Analysis of Metals in Sediments from the Bayou Creek System

DRAFT REPORT

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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-one sediment samples collected from Big and Little Bayou Creeks on September 9, 1999. Sampling stations BB1 through BB9 on Big Bayou Creek (15 samples) and LB2 through LB4 on Little Bayou Creek (4 samples) were included in this field survey. Samples also were taken at the new reference station, upstream of BB1 and designated BB1A. In addition, Massac Creek (MC) was sampled and served as a reference station independent of the Bayou Creek system. Duplicate samples were analyzed for MC, BB1, BB4, BB5, and BB6. Analyses of MOC in water column samples were presented previously in the December report (Birge and Price, 1999a).

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 chemically clean I-chem® 250 mL glass jars with teflon-lined lids. Stainless steel spoons and scoops used for collections were acetone-rinsed between sampling stations. Samples for station LB2A were taken at the confluence with 011 effluent. Samples were maintained on ice (4 ^{o}C) from collection through storage at the UK laboratory. Formal chain of custody documentation was observed for all samples.

A 2.0 g sample was digested and extracted according to procedures described in

EPA Method 3050B and ASTM Method D 3974-81 (U.S. EPA, 1997 and ASTM, 1989). All chemicals used were ACS grade or better and all acids were TraceMetal grade. Metal analyses of sediments were performed by atomic absorption spectrophotometry (AAS), using graphite furnace atomization techniques. Analyses were 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_3) and check standards were processed with all samples. Sample concentrations were then corrected for deviations from the standards.

QUALITY ASSURANCE

Permanent bench records were kept of all assays and annotated as required under Good Laboratory Practices (Federal Register, 40 CFR, Part 160, August 17, 1989). All printouts and graphic recordings were filed and are open for inspection. These bench records will be archived within two years after the close of the project but retrievable upon request. Chain of Custody were maintained for all samples collected. Quality assurance included 1) assays for certified and prepared standards, 2) duplicate assays, and 3) glassware solvent blanks. Five stations were analyzed in duplicate (*i.e.* MC, BB1, BB4, BB5, BB6) by weighing an additional sub-sample from the same jar. These duplicates were prepared and analyzed as a regular sample.

RESULTS

Metal concentrations found in Big and Little Bayou Creeks are presented in Tables 1 and 2, respectively. Comparisons between metal concentrations in sediments and water samples are shown in Figures 1 through 8 for Big Bayou Creek and Figures 9 through 15 for Little Bayou Creek. The location of the major collecting sites and effluents for the Bayou Creek System are shown in Figure 16. The assays for water samples were reported in December, 1999 (Birge and Price, 1999a). Results obtained for the acid blanks are presented in Table A1.

Big Bayou Creek

Several metals were detected at elevated sediment concentrations at stations BB1A and BB1, as compared with results for Massac Creek (MC). These included Be, Cr, Cu, Pb, and Zn. Similar results were given in earlier reports and there is a need to inspect this area and determine the source(s) of contaminant.

Also as noted in previous reports, Ag, Be, Cd, Cr, Cu, Ni, and Zn were detected at elevated concentrations at one or more stations from BB3 through BB6. The possible sources of contamination includes the continuously flowing effluents 009, 008, 006, and/or 001, as well as runoff via intermittent point-sources (*e.g.* 017, 016, 015, and 014). Maximum concentrations were 0.21 µg/g Ag at BB4; 1.04 µg/g Be at BB7, 0.12 µg/g Cd at BB6, 12.8 µg/g Cu at BB7, 10.6 µg/g Pb at BB7, 32.1 µg/g Ni at BB7, and 50.6 µg/g Zn at BB7 (Table 1). Several metals were detected at increased concentrations at stations BB2/BB2A on the unnamed tributary that enters Big Bayou

Creek just upstream of station BB3. These values ranged up to 1.08 µg/g Be, 0.11 µg/g Cd, 6.6 µg/g Cr, 4.66 µg/g Cu, 9.72 µg/g Pb, 28.4 µg/g Ni and 40.4 µg/g Zn. Leachates from the nearby ash landfill possibly could be contributing to metal contamination of the unnamed tributary.

The relationships between metal assays for water and sediment samples for September 1999 are shown for Big Bayou Creek in Figures 1 through 8. The probable source for most silver contamination would appear to be effluent 008 which is located just upstream of monitoring station BB4 where water and sediment Ag were most elevated (Figure 1). There also appears to be a source of silver from effluent 001. Water column silver concentrations at BB4 and BB6 exceeded the chronic threshold for toxicological effects (Hogstrand and Wood, 1998). Beryllium contamination appears traceable to the unnamed tributary (BB2A), effluent 009 and, possibly, in part to some contamination from effluents 008, 006, and 001 (Figure 2). As noted above, some Be water and sediment contamination may originate from sources upstream of the PGDP plant (*e.g.* BB1A, BB1). Sources of cadmium appear to originate from the unnamed tributary, especially at station BB2. Although cadmium was not detected in water samples in September 1999 at stations BB5 through BB9, prior contamination from such effluents as 006 and 001 possibly contributed to the sediment contamination observed at these stations (Figure 3). Chromium in Big Bayou Creek was variable as reflected in the September survey and both upstream and PGDP sources may have contributed to the results (Figure 4). Further study will be required to evaluate sources and magnitude of Cr contamination. The major sources of copper outfall to Big Bayou Creek appeared to be effluents 008, 006, and 001 which likely affected sediments at

monitoring stations BB5 through BB7 (Figure 5). The pattern observed, like that for Cr, was somewhat variable and will require further study. Sediment lead values were elevated throughout Big Bayou Creek, with concentrations at most stations ranging from about 6.00 to more than 10 µg/g (ppm). Values for analysis of water samples peaked at BB2, BB4, and BB6 (Figure 6). These data indicate that probable sources of Pb contamination in September 1999 were the unnamed tributary, as well as effluents 008 and 001. Stream water values reported for lead exceeded the aquatic life criterion if a water hardness of 100 mg $CaCO_3$/L is used in the calculation. Hardness has been reported to range from 54 to 99 mg $CaCO_3$/L at station BB4, with a mean value of 72 mg $CaCO_3$/L (Birge *et al.*, 1989, 1992). The likely sources of nickel contamination appeared to be the unnamed tributary (*i.e.* ash landfill) and, possibly, effluents 008 through 001 (Figure 7). Sediment zinc concentrations were elevated at BB2, BB6, BB7, and BB9 (Figure 8). Although Zn was not prevalent in the water column at these stations, previous reports indicate that PGDP effluents contribute to Zn contamination, especially effluent 001. The absence of peaks for Zn and certain other metals in water at these stations may be a factor of timing. For example, Zn was elevated in the water column at station BB4 through BB8 in previous studies (Birge and Price, 1997; Birge and Price, 1999b).

