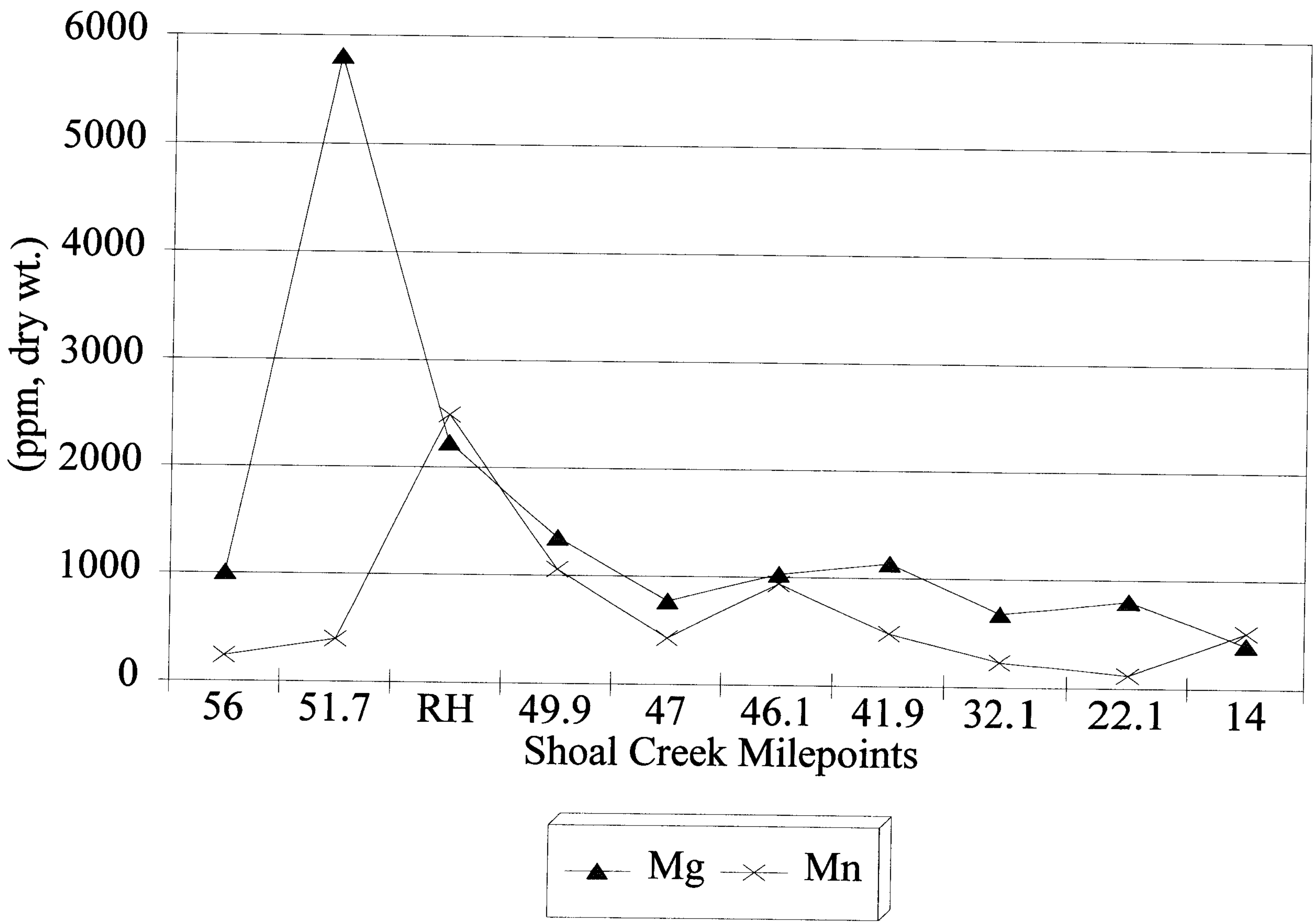


Fig. 4. Metals in Shoal Cr. Sediments
(Ba, Cr, Ni, V, Zn)

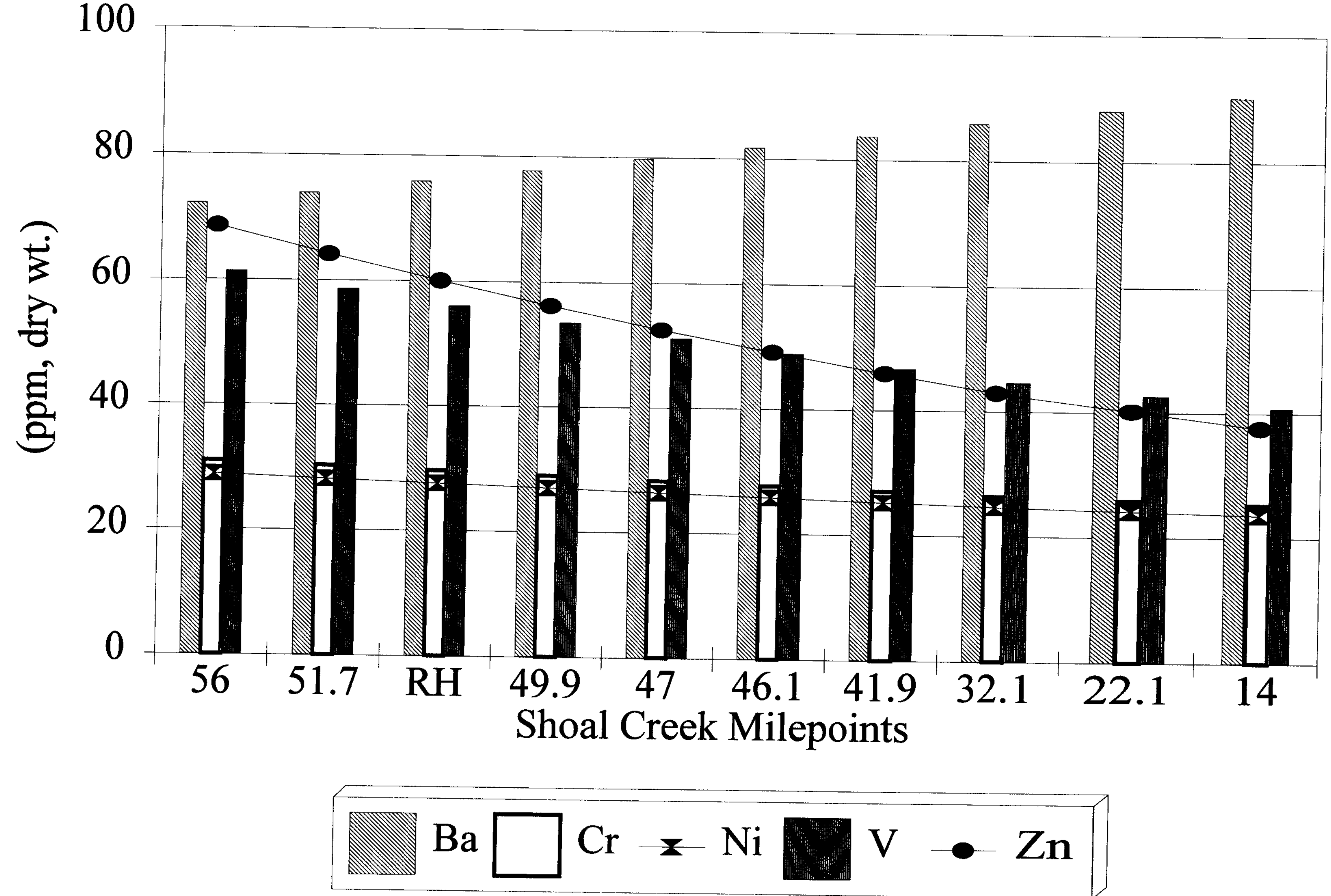


Fig. 5. Metals in Shoal Cr. Sediments

(As, B, Cu, Pb, Sr)

