

# **Analysis of Metals in Sediments from the Bayou Creek System**

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**February 11, 1998**

**FINAL REPORT**

## INTRODUCTION

This report presents the results for eight metals of concern (MOC, *i.e.* Ag, Be, Cd, Cr, Cu, Ni, Pb and Zn) analyzed in twenty-six sediment samples collected from Big and Little Bayou Creeks on July 15-16, 1997. Sampling was conducted jointly by personnel from UK and FFOU. Samples for station LB2A were taken just below the 011 outfall down to the beginning of the LB2 monitoring station. Analyses of MOC in water column samples were presented previously in the December report (Birge and Price, 1997). Within the effluent receiving zone of Big Bayou Creek, water column concentrations of copper, chromium and zinc generally increased in a downstream progression, with highest concentrations usually noted at stations BB6 and BB7. These stations are downstream of effluent 001. Beryllium, cadmium, lead, nickel and silver were sharply elevated at station BB6, presumably due to the effluent 001 discharge. Chromium and lead were the metals most elevated in Little Bayou Creek, especially at station LB2A/LB2.

## METHODS

Sediment samples were restricted to the upper 5-10 cm of sediment soil, including depositional areas where found. All sediment samples were collected in acetone-rinsed 0.47L glass jars with teflon or aluminum foil-lined lids. Stainless steel spoons and scoops used for collections were acetone-rinsed between sampling stations. Samples were maintained on ice (4 °C) from collection to the UK laboratory, where they were refrigerated. Formal chain of custody documentation was observed for all samples.

Sediment samples were air dried for 7 days on pre-weighed acetone-rinsed stainless steel pans, reweighed, and sieved. Sub-samples of the 7-day air-dried samples were sieved to obtain the clay-silt fraction, *i.e.* past 180- $\mu$ m mesh (Hynes, 1970; Gee and Bauder, 1986). All sieves were solvent-cleaned stainless steel. Clay-silt fractions were stored in chemically cleaned 0.24L glass jars with teflon or aluminum foil-lined lids until extraction.

A 2.0 g sample per station was digested and extracted according to procedures described in EPA Method 3050 and ASTM Method D 3974-81 (U.S. EPA, 1986; ASTM, 1989). All chemicals used were ACS grade or better and all acids were TraceMetal grade. Metal analysis of sediments was performed by atomic absorption spectrophotometry (AAS), using graphite furnace atomization techniques. Analysis was performed using a Varian AAS (Model Spectra AA-20), equipped with a GTA-96 graphite furnace. All gases used were ultra pure carrier grade. Calibration curves were based on five standards. The instrument was programmed to take three readings per sample and average the absorbance. Instrument blanks (0.5 % HNO<sub>3</sub>) and check standards were processed with all samples. Sample concentrations were then corrected for deviations from the standards, and sediment dry weight was factored into calculation of final values.

## RESULTS

Beryllium (Be) sediment concentrations were elevated at stream stations BB6 and BB9 in Big Bayou Creek (Table 1, Figure 1) and at stations LB2 and LB2A in Little Bayou Creek (Table 2). More sediment sampling will be required to establish a more accurate Be profile in Big Bayou Creek. Some of the variability (e.g. BB8) appears to be due to the sampling pattern and the low number of samples taken. The maximum concentration recorded was 1.34  $\mu\text{g/g}$  (i.e. ppm) at BB6.

Only slight elevations in sediment cadmium were observed within the two streams. Highest concentrations were at stations BB5 and BB6 on Big Bayou Creek, below effluents 006 and 001, and at LB3 on Little Bayou Creek. Station LB3 is downstream of effluent 010 (Figure 2). Highest water concentrations previously reported for cadmium were observed at and below BB6 on Big Bayou Creek, and elevated sediment cadmium generally was not observed on Little Bayou Creek. Mean concentrations are shown in Figure 2. The highest sediment cadmium concentration was 2.8  $\mu\text{g/g}$  at station LB3 on Little Bayou Creek (Table 2).

Sediment concentrations of chromium increased from stations BB5 to BB7 on Big Bayou Creek (Figure 3), and chromium was elevated at LB2A and LB3 on Little Bayou Creek. The highest concentrations were 107.6 and 93.5  $\mu\text{g/g}$  at stations BB7 and LB3, respectively (Tables 1,2). Highest mean chromium values for water samples collected in July 1997 occurred at stations BB6 and LB2. It is not unusual for sediment metal contaminations to peak some distance downstream of the source, as shown for mean values in Figure 4.