Little Bayou Creek

High levels of sediment metal contamination were observed at most stations on Little Bayou Creek. Maximum sediment values in µg/g (ppm) were 0.16 for Ag at LB2,

2.47 for Be at LB3, 0.10 for Cd at LB2, 14.4 for Cr at LB3, 34.7 for Cu at LB3, 33.2 for Pb at LB3, 51.1 for Ni at LB3, and 159.5 for Zn at LB3 (Table 2). Highest sediment metal contamination was observed for Little Bayou Creek station LB3 which is downstream of effluent 002. However, substantial metal contamination also was observed at other stations. For example, concentrations (µg/g) were 0.12, 0.76, 27.1, 12.3 at LB2A for Ag, Be, Ni and Zn, respectively. In addition, values (µg/g) of 0.91, 10.4, 23.6 and 34.2 were observed at LB2 for Be, Pb, Ni, and Zn. Contamination for Be, Cu, Pb, Ni and Zn was still evident at station LB4 which is situated about 4.3 Km downstream of effluent 002. Based on past data, all continuously flowing effluents that enter Little Bayou Creek potentially contribute to metal contamination. This includes effluents 012, 011, 010, and 002. Effluents 010 and/or 002 are the most likely sources for Ag, Be, Cd, Cu, and Pb, whereas 011 also may contribute to Ni and Zn pollution (Figures 9-15). In the metal assays of blanks, all values were below detection (Table A1).

It is recommended that future studies include a comprehensive analysis of metal contamination in Little Bayou Creek. Attention also should be given to the ash landfill and other sources of metal pollution affecting Big Bayou Creek.

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Table 1. Metal concentrations in Stream Sediments from Big Bayou Creek Collected September 9, 1999.

Station	Sample Number	Metal Concentration (µg/g)							
		Ag	Be	Cd	Cr	Cu	Pb	Ni	Zn
MC	MSIAR	0.05	<0.36	<0.04	<3.57	1.17	2.93	<19.79	<9.89
MC	MSIBR	0.06	<0.38	<0.04	<3.84	1.39	2.88	<23.25	<11.62
BB1A	MSIAR	0.03	1.39	0.04	7.46	4.15	10.13	<21.60	17.43
BB1	MSIAR	0.06	1.21	<0.04	<3.87	5.67	10.39	<22.36	14.58
BB1	MSIBR	0.10	0.71	<0.04	<4.33	4.43	10.06	<23.55	18.40
BB2[a]	MSIAR	0.03	0.34	0.11	<3.08	4.22	6.35	23.38	40.38
BB2A[a]	MSIAR	0.06	1.08	0.04	6.64	4.66	9.72	28.44	20.43
BB3	MSIAR	0.14	0.50	0.03	<2.63	3.98	8.35	<19.15	16.95
BB4	MSIAR	0.16	0.95	0.03	<2.80	4.17	6.42	16.91	12.13
BB4	MSIBR	0.21	0.84	<0.04	<3.97	4.34	8.31	16.52	12.04
BB5	MSIAR	0.07	0.50	0.05	<2.90	5.22	5.43	<19.20	12.89
BB5	MSIBR	0.10	0.49	0.06	<3.56	7.39	5.63	<23.32	17.54
BB6	MSIAR	0.11	0.77	0.11	<2.67	12.46	6.69	<22.62	40.58
BB6	MSIBR	0.14	0.57	0.12	<3.40	10.80	6.94	<22.90	15.82
BB7	MSIAR	0.08	1.04	0.07	5.98	12.84	10.59	32.09	50.61
BB8	MSIAR	0.05	0.55	0.07	3.20	2.92	6.90	<18.92	10.89
BB9	MSIAR	0.08	0.79	0.08	<2.53	6.51	7.78	<24.95	28.81

[a] Stations on unnamed tributary entering Big Bayou Creek.

Table 2. Metal concentrations in Stream Sediments from Little Bayou Creek Collected September 9, 1999.

Station	Sample Number	Metal Concentration (µg/g)							
		Ag	Be	Cd	Cr	Cu	Pb	Ni	Zn
MC[a]	MSIAR	0.05	<0.36	<0.04	<3.57	1.17	2.93	<19.79	<9.89
MC	MSIBR	0.06	<0.38	<0.04	<3.84	1.39	2.88	<23.25	<11.62
LB2A	MSIAR	0.12	0.76	0.03	<2.48	3.34	4.05	27.12	12.30
LB2	MSIAR	0.16	0.91	0.10	<4.06	6.28	10.38	23.58	34.21
LB3	MSIAR	0.04	2.47	0.07	14.38	34.68	33.16	51.15	159.53
LB4	MSIAR	0.04	0.28	<0.04	<3.65	2.70	4.13	18.52	12.40

[a] Reference site on Massac Creek.

Table A1. Metal concentrations in Blanks for Stream Sediments from the Bayou Creek System, Collected September 9, 1999.