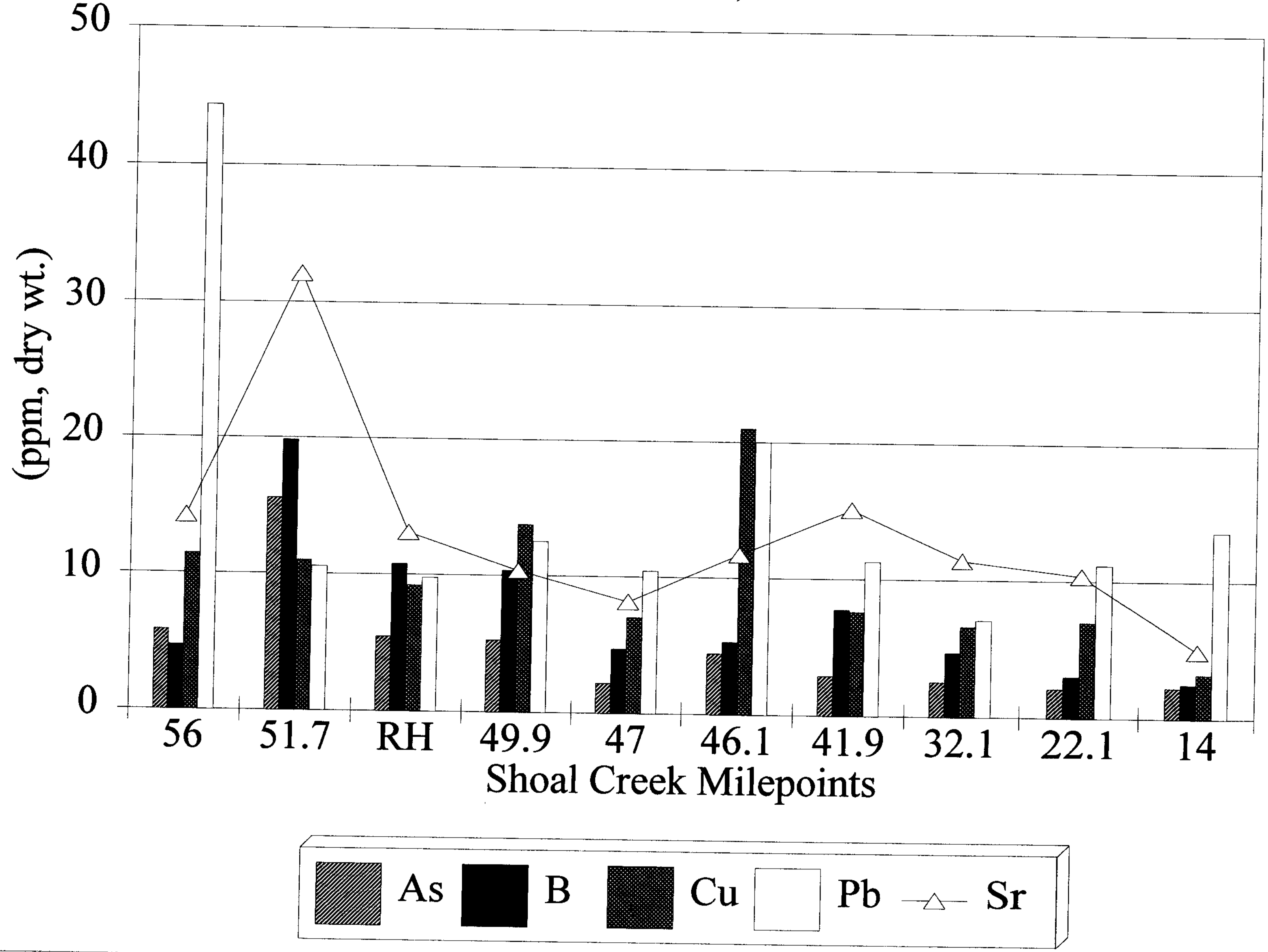


Fig. 6. Metals in Shoal Cr. Sediments
(Be, Cd, Hg, Mo, Se)