Sediment copper contamination also increased in the effluent receiving zone of Big Bayou Creek (BB4, BB5) and was elevated at BB7 (Table 1, Figure 5). The lower values obtained for BB6 probably reflect variability in sampling. The highest sediment value for copper was 26.6  $\mu\text{g/g}$  at BB7. Sediment copper was not consistently elevated in Little Bayou Creek, but the highest concentration approached 11  $\mu\text{g/g}$  at LB3. Water column copper was elevated at stations BB3, BB6, and BB7 (Birge and Price, 1997).

With the exception of BB6, mean lead concentrations in Big Bayou Creek sediments increased slightly within the effluent-receiving zone from BB4 through BB7 (Figure 6). The lower values for BB6 were likely due to sampling. Lead was detected in the water column from BB6 through BB9 at concentrations ranging from 2.34  $\mu\text{g/L}$  to 3.06  $\mu\text{g/L}$  (Birge and Price, 1997). In Little Bayou Creek, both sediment and water column data were more uniform, but there was a decrease in the LB4 sediment, which was the most downstream sector sampled (Birge and Price, 1997). The highest sediment lead concentrations were 8.8 and 8.1  $\mu\text{g/g}$  at stations BB7 and BB5, respectively, and 8.4  $\mu\text{g/g}$  at LB3 (Tables 1, 2).

Nickel was not detected at stations BB8, LB2 and LB4 (Figure 7), nor in one of the samples from stations BB1, BB3, BB4, BB7, and LB3 (Tables 1, 2). As indicated above, sampling may have contributed to the variability in this set of analyses. The highest value observed for nickel was 38.4  $\mu\text{g/g}$  at station BB7 (Table 1). Otherwise, nickel

concentrations were generally consistent, ranging from 11.5  $\mu\text{g/g}$  (BB3) to 15.9  $\mu\text{g/g}$  (BB9) in Big Bayou Creek and 12.5  $\mu\text{g/g}$  (LB2A) to 14.9  $\mu\text{g/g}$  (LB3) in Little Bayou Creek (Tables 1, 2). Elevated water concentrations were observed for nickel at BB6 (24.1  $\mu\text{g/L}$ ) and BB7 (25.7  $\mu\text{g/L}$ ), but it was not detected from BB1 through BB5, or from LB2 through LB4 (Birge and Price, 1997).

Only low concentrations of silver were detected at stream stations BB1 (*i.e.* reference) and BB3 (Table 1). However, silver contamination increased progressively from BB4 to BB6, with a maximum concentration of 1.29  $\mu\text{g/g}$ . As shown in Figure 8, mean silver concentrations decreased nearly linearly below BB7. Water sample analyses reported previously (Birge and Price, 1997) revealed an abrupt increase in silver at BB6. The sediment results indicate that silver contamination from effluents upstream of 001 (*i.e.* 009, 008, 006) may fluctuate with time. More frequent water sampling will be required to clarify all sources of silver.

Like chromium, zinc sediment concentrations were more elevated throughout the Bayou system than those for other MOC (Tables 1,2). Maximum sediment zinc concentrations were observed at BB7 (127.6  $\mu\text{g/g}$ , Table 1) and at LB3 (85.7  $\mu\text{g/g}$ , Table 2). The highest mean zinc values for water samples collected from Big Bayou Creek in July 1997 occurred at BB6 (15.1  $\mu\text{g/L}$ ) and BB8 (22.9  $\mu\text{g/L}$ ). Sediment zinc concentrations generally increased in the effluent receiving zone from BB4 through BB7 (Figure 9), reflecting stream metal loading by PGDP discharges. There was a reasonable correlation between water column and sediment zinc. As noted above, sediment metal loading often is greater one station below that where peak water concentrations occur (Figure 10).

In summary, these data indicate that Bayou Creek sediments are moderately impacted by metals, and this contamination appears traceable to metals discharged in PGDP effluents. It should be noted further that impact on macroinvertebrate communities has been reported for most sectors of Big Bayou Creek that experience sediment metal enrichment (Birge *et al.*, 1992).

Table 1. Metal concentrations in Stream Sediments from Big Bayou Creek Collected July 15, 1997.