Station	Sample Number	Metal Concentration (µg/g)							
		Ag	Be	Cd	Cr	Cu	Pb	Ni	Zn
BLNK	1	<0.001	<0.01	<0.001	<0.10	<0.001	<0.001	<0.5	<0.25
BLNK	2	<0.001	<0.01	<0.001	<0.10	<0.001	<0.001	<0.5	<0.25
BLNK	3							<0.5	<0.25
BLNK	4							<0.5	<0.25

Figure 1. Silver concentrations in sediment and water samples collected September 9, 1999 from Big Bayou Creek.

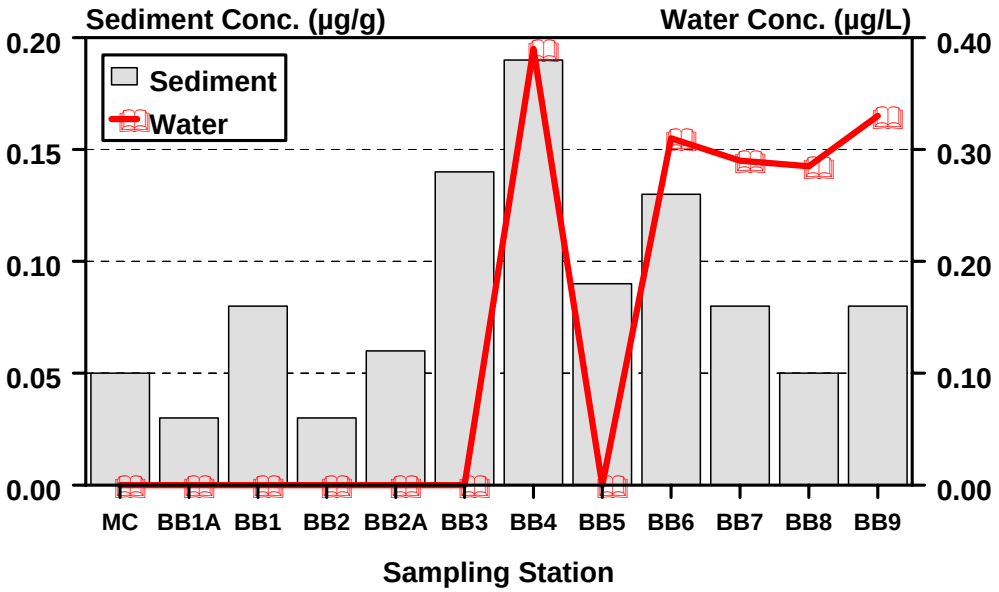


Figure 2. Beryllium concentrations in sediment and water samples collected September 9, 1999 from Big Bayou Creek.

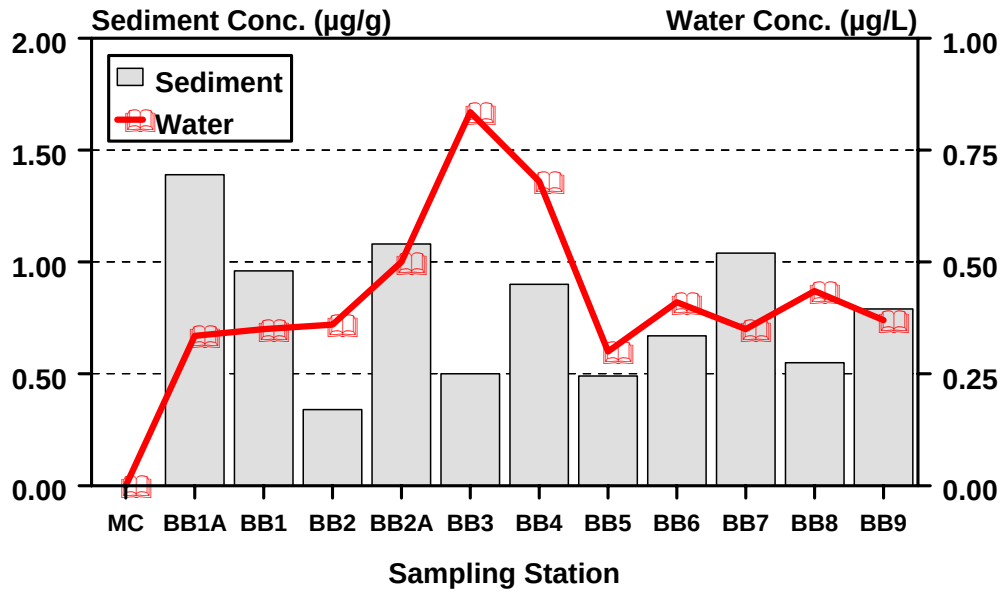


Figure 3. Cadmium concentrations in sediment and water samples collected September 9, 1999 from Big Bayou Creek.

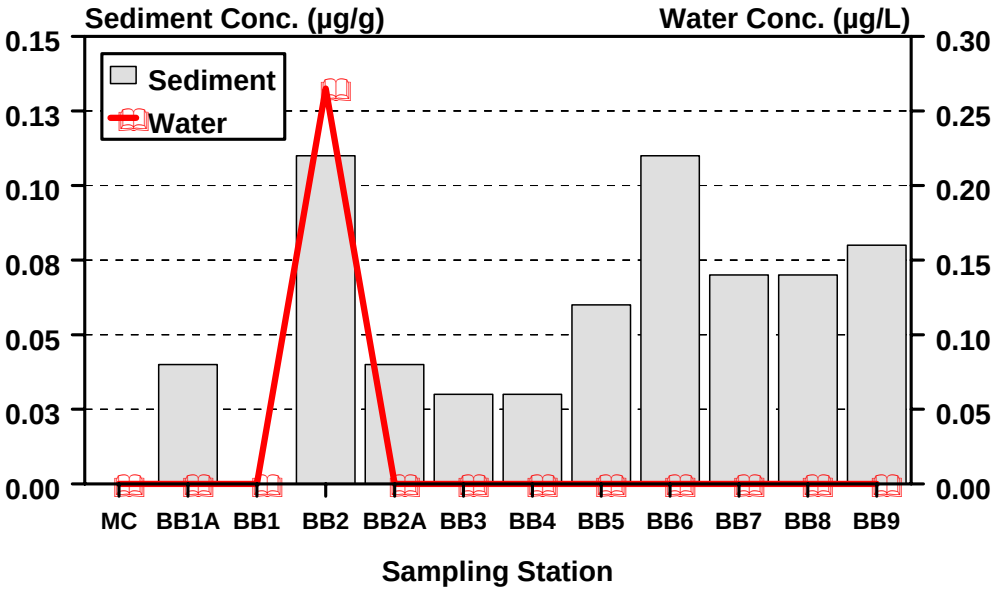


Figure 4. Chromium concentrations in sediment and water samples collected September 9, 1999 from Big Bayou Creek.