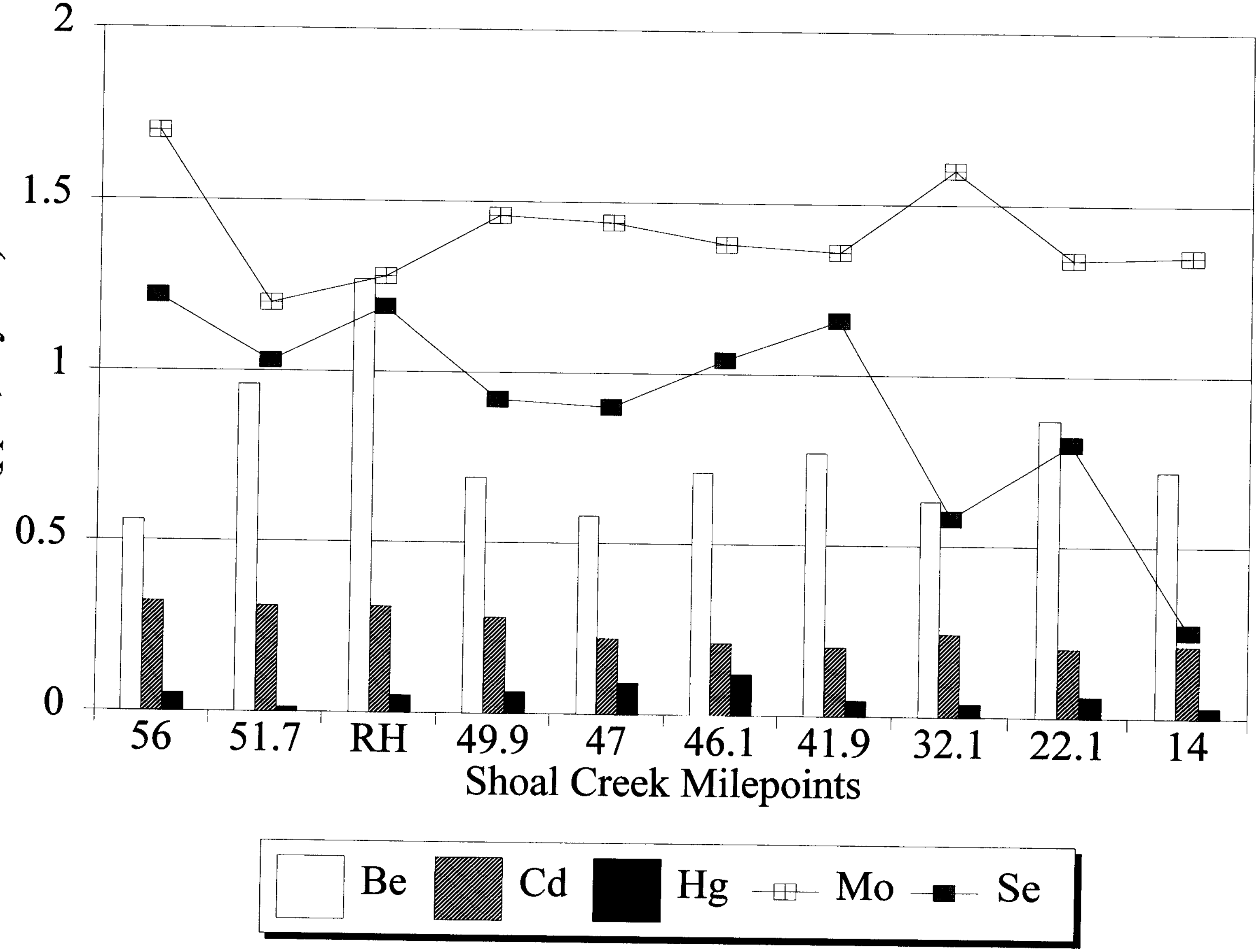


Fig. 7. Metals in Shoal Cr. Sediments
(Exponential Fit: Al, Fe)

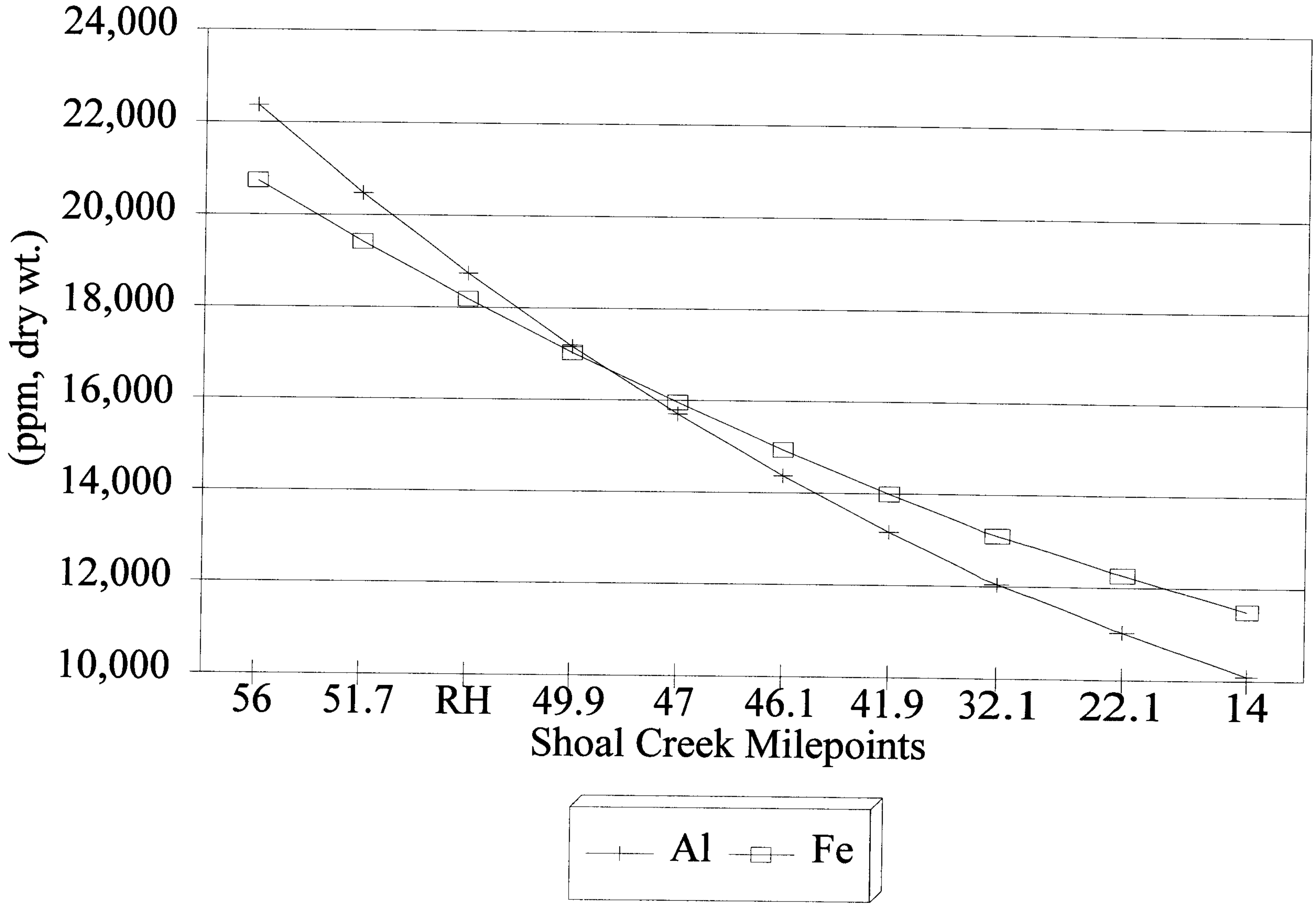


Fig. 8. Metals in Shoal Cr. Sediments
(Exponential Fit: Mg, Mn)