Sample Number	Sediment Wt. (g)	Metal Concentrations (µg/g)							
		Ag	Be	Cd	Cr	Cu	Ni	Pb	Zn
BB1071597MSED1	2.11	<0.047	1.12	1.16	18.72	7.68	11.64	6.40	31.28
BB1071597MSED2	2.07	0.090	0.81	<1.21	20.29	7.34	<12.08	6.52	38.41
BB3071597MSED1	2.00	0.094	<0.50	<1.25	15.65	<5.00	<12.50	5.70	<25.00
BB3071597MSED2	2.19	0.060	0.72	1.19	20.00	6.21	11.45	6.26	34.20
BB4071597MSED1	1.96	0.387	<0.51	<1.28	17.14	<5.10	<12.76	7.19	<25.51
BB4071597MSED2	2.12	0.361	0.78	1.18	25.75	9.62	13.13	6.46	53.11
BB5071597MSED1	2.07	0.196	1.03	1.61	35.89	12.66	15.36	8.12	51.69
BB5071597MSED2	2.19	0.817	0.96	1.38	31.78	11.51	12.94	6.58	45.21
BB6071597MSED1	2.04	1.292	1.34	1.53	30.54	5.74	12.78	4.85	27.84
BB6071597MSED2	2.25	0.132	1.08	1.30	28.76	7.33	12.81	4.58	34.18
BB7071597MSED1	1.97	1.026	1.28	1.43	107.56	26.60	38.43	8.78	127.56
BB7071597MSED2	2.28	0.203	0.65	<1.10	28.38	5.96	<10.96	5.75	28.46
BB8071597MSED1	2.03	0.206	0.79	1.23	28.42	7.19	<12.32	7.19	35.67
BB8071597MSED2	1.97	0.802	0.64	<1.27	25.33	5.94	<12.69	6.19	30.61
BB9071597MSED1	1.95	0.370	1.30	1.56	28.46	10.36	15.92	6.21	53.33
BB9071597MSED2	2.04	0.348	1.32	1.44	31.37	6.47	15.51	6.13	47.79

Table 2. Metal Concentrations in Stream Sediments from Little Bayou Creek Collected July 16, 1997.

Sample Number	Sediment Wt. (g)	Metal Concentrations (µg/g)							
		Ag	Be	Cd	Cr	Cu	Ni	Pb	Zn
LB1071697MSED1	2.06	0.451	0.91	1.21	24.47	8.50	13.13	6.17	52.48
LB1071697MSED2	2.13	0.054	1.08	1.22	27.42	9.58	14.51	7.18	56.90
LB2A071697MSED1	2.23	0.126	1.24	1.17	78.48	7.85	12.99	6.19	50.90
LB2A071697MSED2	2.03	<0.049	1.09	1.39	62.81	6.90	12.54	6.80	48.67
LB2071697MSED1	2.08	<0.048	1.16	1.25	31.11	6.06	<12.02	5.91	43.08
LB2071697MSED2	1.99	<0.050	1.17	<1.26	38.39	6.33	<12.56	6.58	38.89
LB3071697MSED1	2.06	0.785	1.20	1.21	93.45	10.87	14.91	8.35	85.73
LB3071697MSED2	2.05	0.129	0.84	2.80	64.63	6.83	<12.20	5.17	65.80
LB4071697MSED1	2.15	0.063	0.58	<1.16	37.40	5.63	<11.63	5.26	28.19
LB4071697MSED2	2.18	0.233	0.71	<1.15	67.66	9.45	<11.47	5.50	53.72

Figure 1. Mean Beryllium Concentrations in Stream Sediments from Bayou Creek Collected July 15-16, 1997.