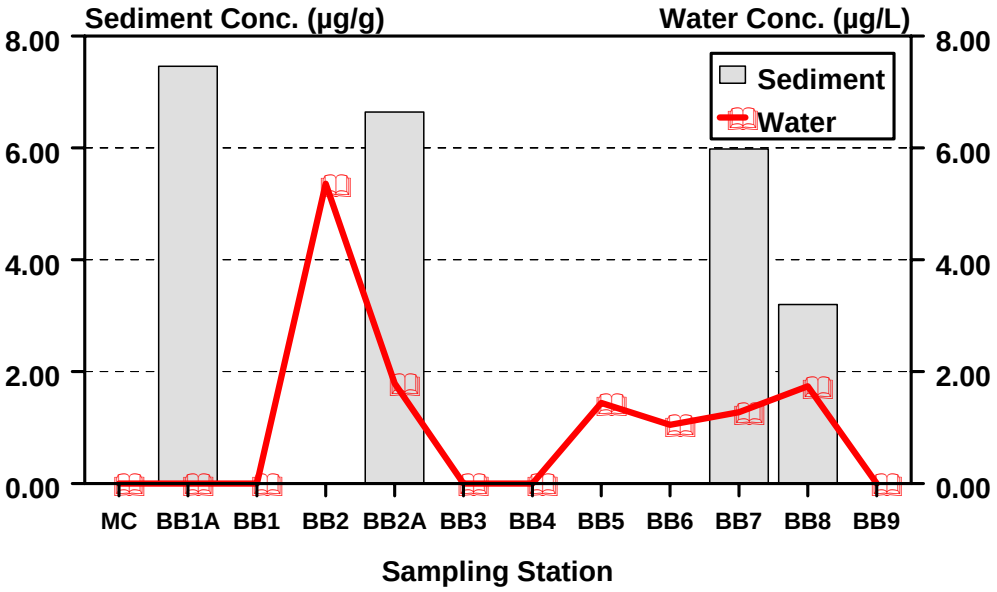


Figure 5. Copper concentrations in sediment and water samples collected September 9, 1999 from Big Bayou Creek.

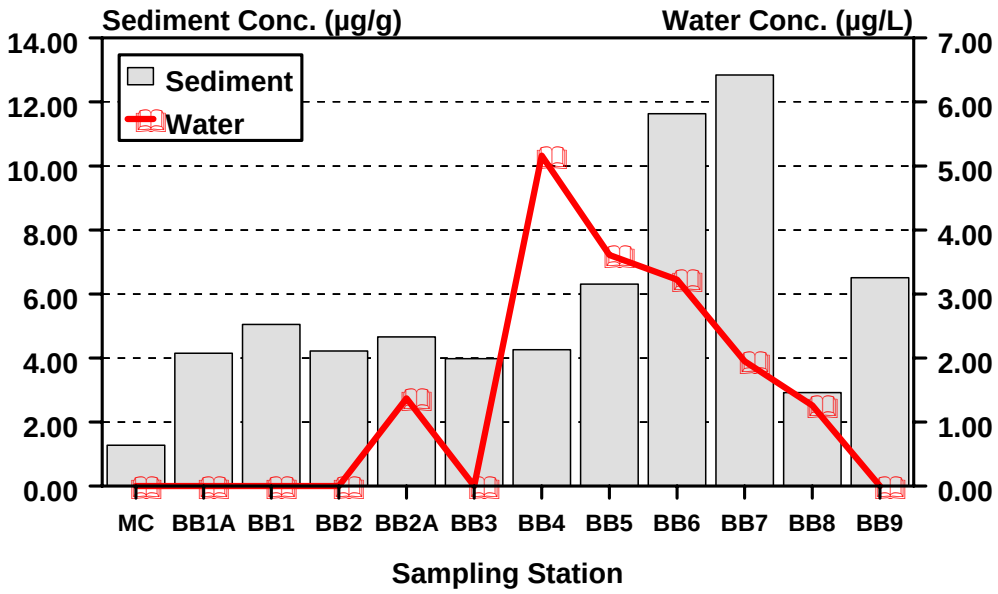


Figure 6. Lead concentrations in sediment and water samples collected September 9, 1999 from Big Bayou Creek.