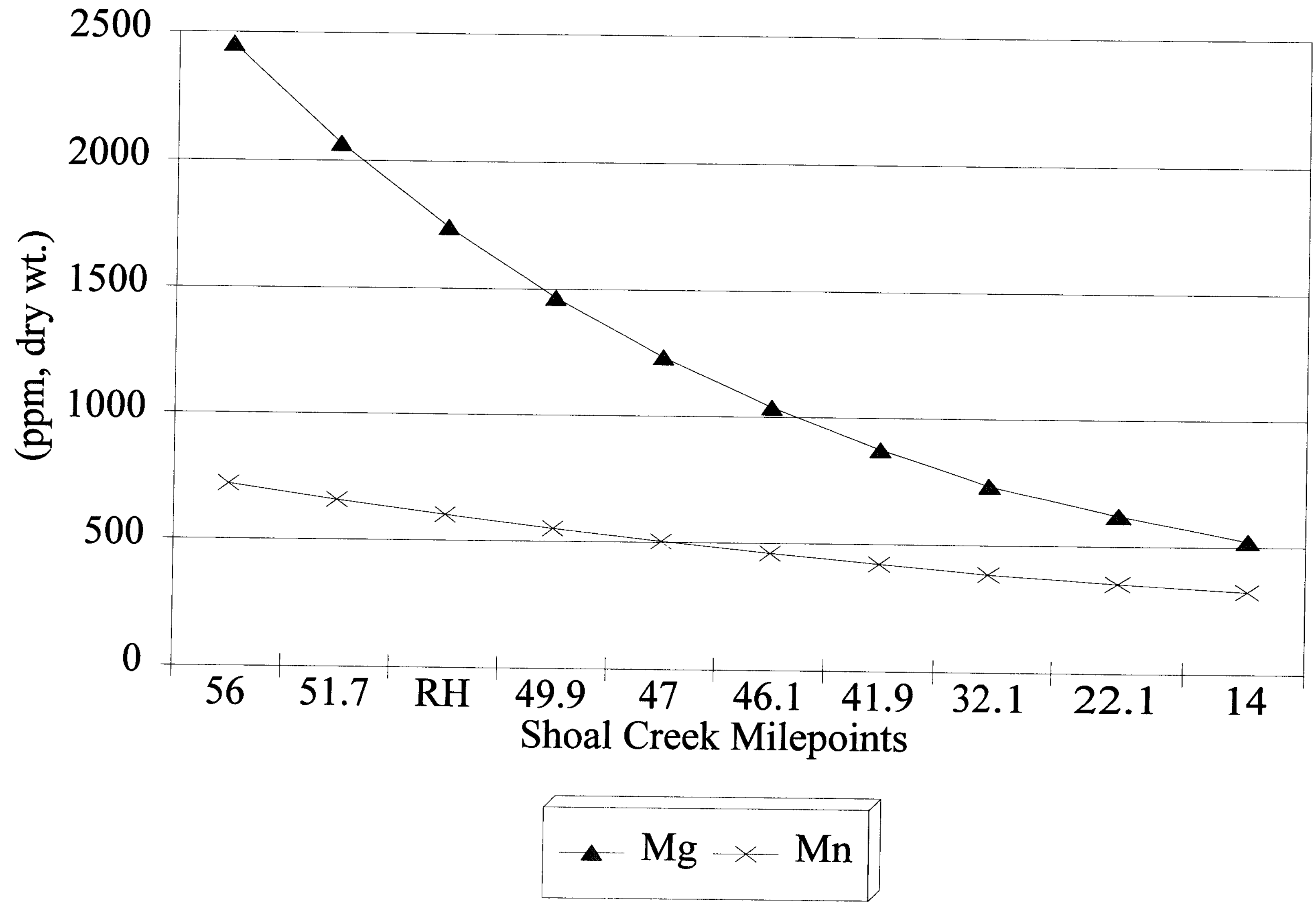


Fig. 9. Metals in Shoal Cr. Sediments
(Exponential Fit: Ba, Cr, Ni, V, Zn)

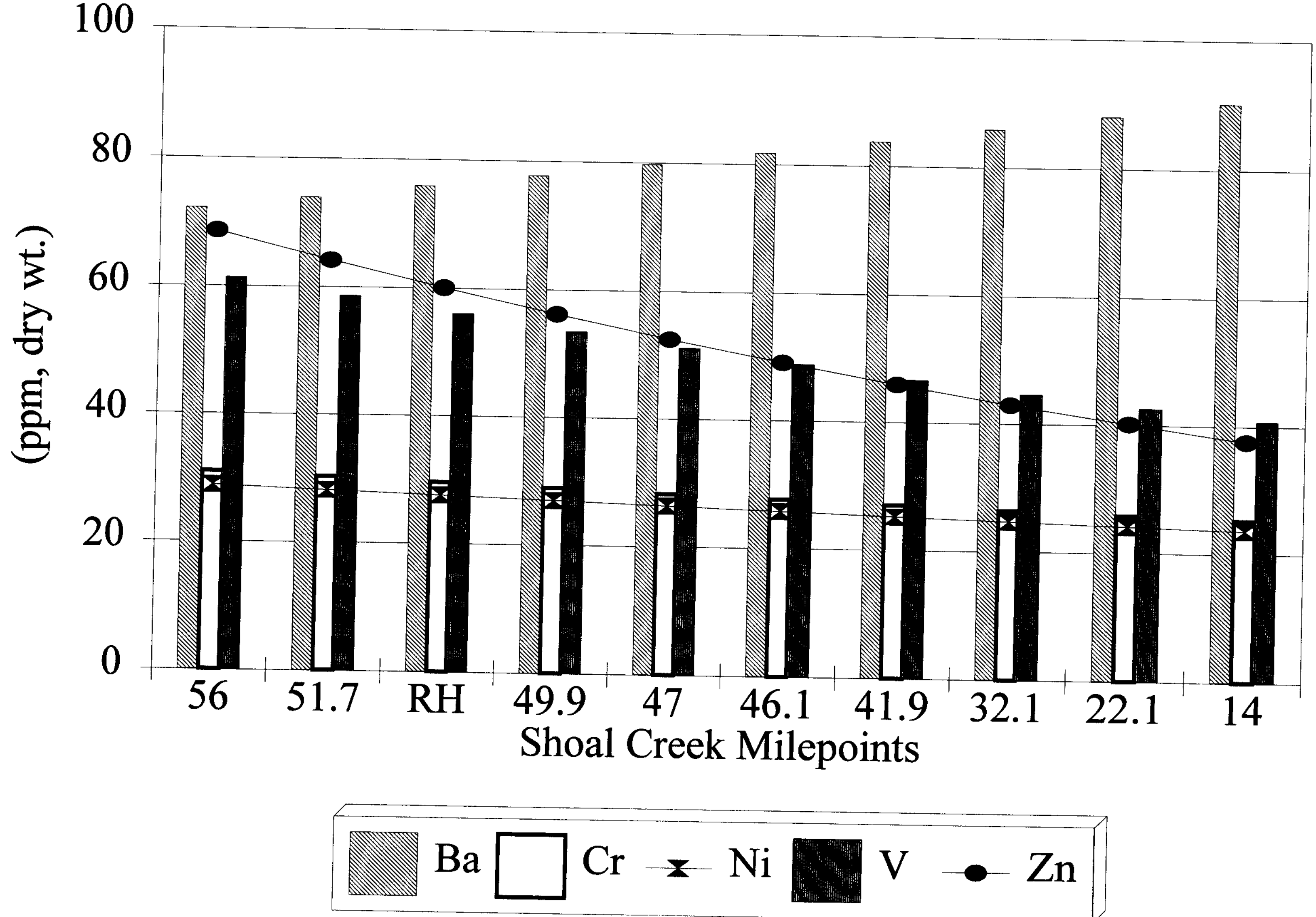


Fig. 10. Metals in Shoal Cr. Sediments
(Exponential Fit: As, B, Cu, Pb, Sr)