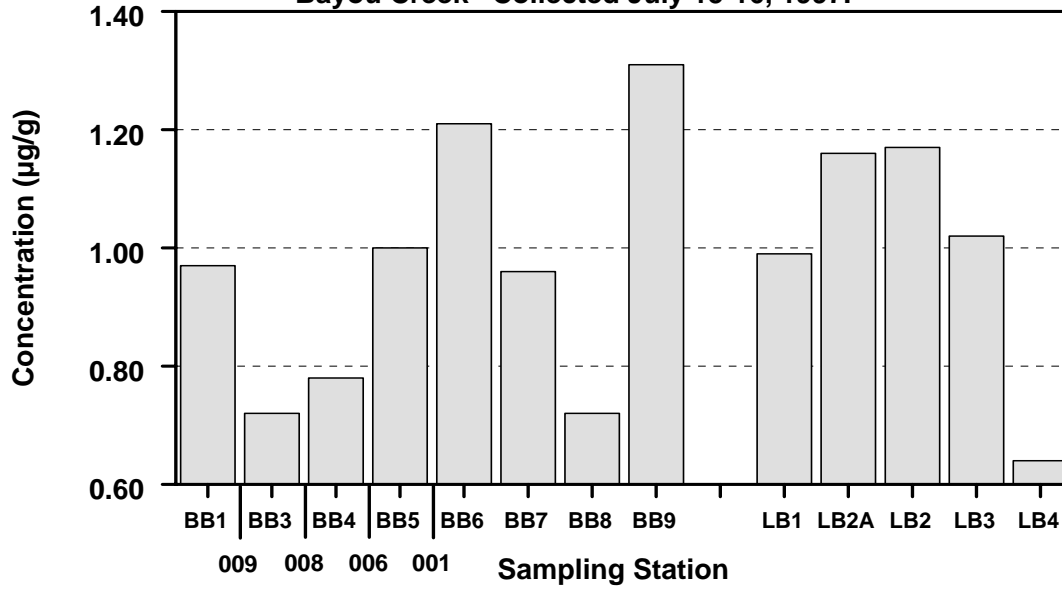


Figure 2. Mean Cadmium Concentrations in Stream Sediments from Bayou Creek Collected July 15-16, 1997.

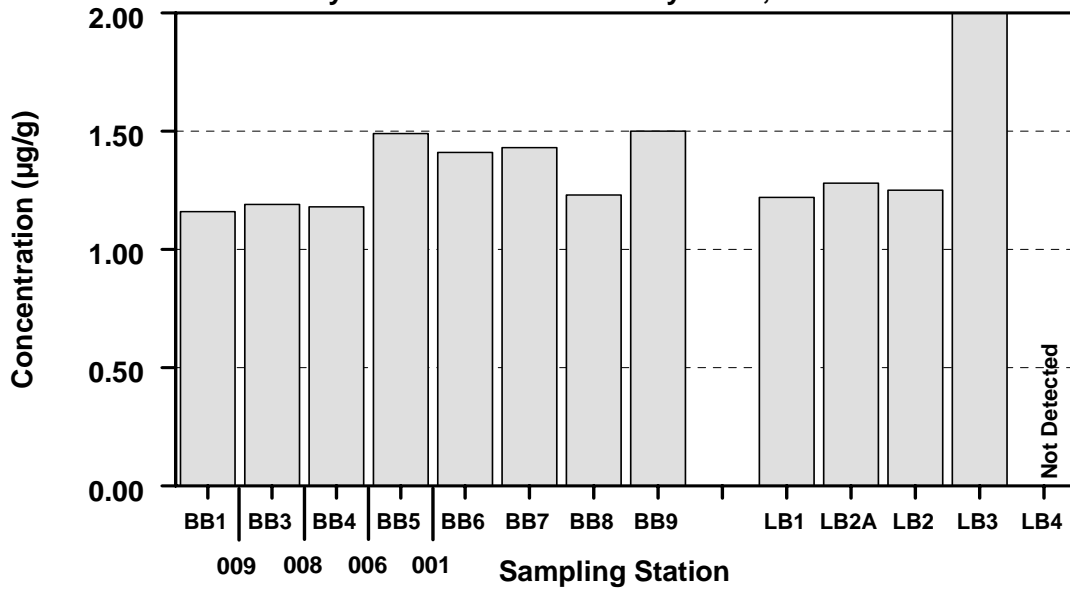


Figure 3. Mean Chromium Concentrations in Stream Sediments from Bayou Creek Collected July 15-16, 1997.