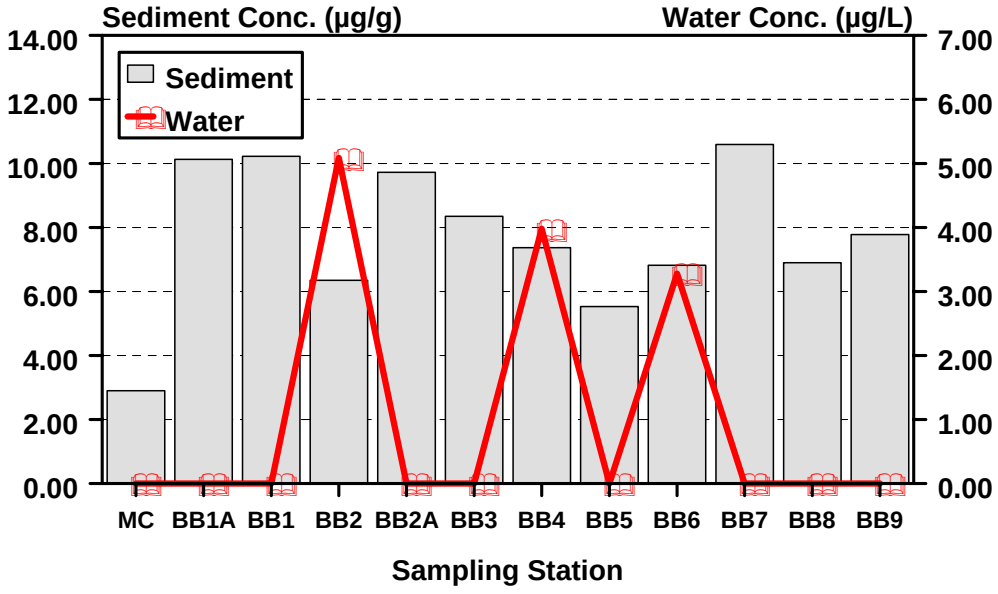


Figure 7. Nickel concentrations in sediment and water samples collected September 9, 1999 from Big Bayou Creek.

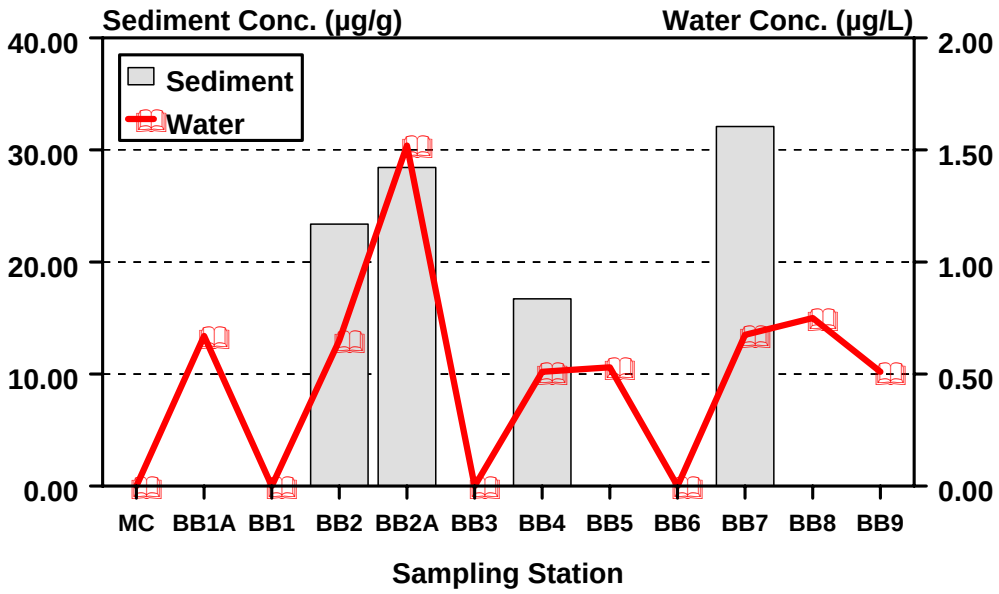


Figure 8. Zinc concentrations in sediment and water samples collected September 9, 1999 from Big Bayou Creek.

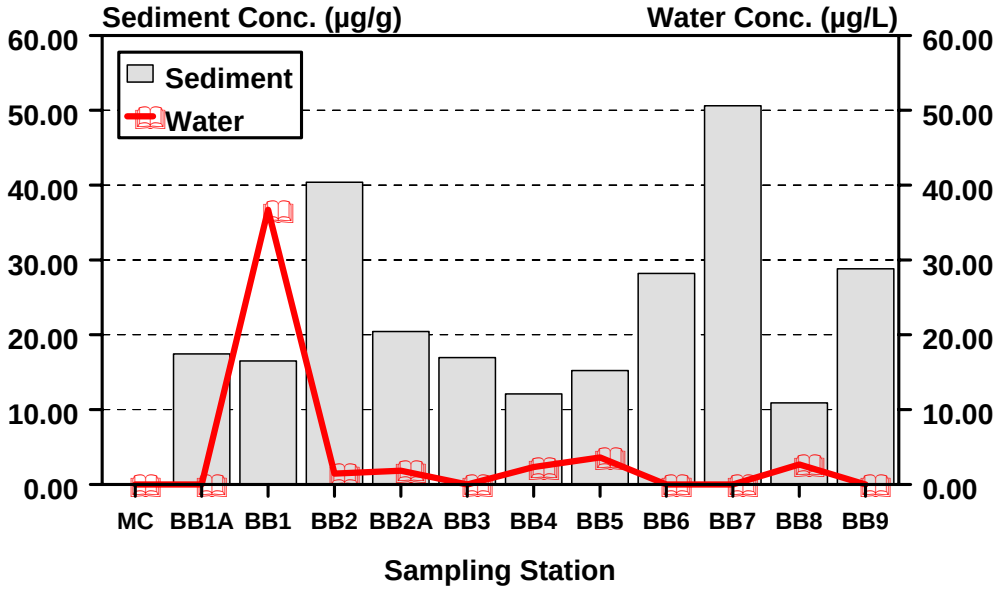


Figure 9. Silver concentrations in sediment and water samples collected September 9, 1999 from Little Bayou Creek.