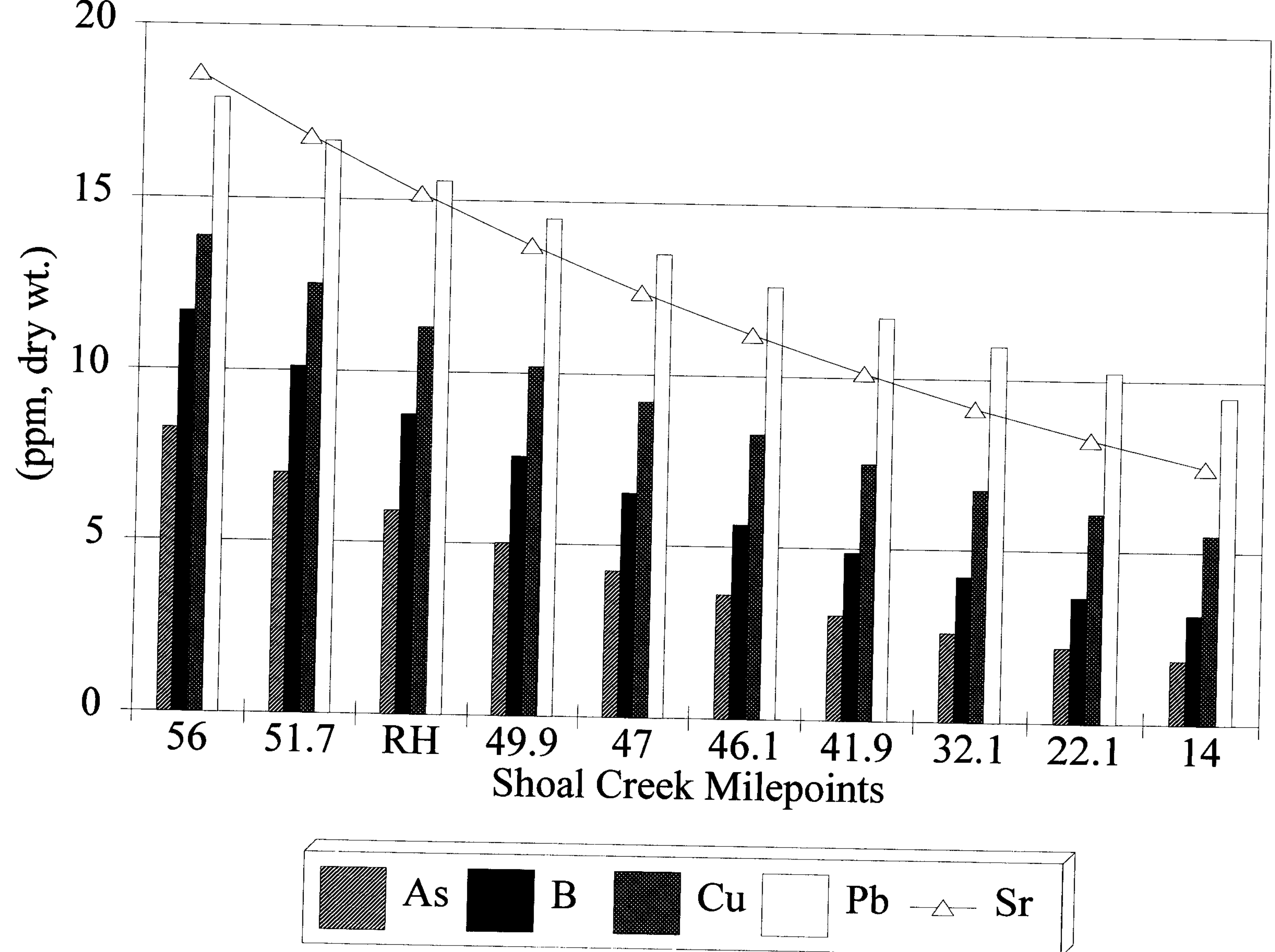
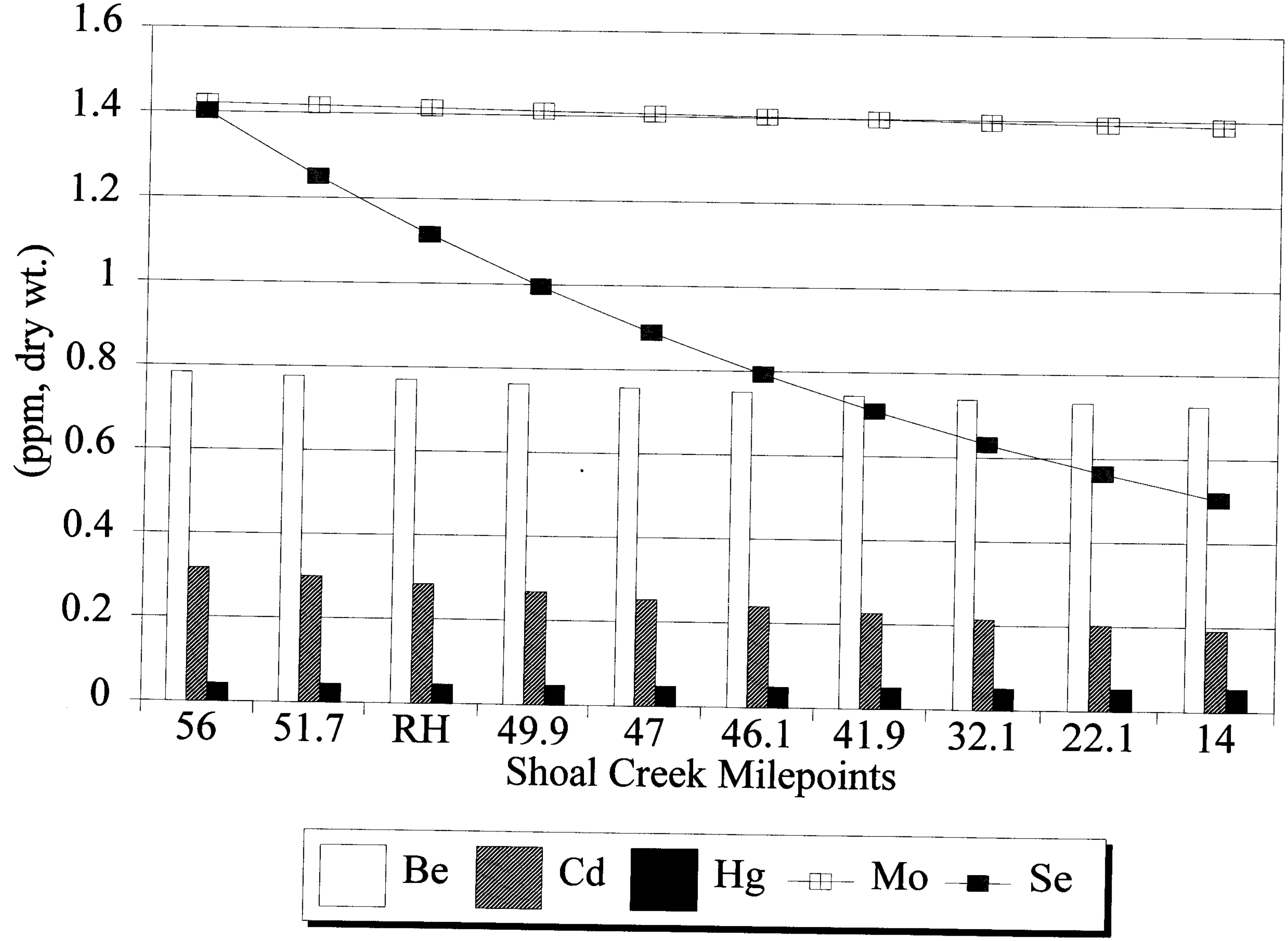


Fig. 11. Metals in Shoal Cr. Sediments

(Exponential Fit: Be, Cd, Hg, Mo, Se)



DISCUSSION

Concentrations for five metals (Be, Mn, Mo, Ni, and Se) in Shoal Creek sediments ranged from two to ten times higher than the respective geometric means reported by Shacklette and Boerngen (1984) for soils in the eastern United States (Table 4). Values for Al, B, Ba, and Sr were notably less than the respective geometric means for the eastern United States (Table 4), while the remaining Shoal Creek mainstem averages and Rigsby Hollow values were comparable to those reported by Shacklette and Boerngen (1984). No individual values for Al, Ba, B, or Sr exceeded the respective geometric mean for the eastern United States (Shacklette and Boerngen, 1984), while all values for Mo and Ni did.