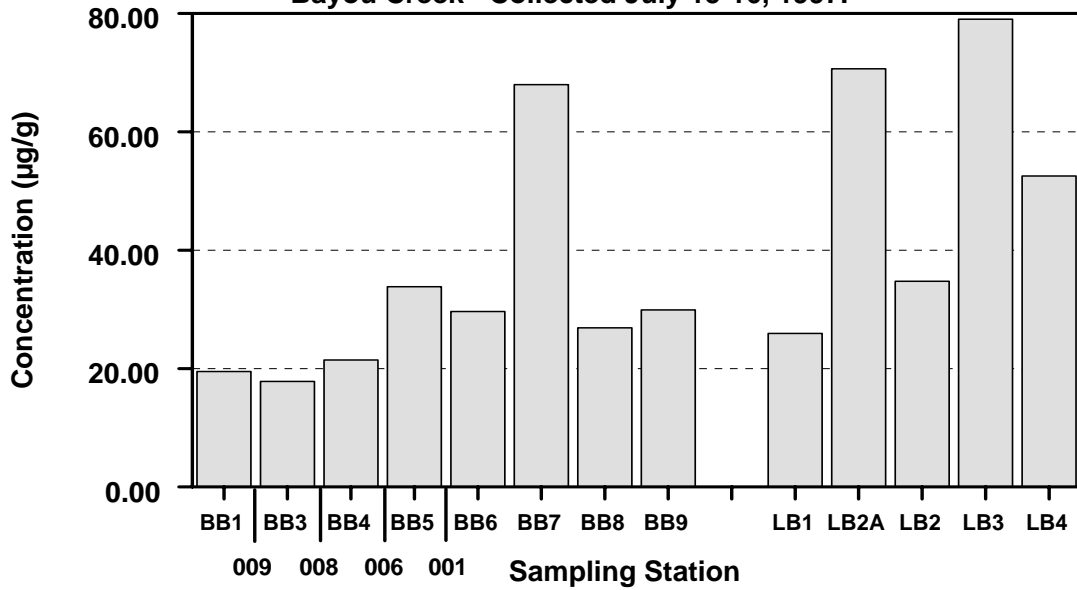
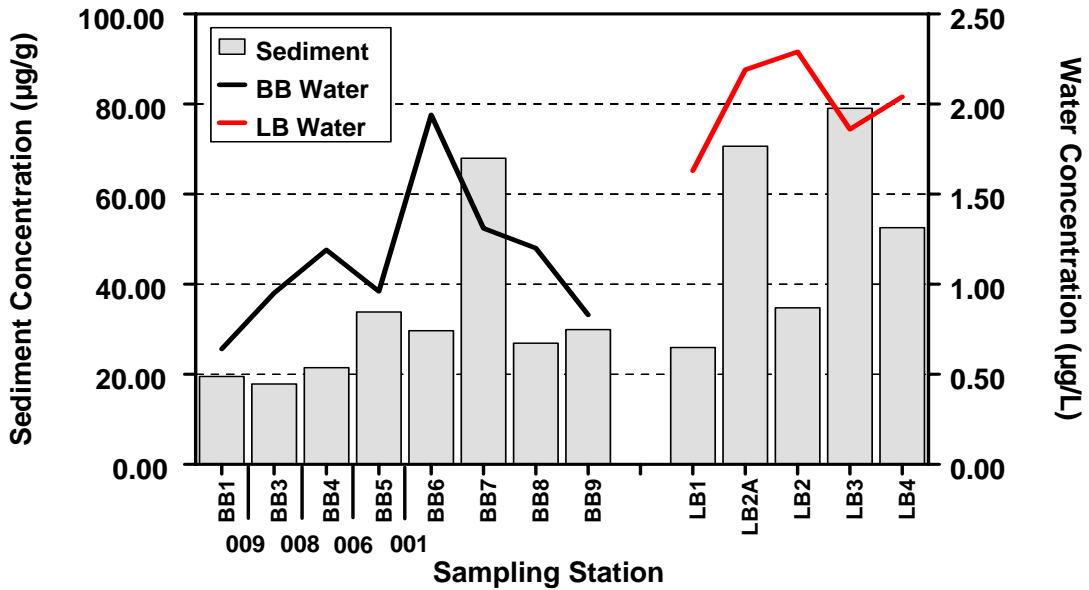
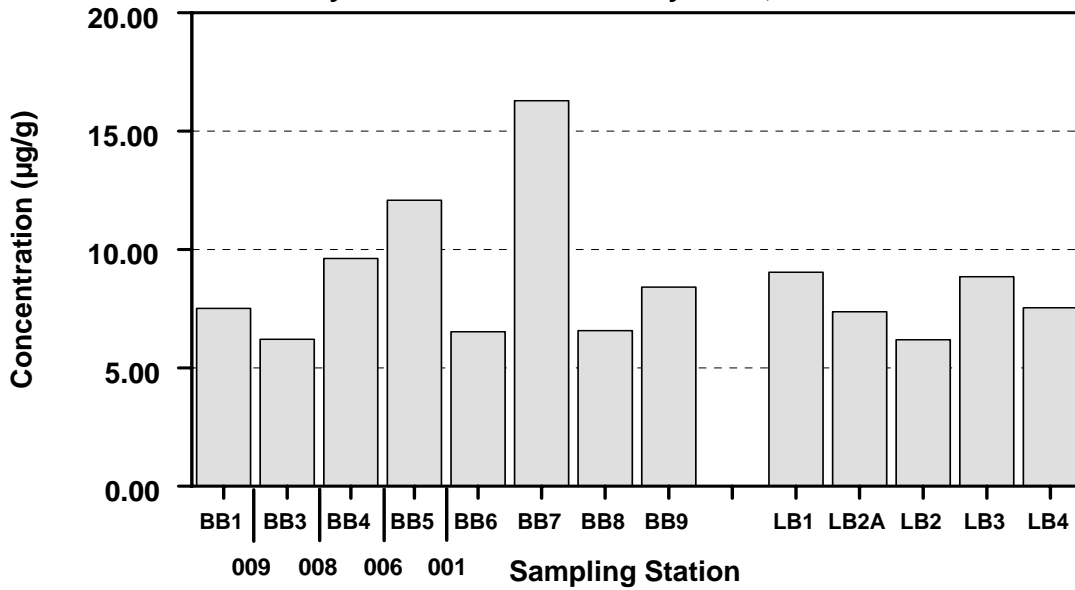