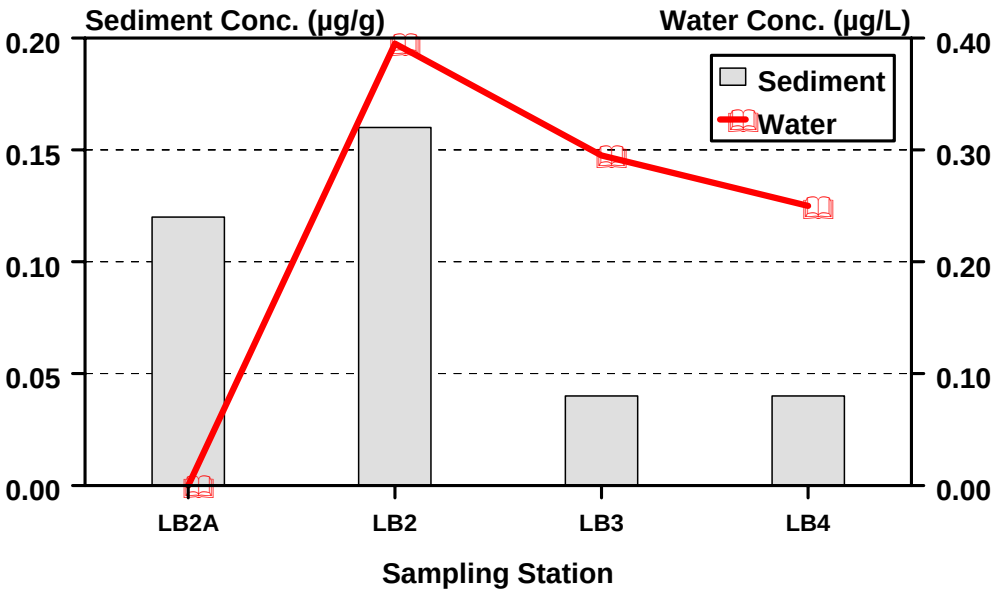


Figure 10. Beryllium concentrations in sediment and water samples collected September 9, 1999 from Little Bayou Creek.

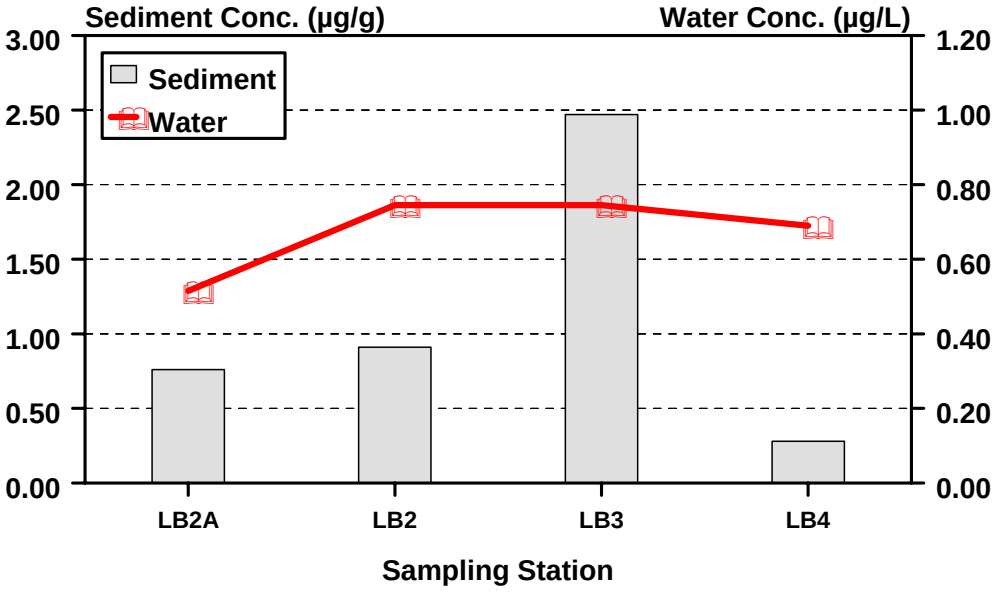


Figure 11. Cadmium concentrations in sediment and water samples collected September 9, 1999 from Little Bayou Creek.

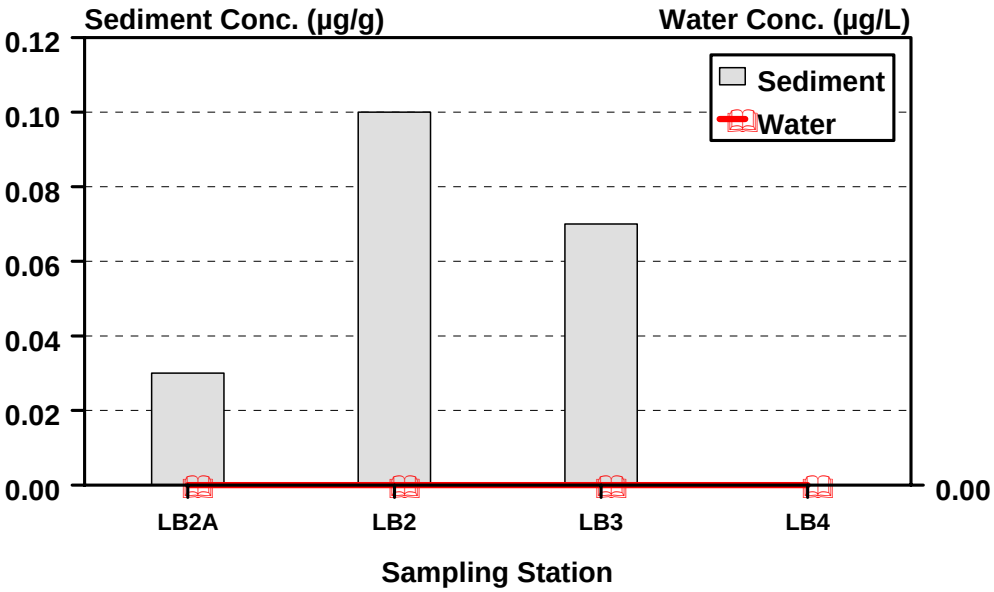


Figure 12. Copper concentrations in sediment and water samples collected September 9, 1999 from Little Bayou Creek.