Stewart *et al.* (1992) reported ppm concentrations of Cd (13), Cr (298), Cu (339), Hg (56), Mn (565), Ni (164), and Zn (954) in sediment samples from East Fork Poplar Creek near Oak Ridge, Tennessee. Our results for the same metals in Shoal Creek were typically well below theirs, except for Mn at three sites. Also, our mean results for most metals observed in the Shoal Creek sediments were generally in the same range as, or slightly less than, those reported for sites along the Clinch River (Robison *et al.* 1996).

A comparison with the Illinois stream sediment classification developed by Kelly and Hite (1984) indicated that only Site 2 (MP 22.2) had no elevated metals concentrations (Table 5). Only Cr was elevated at three of the four sites furthest downstream. Of the 17 elevated metals concentrations observed, 14 (82%) occurred in the 28 mile segment from MP 28.0 to MP 56.0. Although no site had more than three elevated metals, the following three sites each had three elevated metals: Site 4 at MP 46.1 (Cr, Hg, Zn); Site 8 at MP 49.8 (Cr, Fe, Zn); and Rigsby Hollow (Cr, Fe, Mn). Lead was elevated at MP 56.0 near the Lawrenceburg Water Department intake.

The Ontario Ministry of the Environment (Persaud *et al.* 1989; Jaagumagi 1992) has developed sediment criteria for ten metals (Table 6). Of our 100 results available for comparison with these criteria, Mn at Rigsby Hollow and Ni at Site 4 (MP 46.1) exceeded the respective limit of tolerance or severe effect level. At four and six additional sites, Mn and Ni, respectively, exceeded the Canadian lowest effect levels, and the overall averages for these two metals in Shoal Creek also exceeded the lowest effect levels. Although Cr exceeded its lowest levels at five sites, Cd was below its respective no effect level at all sites. Except for Site 4, Hg was below its no effect level at all sites.

Becker *et al.* (1995) observed reduced amphipod and chironomid survival at three and five sites, respectively, using 10-d sediment toxicity tests. At these sites, their sediments contained ppm concentrations of Cd (0.9-3), Cr (19-2,000), Cu (49-170), Pb (70-240), Hg (3.2-69), Ni (7-650), and Zn (77-220). In our Shoal Creek samples, Cr, Cu, Pb, Ni, and Zn fell within, or exceeded,

Table 4. Comparison of Rigsby Hollow metals results and geometric means for metals (ppm, dry weight) in Shoal Creek mainstem sediments with those reported by Shacklette and Boerngen (1984).

Metals	Eastern United States	Rigsby Hollow	Shoal Creek Mainstem
Al (%)	3.30	1.930	1.460
As	4.80	5.44	3.77
B	31	10.77	5.70
Ba	290.00	151.72	75.23
Be	0.55	1.27	0.71
Cr	33.00	24.01	28.42
Cu	13.00	9.21	8.69
Fe (%)	1.40	2.18	1.49
Hg	0.081	0.050	0.048
Mg (%)	0.21	0.22	0.10
Mn	260	2493	402
Mo	0.32	1.28	1.42
Ni	11.00	37.86	25.05
Pb	14.00	9.76	13.48
Se	0.30	1.19	0.81
Sr	53.00	13.07	11.65
V	43.00	66.75	48.42
Zn	40.00	58.84	49.96

*Values for Al, Fe and Mg are expressed as percent.

Table 5. Comparison of metals detected in Shoal Creek sediment samples (ppm, dry weight) with the Illinois stream sediment classification* developed by Kelly and Hite (1984).

	Sites									
Metals	MP56.0	MP51.7	RH**	MP49.8	MP47.0	MP46.1	MP41.9	MP32.1	MP22.2	MP14
As	NE	E	NE	NE	NE	NE	NE	NE	NE	NE
Cd	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE
Cr	HE	NE	E	E	SE	Ex	E	SE	NE	E
Cu	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE
Fe	NE	E	SE	SE	NE	NE	NE	NE	NE	NE
Hg	NE	NE	NE	NE	NE	E	NE	NE	NE	NE
Mn	NE	NE	E	NE	NE	NE	NE	NE	NE	NE
Pb	E	NE	NE	NE	NE	NE	NE	NE	NE	NE
Zn	NE	NE	NE	SE	NE	SE	NE	NE	NE	NE
Site No.	5	10	7	8	6	4	9	3	2	1

*NE-non-elevated; SE-slightly elevated; E-elevated; HE-highly elevated; Ex-extremely elevated

**RH-Rigsby Hollow

Table 6. Sediment quality criteria (ppm, dry weight) developed by the Ontario Ministry of the Environment.

Metals	No Effect Level*	Lowest Effect Level 1989*	Lowest Effect Level 1992**	Limit of Tolerance*	Severe Effect Level**
As	4.0	5.5	6.0	33.0	33.0
Cd	0.6	1.0	0.6	10.0	10.0
Cr	22.0	31.0	26.0	111.0	110.0
Cu	15.0	25.0	16.0	114.0	110.0
Fe (%)	2.0	3.0	2.0	4.0	4.0
Pb	23.0	31.0	31.0	250.0	250.0
Mn	400.0	457.0	460.0	1,110.0	1,100.0
Hg	0.1	0.12	0.20	2.0	2.0
Ni	15.0	31.0	16.0	90.0	75.0
Zn	65.0	110.0	120.0	800.0	820.0

* Persaud, et al. (1989).
** Jaagumaji (1992).

the values reported by Becker *et al.* (1995) at several sites, while Cd and Hg were below their ranges at all sites. Although we only detected one organochlorine compound at one site, polycyclic aromatic hydrocarbons (PAHs) were not analyzed. In the samples tested by Becker *et al.* (1995), PCBs ranged from 0.10-0.36 ppm in three samples, and PAHs varied from 28-330 ppm in four samples, where survival was reduced.

Our results for Cd, Fe, and Zn were less than those reported by Birge *et al.* (1987) and Francis *et al.* (1984) for control sediments used in toxicity tests. The average Hg value in our Shoal Creek sediment samples (0.057 ppm) was similar to that in the control sediments (0.052 ppm) used by Birge *et al.* (1987) and Francis *et al.* (1984). Their investigations noted that rainbow trout (Salmo gairdneri) early life stage survival was reduced to 70% and 45% when exposed to sediment containing 0.180 ppm and 1.050 ppm of Hg, respectively. They also reported significant reductions in rainbow trout early life stage survival using sediment with 2.15 ppm Cd, and also using sediment containing Zn at 121.4 ppm. All of the Cd, Hg, and Zn values which we observed in our Shoal Creek sediment samples were below those associated with toxicity by Birge *et al.* (1987) and Francis *et al.* (1984).