Figure 4. Mean Chromium Concentrations in Stream Sediments and Water Samples from Bayou Creek Collected July 15-16, 1997.





**Figure 5. Mean Copper Concentrations in Stream Sediments from Bayou Creek Collected July 15-16, 1997.**



**Figure 6. Mean Lead Concentrations in Stream Sediments from Bayou Creek Collected July 15-16, 1997.**

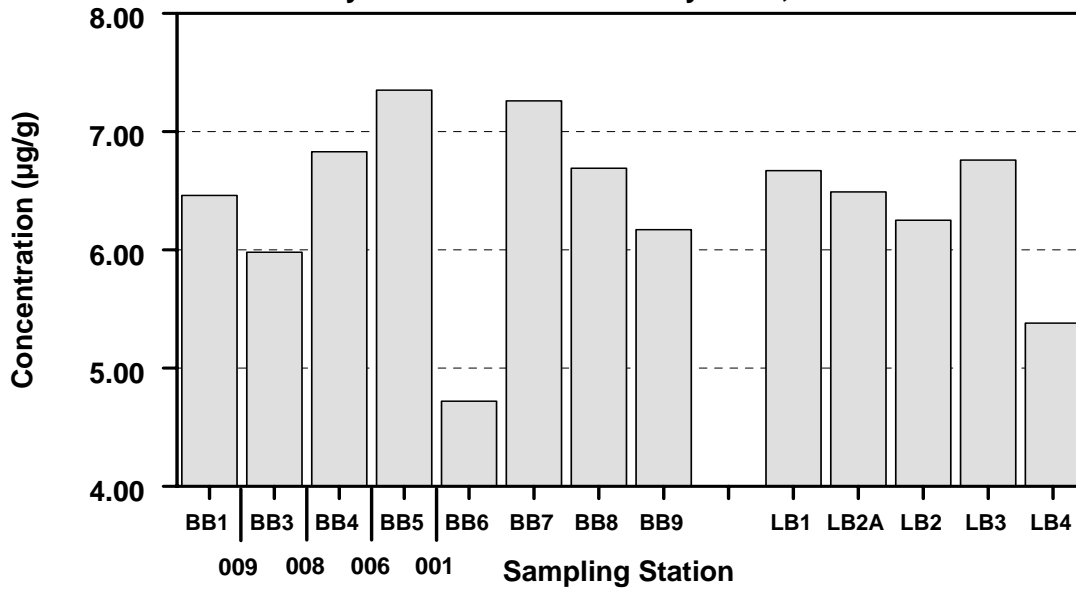


Figure 7. Mean Nickel Concentrations in Stream Sediments from Bayou Creek Collected July 15-16, 1997.