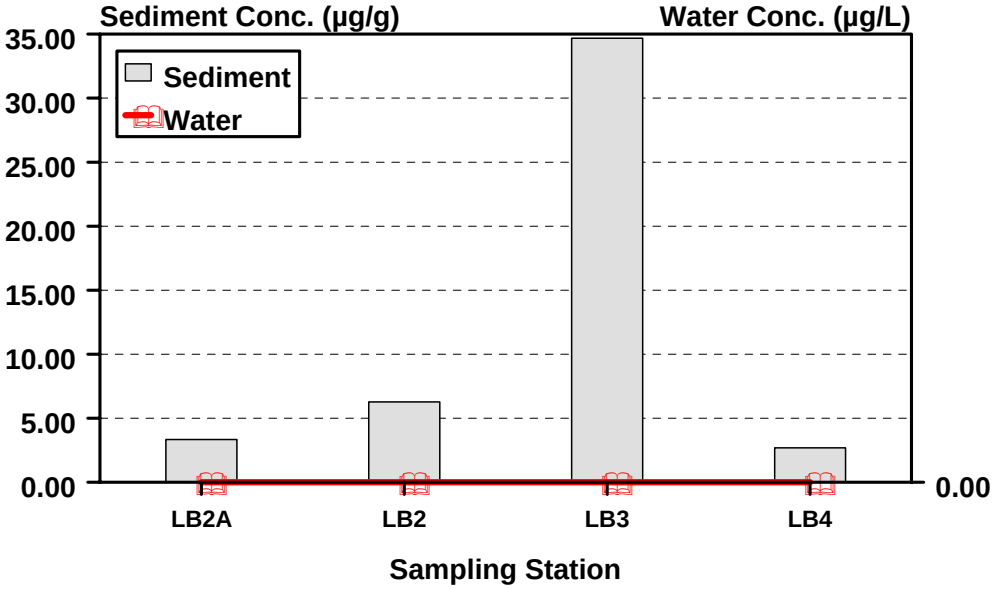


Figure 13. Lead concentrations in sediment and water samples collected September 9, 1999 from Little Bayou Creek.

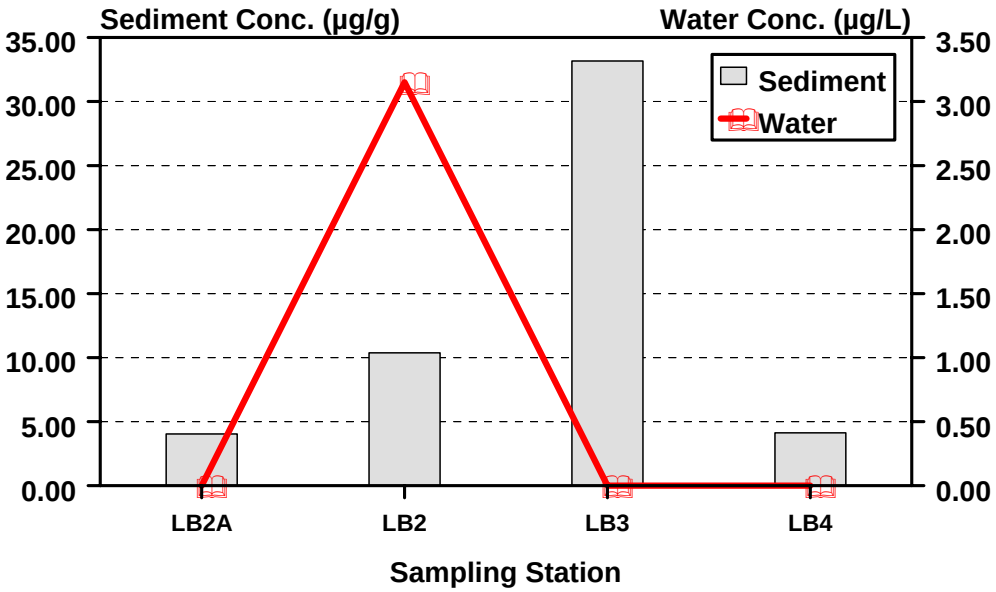


Figure 14. Nickel concentrations in sediment and water samples collected September 9, 1999 from Little Bayou Creek.

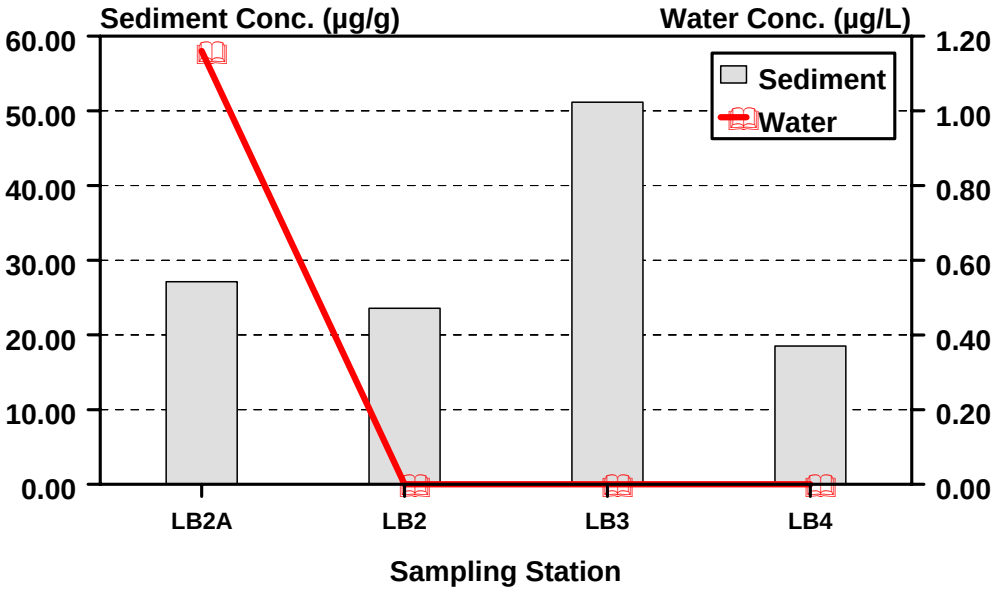


Figure 15. Zinc concentrations in sediment and water samples collected September 9, 1999 from Little Bayou Creek.