SUMMARY

Our study was limited to the collection and analysis of sediment samples. The current lack of national sediment quality criteria in the United States prompted us to use sediment quality guidelines developed in Canada. Based on these, our study did not indicate overall impacts from most individual metals at most sites. Beryllium, Mn, Mo, Ni, and Se may play important roles in impacts to mussel populations in Shoal Creek. On average, these metals ranged from two to ten times higher than mean values for soils in the Eastern United States. While Mn and Ni exceeded Canadian limit of tolerance or severe effect levels at Rigsby Hollow, they also exceeded the Canadian lowest effect levels at four and six additional sites, respectively.

It should be noted that the Canadian sediment quality guidelines were not developed specifically for freshwater mussels. While these guidelines were developed for several individual metals, they do not address cumulative impacts from exposure to multiple metals. Although they are useful, we do not necessarily consider them to be strictly protective of mussel species, particularly species listed as threatened or endangered.

RECOMMENDATIONS

We recommend that the following activities be included in any additional investigations on Shoal Creek:

1) If suitable habitat is present, conduct initial mussel/fish relocation efforts downstream of MP 42;

2) determine contaminant residues in nonlisted mussel species which are co-located with listed mussel species;

3) conduct larval and juvenile mussel toxicity tests using sediment and water from Shoal Creek;

4) measure contaminants in water and sediment in conjunction with the toxicity tests;

5) conduct cholinesterase inhibition assays on non-listed mussel species;

6) utilize benthic invertebrate surveys to help assess relocation areas;

7) analyze sediment samples for polycyclic aromatic hydrocarbons; and

8) analyze sediment samples for acid volatile sulfide and simultaneously extracted metals.

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APPENDIX I

ANALYTICAL METHODS

HAZELTON ENVIRONMENTAL SERVICES, INC.
METHOD SUMMARIES

DECEMBER 1996

A. MOISTURE DETERMINATION

METHOD CODE 019

SCOPE:

This method is applicable to plant tissue, animal tissue, soil, and sediment.

PRINCIPLE:

A representative portion of the homogenized sample is weighed into a tared aluminum dish and is dried in an oven to constant weight (approximately 12-18 hours) at 100°C. The moisture content is the weight loss after heating.

SENSITIVITY:

This method is capable of detecting 0.1% moisture.

REFERENCES:

- Association of Official Analytical Chemicals (AOAC). 1990. Official Methods of Analysis, 15th ed. Methods 926.08 and 925.09. AOAC, Arlington, VA. Modified by lab.
- USEPA Contract Laboratory Program, Statement of Work for Inorganics Analysis. 1990. Exhibit D, Document No. ILM01.0.

B. ELEMENTAL ANALYSIS BY INDUCTIVELY COUPLED PLASMA SPECTROSCOPY

METHOD CODE 001

SCOPE:

This method is applicable to plant and animal tissue, soil/sediment, and water.

INSTRUMENTATION:

Thermo Jarrell Ash ICAP 61E Argon Plasma Emission Spectrometer

SAMPLE PREPARATION:

- Plant and Animal Tissue

  Digest 5.00 g of homogenized tissue in Telfon^R vessel with 5 ml nitric acid in microwave digester. Transfer into 50 ml volumetric flask and dilute to volume with .005% Triton X-100^R solution. Filter.

- Soil/Sediment

  Digest 2.00 g of soil in covered Teflon beaker on hot plate using 10 ml nitric acid. Add 30% hydrogen peroxide in 1 ml aliquots until effervescence no longer occurs. Add 1.25 ml hydrochloric acid, heat 10 minutes, and transfer to a 50 ml volumetric flask. Dilute to volume with DDI water. Filter.

- Water

  Digest 125.0 ml sample in Teflon beaker on hot plate with 0.5 ml nitric acid and 2.5 ml hydrochloric acid. Reduce volume to 15 to 20 ml. Transfer into a 25.0 ml volumetric flask. Dilute to volume with DDI water. Filter.

PRINCIPLE:

- Each analyte concentration in the sample solution is determined by comparing its emission intensity with the emission intensities of a known series of analyte standards. Analytical data is corrected for background and interfering element effects by the spectrometer program.

The detection limit of each analyte is listed in the data report with each respective unknown value. This detection limit is a function of the instrument detection limit (IDL), and the sample mass and volume to which it is diluted. With each batch of 20 samples of the same matrix type, at least one duplicate, one sample spike, one analytical blank, and one appropriate reference material are assayed.

REFERENCES:

- Dahlquist, R.L. and J.W. Knoll. 1978. Inductively Coupled Plasma - Atomic Emission Spectrometry: Analysis of Biological Materials and Soils for Major, Trace, and Ultra-Trace Element. Applied Spectroscopy 32(1):1-29.
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- Thermo Jarrell Ash ICAP 61E Instrument Manual.
- USEPA. 1987. Test Methods for Evaluating Solid Waste. SW-846, 3rd ed. Methods 3030, 3040, 3050, and 6010. USEPA, Washington, D.C.

C. MERCURY BY COLD VAPOR ATOMIC ABSORPTION

METHOD CODE 002

SCOPE:

This method is applicable to animal tissues, plants, and soils.

INSTRUMENTATION:

Leeman Labs PS-200 Automated Mercury Analyzer

PRINCIPLE:

Sample weight: 2.00 g.
Sample volume: 100 ml.

Homogenized samples are digested with a mixture of sulfuric and nitric acid. The mercury in the digestate is reduced with stannous chloride for determination. The amount of mercury is determined at a wavelength of 253.7 nm by comparing the signal of the unknown sample to a standard curve prepared by linear regression.

REFERENCES:

- o Digestion: Analyst 86:608 (1961) with modifications.
- o USEPA. 1986. Test Methods for Evaluating Solid Waste. SW-846, 2nd ed. Method 7471. USEPA, Washington, D.C.

D. ARSENIC BY GRAPHITE FURNACE

METHOD CODE 004

SCOPE:

This method is applicable to animal tissues, plants, sediments, sludges, and soils.

INSTRUMENTATION:

Perkin Elmer Zeeman 5100 PC
Atomic Absorption Spectrophotometer

SAMPLE PREPARATION:

Animal or Plant Tissue

Digest 5.0 g homogenized sample with nitric acid in a microwave digester. Transfer to 50 ml, then filter.

Sediment or Soil

Digest 1.0 g homogenized sample with nitric acid and 30% hydrogen peroxide using covered glass beakers on hot plates. Transfer to 100 ml, then filter.

PRINCIPLE:

The amount of arsenic is determined at a wavelength of 193.7 nm by comparing the signal of the unknown sample, measured by the graphite furnace atomic absorption spectrophotometer, with the signal of the standard solutions. Nickel is used as a matrix modifier.

REFERENCES:

o USEPA. 1986. Test Methods for Evaluating Solid Waste. SW-846, 2nd ed. Methods 3030, 3040, 3050, and 7060. USEPA, Washington, D.C.

E. SELENIUM BY GRAPHITE FURNACE

METHOD CODE 006

SCOPE:

This method is applicable to animal tissue, plants, sediments, sludges, and soils.

INSTRUMENTATION:

Perkin Elmer Zeeman 5100 PC
Atomic Absorption Spectrophotometer

SAMPLE PREPARATION:

Animal or Plant Tissue

Digest 5.0 g homogenized sample with nitric acid in a microwave digester. Transfer to 50 ml, then filter.