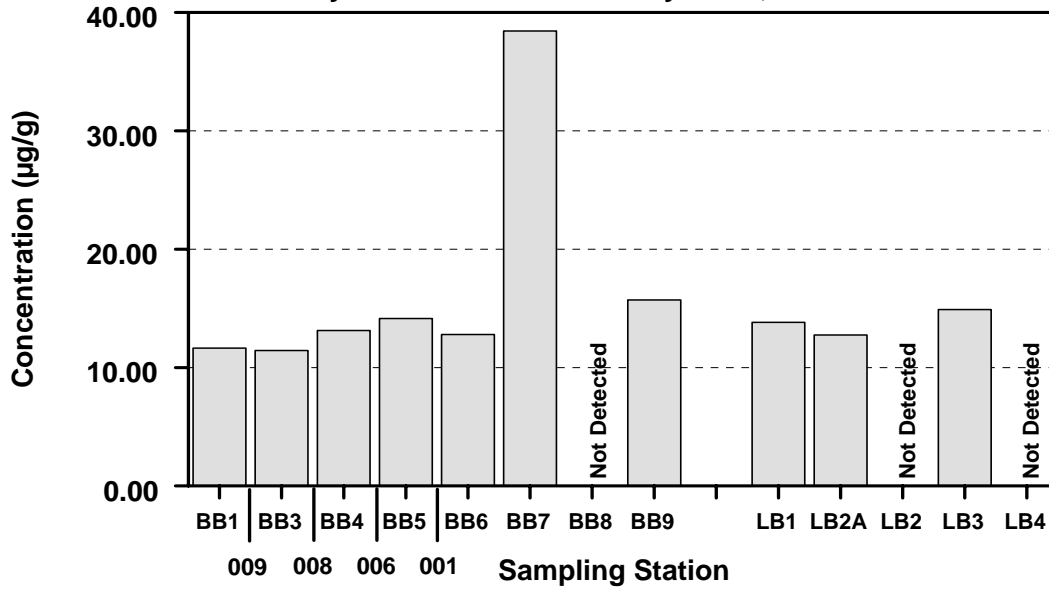


Figure 8. Mean Silver Concentrations in Stream Sediments from Bayou Creek Collected July 15-16, 1997.

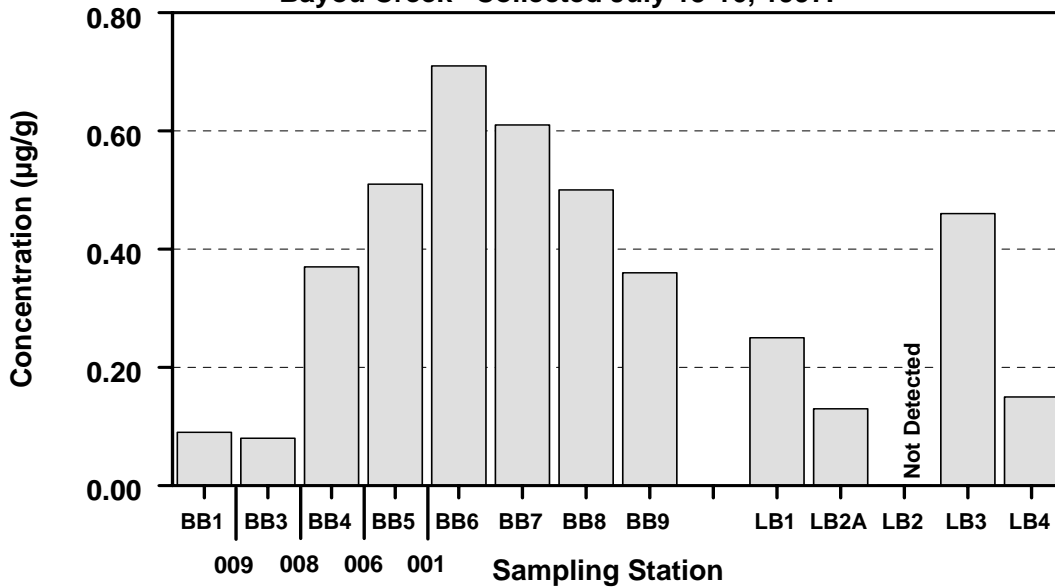


Figure 9. Mean Zinc Concentrations in Stream Sediments from Bayou Creek Collected July 15-16, 1997.