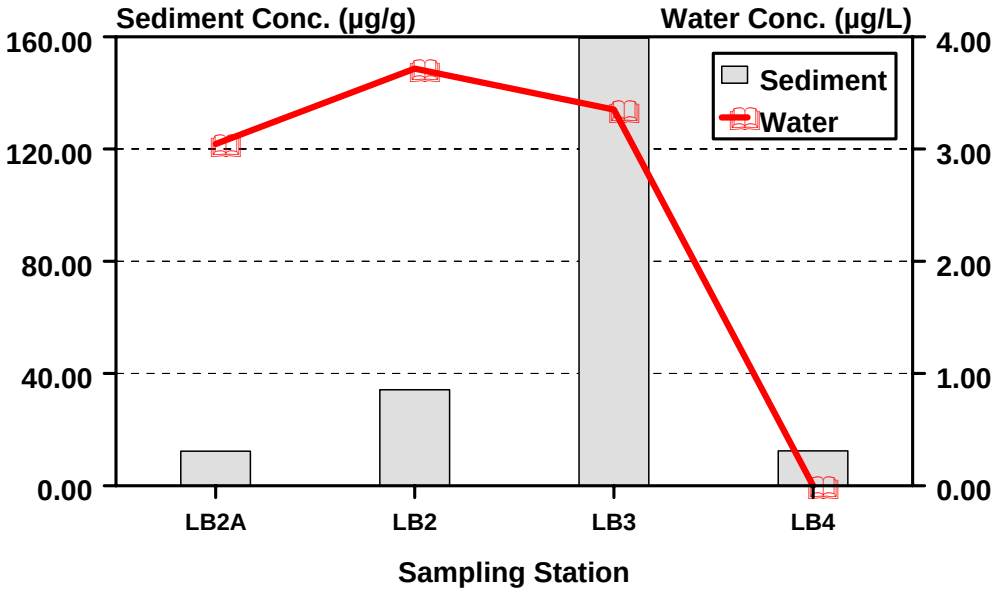
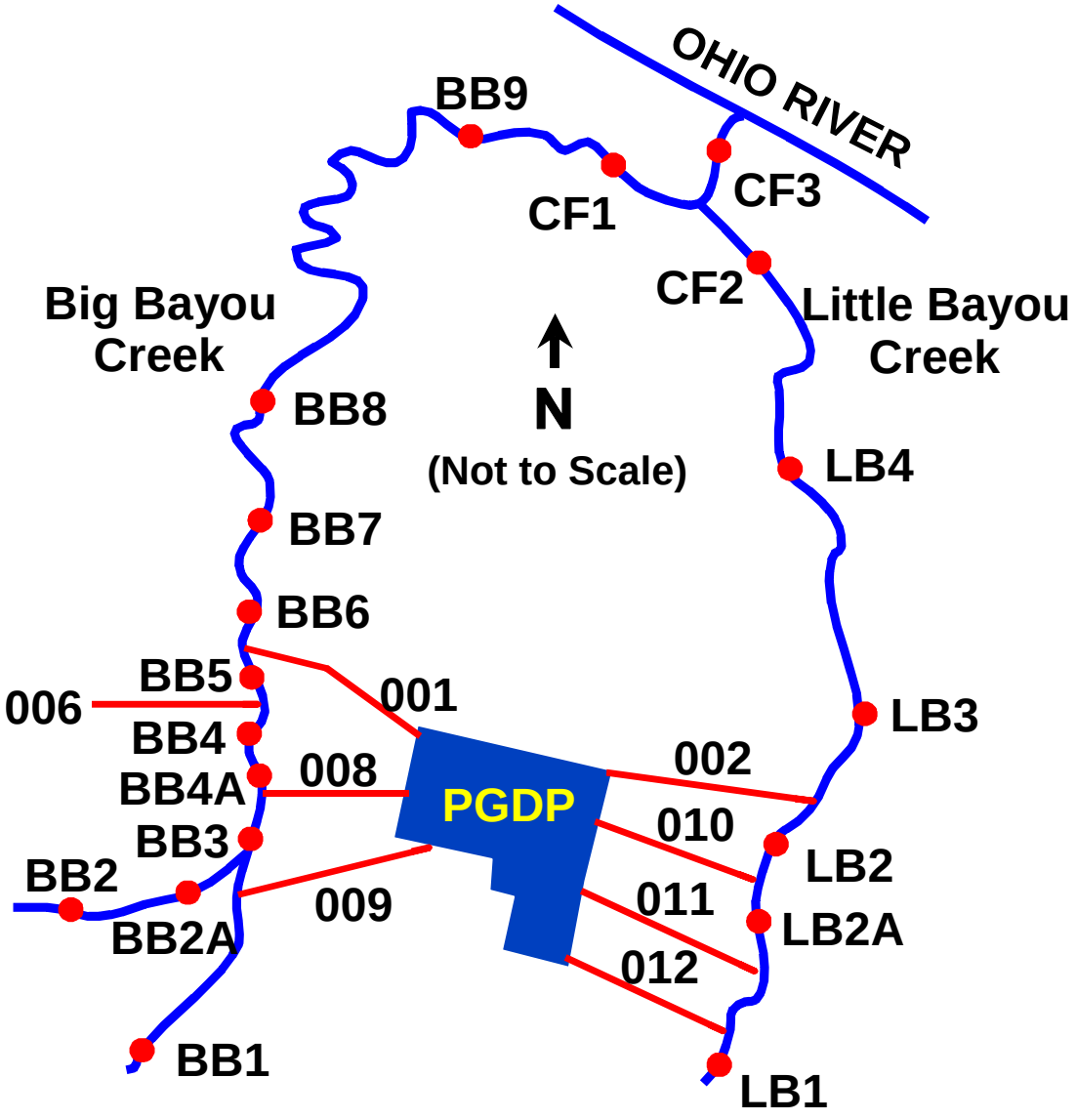


Figure 1. Location of Monitoring Stations and Continuously Flowing Effluents on Big and Little Bayou Creeks



BB1 to BB8 6.1 km
BB8 to Ohio River 7.4 km