Sediment or Soil

Digest 1.0 g homogenized sample with nitric acid and 30% hydrogen peroxide using covered glass beakers on hot plates. Transfer to 100 ml, then filter.

PRINCIPLE:

The amount of arsenic is determined at a wavelength of 196.0 nm by comparing the signal of the unknown sample, measured by the graphite furnace atomic absorption spectrophotometer, with the signal of the standard solutions. Nickel is used as a matrix modifier.

REFERENCES:

- USEPA. 1986. Test Methods for Evaluating Solid Waste. SW-846, 2nd ed. Methods 3030, 3040, 3050, and 7740. USEPA, Washington, D.C.

APPENDIX II

QA/QC RESULTS FOR METALS ANALYSES OF SHOAL CREEK SEDIMENT SAMPLES

DECEMBER 1996

Table II-A. Duplicate Analyses of Shoal Creek Sediments Collected at MP 51.7 (Site 10).

Analyte	Initial Result*	Duplicate Result	Average	Relative Percent Difference
% Moisture	17.7	18.3	18.0	3.3
Al (%)	1.40	1.36	1.38	2.9
As	12.8	12.6	12.7	1.6
Ba	21.9	21.4	21.6	2.3
Be	0.79	0.75	0.77	5.0
B	16.3	15.7	16.0	3.7
Cd	0.26	0.29	0.28	11.6
Cr	12.1	11.5	11.8	5.1
Cu	9.04	8.90	8.97	1.6
Fe (%)	2.32	2.21	2.27	4.9
Pb	8.68	7.16	7.92	19.2
Mg (%)	0.48	0.46	0.47	4.1
Mn	324	308	316	5.1
Hg	<0.010	<0.010	---	---
Mo	<0.098	<0.097	---	---
Ni	14.0	14.2	14.1	1.4
Se	0.85	0.75	0.80	12.5
Sr	26.4	25.7	26.0	2.7
V	28.6	27.2	27.9	5.0
Zn	40.7	38.8	39.7	4.8

*Results are ppm (dry weight) unless indicated otherwise.

Table II-B. Recovery Results for Spiked Shoal Creek Sediment Samples.

Analyte	Concentration	Amount Added	Amount Analyzed	Percent Recovery
Al	14000	2480	17100	—*
As	12.8	4.9	16.7	—*
Ba	21.9	124	128	85.6
Be	0.79	2.48	2.85	83.0
B	16.3	124	120	83.6
Cd	0.26	2.48	2.17	77.1
Cr	12.1	12.4	21.5	75.8
Cu	9.04	12.4	20.3	90.8
Fe	23200	2480	24800	—*
Pb	8.68	12.4	23.9	122.7
Mg	4780	2480	6940	—*
Mn	324	124	438	—*
Hg	<0.010	0.049	0.049	100
Mb	<0.98	124	98.4	79.4
Ni	14.0	12.4	24.0	—*
Se	0.85	9.79	7.96	72.6
Sr	26.4	12.4	38.8	—*
V	28.6	12.4	39.6	—*
Zn	40.7	12.4	50.9	—*

*Percent recovery not calculated because the spike/background ration was less than 1.

Table II-C. Results (ppm, dry weight) for Certified Reference Material* Analyzed with Shoal Creek Sediment Samples.

Analyte	Certified Value	Analytical Result	Percent Recovery
Al	4010	5340	133.2
As	144	136	94.4
Ba	206	206	100
Be	85.7	88.7	103.5
B	NCV**	<8.0	NA***
Cd	129	137	106.2
Cr	100	103	103
Cu	101	100	99
Fe	7990	11200	140.2
Pb	118	124	105.1
Mg	1980	1890	95.5
Mn	260	251	96.5
Hg	4.88	4.84	99.2
Mo	89.6	98.4	109.8
Ni	136	147	108.1
Se	165	136	82.4
Sr	NCV	10.30	NA
V	74	96.2	130
Zn	160	154	96.2

*Certified Reference Material No. 214 obtained from ERA, Inc.

** NCV - No certified value.

***NA - Not applicable.

Table II-D. Detection Limits (ppm, dry weight) for Metals Analyzed in Shoal Creek Sediments.

Element	Detection Limit
Al	2.50
As	0.10
Ba	0.50
Be	0.05
B	1.00
Cd	0.15
Cr	0.25
Cu	0.25
Fe	2.50
Pb	1.25
Mg	2.50
Mn	0.25
Hg	0.010
Mo	1.00
Ni	0.30
Se	0.10
Sr	0.13
V	0.13
Zn	0.50

APPENDIX III

METALS RESULTS (ppm, wet weight) FOR SHOAL CREEK SEDIMENT SAMPLES

DECEMBER 1996

Table III-A. Metals Results (ppm, wet weight) for Shoal Creek Sediment Samples.

	MP 56.0	MP 51.7	UT in Rigsby Hollow	MP 49.8	MP 47.0	MP 46.1	MP 41.9	MP 32.1	MP 22.2	MP 14.0	Average	Geometric Mean
Al	10600	14000	14600	12600	11600	13900	13500	5670	10800	4340	10779	10088
As	3.34	12.80	4.12	3.52	1.45	3.19	2.07	1.51	1.52	1.64	3.45	2.60
Ba	40.30	21.90	115.00	53.30	64.90	88.40	89.50	42.10	72.10	37.40	56.66	51.92
Be	0.32	0.79	0.97	0.46	0.39	0.51	0.55	0.38	0.63	0.52	0.51	0.49
B	2.71	16.30	8.16	6.96	3.18	3.81	5.55	2.80	2.18	1.79	5.03	3.93
Cd	0.18	0.26	0.24	0.19	0.15	0.15	0.15	0.15	0.15	0.15	0.17	0.17
Cr	27.20	12.10	18.20	23.90	12.70	65.10	22.80	12.50	11.10	20.90	23.14	19.62
Cu	6.57	9.04	6.98	9.23	4.74	15.10	5.43	3.98	5.05	2.34	6.83	6.00
Fe	9490	23200	16500	12100	7140	11000	9510	7210	7280	12000	10992	10254
Pb	25.50	8.68	7.40	8.40	7.08	14.40	8.06	4.25	8.07	9.96	10.49	9.30
Mg	579	4780	1690	909	523	742	813	410	581	293	1070	725
Mn	135	324	1890	709	289	677	348	140	87.1	376	343	277
Hg	0.030	0.010	0.038	0.042	0.061	0.085	0.033	0.023	0.044	0.022	0.039	0.033
Mo	0.98	0.98	0.97	0.98	0.98	0.99	0.97	0.97	0.97	0.99	0.98	0.98
Ni	10.10	14.00	28.70	37.70	7.95	90.90	19.90	12.60	12.10	11.80	24.12	17.29
Se	0.70	0.85	0.90	0.62	0.61	0.75	0.83	0.35	0.58	0.18	0.61	0.56
Sr	8.19	26.40	9.91	6.96	5.54	8.43	10.80	6.90	7.49	3.59	9.37	8.04
V	39.20	28.60	50.60	42.10	36.50	40.90	42.10	20.20	33.50	25.90	34.33	33.42
Zn	38.30	40.70	44.60	59.10	23.10	59.50	33.60	25.00	26.00	24.90	36.69	34.48