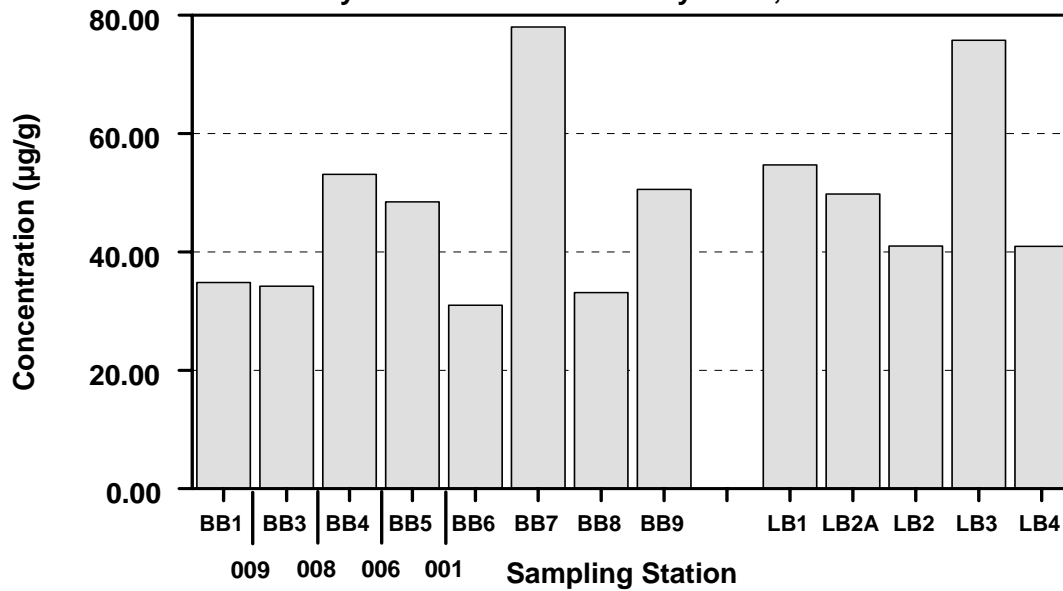
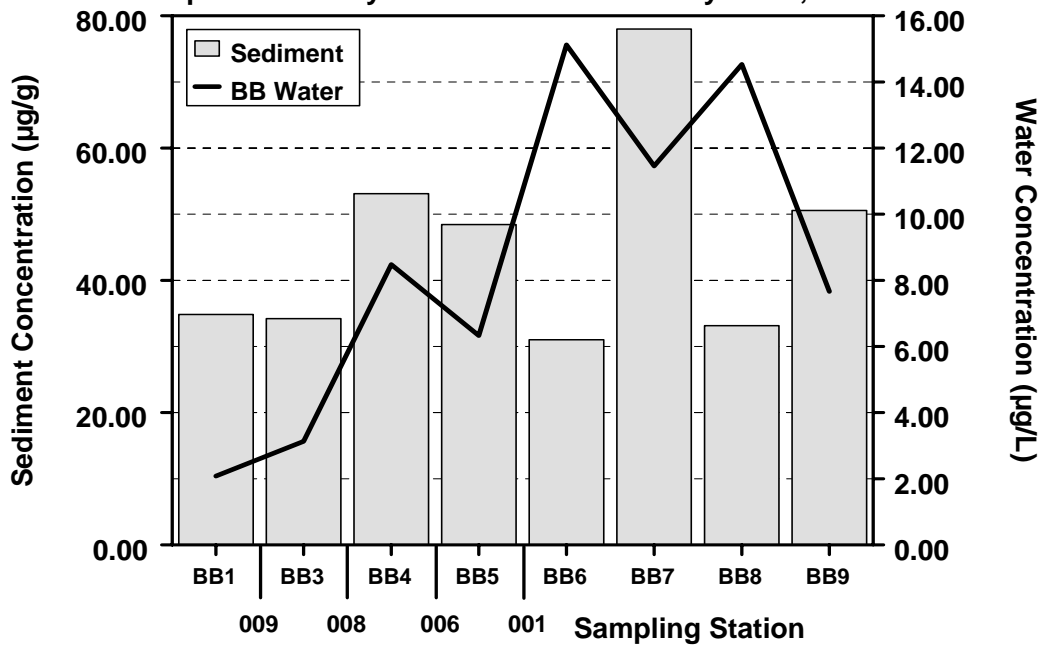


Figure 10. Mean Zinc Concentrations in Stream Sediments and Water Samples from Bayou Creek Collected July 15-16, 1997.



## REFERENCES

ASTM. 1989. Standard Practice for Preparation of Sediment Samples for Chemical Analysis. D 3976-88. Annual Book of ASTM Standards. Vol. 11.02. pp. 598-600. ASTM, Philadelphia, PA.

Birge, W.J. and D.J. Price. 1997. Analysis of Metals and PCBs in Environmental Samples from the Bayou Creek Systems. Report to FFOU, December 8, 1997. University of Kentucky. Lexington, KY. 40 pp.

Birge, W.J., D.J. Price, D.P. Keogh, J.A. Zuiderveen, and M.D. Kercher. 1992. *Biological Monitoring Program for the Paducah Gaseous Diffusion Plant. Annual Report. October 1990 to March 1992.* University of Kentucky, Lexington, KY.

Hynes, H.B.N., ed. 1970. *The Ecology of Running Waters.* University of Toronto Press. Toronto, Ontario, Canada. p. 24.

Gee, G.W. and J.W. Bauder. 1986. *In: Methods of Soil Analysis. Part 1, Physical and Mineralogical Methods,* second edition. A. Klute, ed. *Agronomy* 9: 383-393.

U.S. EPA. 1986. *Method 3050. Test Methods for Evaluating Solid Waste. Volume IA: Laboratory Manual Physical/Chemical Methods. SW-846, Revision 1, 1987.* Office of Solid Waste and Emergency Response. Washington, DC.