

**Report to FFOU on Metals, Mercury and Polychlorinated Biphenyl (PCB)  
Residues in Water Samples Collected October 20,1998  
from the Bayou Creek System**

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**January 26,1999**

**DRAFT REPORT**

## INTRODUCTION

This report presents the results for water samples collected from Big and Little Bayou Creeks on October 20, 1998. Sampling was conducted jointly by personnel from UK and FFOU. Samples were collected from 11 stations in Big Bayou Creek, 4 in Little Bayou Creek, and 1 in Massac Creek. A new reference station was selected upstream of BB1 and designated BB1A. Samples collected from Massac Creek served as a reference station independent of the Bayou Creek system. Two samples were collected for PCB assays for each of the sampling stations for a total of 32 samples. One sample per station was collected for metal assays and a separate sample per station was collected for mercury assays. Three Aroclors (i.e. 1248, 1254, and 1260) were determined for the 32 samples and 8 metals of concern (MOC, *i.e.* Ag, Be, Cd, Cr, Cu, Ni, Pb and Zn) were analyzed for the 16 stations. On-site water quality was determined by FFOU personnel during collections.

## METHODS

### Water Collection

**PCBs:** Water samples for PCB analyses were collected in chemically cleaned, 1-L amber glass jars with teflon-lined caps. New jars were obtained from I-Chem by FFOU personnel. Samples for PCB determinations were placed on ice until delivery to the laboratory and maintained under refrigeration (4 °C) until extraction.

**Metals:** Water samples for metal assays were collected in acid-cleaned 250-mL polyethylene bottles. Samples were preserved with concentrated HNO<sub>3</sub> upon collection and analyzed for total recoverable (TR) metals.

**Mercury:** Water samples for mercury assays were collected in acid-cleaned 1000-mL polyethylene bottles. Samples were preserved with concentrated HNO<sub>3</sub> upon collection.

### Water Extraction

Liquid-liquid extractions were performed in separatory funnels following SW-846 Method 3510C, Separatory funnel liquid-liquid extraction (U.S. EPA, 1997). Water samples were extracted within 7 days of collection. One-liter aqueous samples were extracted three times with 60-mL methylene chloride each time and concentrated to near dryness in a Roto-evaporator (Buchi Model RE121). The reconstituted samples (2.0 mL in iso-octane) were cleaned of interferences as described below and then analyzed by gas chromatography.

## **PCB Sample Cleanup**

Lipid and pesticide clean-up was performed by eluting a 2.0 mL sample through a micro-column of 2.0 g activated 100-200 mesh Florisil® (100°C/24 h) with 10.0 mL hexanes and evaporated to 2.0 mL (Erickson, 1997; U.S. EPA, 1996, SW-846 Method 3620B, Florisil cleanup). Elemental sulfur was then removed by shaking 2-propanol (2 mL) and tetrabutylammonium sulfite (2 mL), adding ultra-pure water (8 mL) and reshaking. The organic extract was removed and mixed with 2.0-mL concentrated sulfuric acid (Jensen *et al.*, 1977; U.S. EPA, 1997, SW-846 Method 3660B, Sulfur cleanup). A 4 µL sub-sample was then analyzed by gas chromatography.

## **PCB Determinations**

Samples were analyzed for Aroclors 1248, 1254, and 1260 according to SW-846 Method 8082, Polychlorinated biphenyls by gas chromatography (U.S. EPA, 1997). Analysis were performed using a Hewlett-Packard (HP) Model 5890A gas chromatograph equipped with an electron capture detector and an HP Model 7673A Automatic Sampler. Samples were analyzed using a 60m X 0.53mm ID SPB-5 (0.5µm film) fused silica megabore column (Supelco, Inc.) with ultra-high purity helium and nitrogen as carrier and makeup gases, respectively. The temperature program was set at 160°C (6 min)-10°C/ min-235°C (0 min)-0.9°C/min-260°C (10 min); Injector temperature, 280°C; Detector temperature, 300°C. PCB peak heights were quantified : using an HP Model 3396A integrator. Aroclor levels were calculated from heights of 6 to 9 peaks for Aroclors 1248 and 1260 and 4-6 peaks for Aroclor 1254. Five external standards were used for calibration curves and for every tenth sample either a solvent blank or a standard was analyzed. Statistical quantitation of peak heights was

determined by multiple-peak linear regression analysis, which was performed with Lotus-123® software. The Lotus program regresses data from PCB standards to the sample being analyzed. Each peak selected for each Aroclor class was statistically analyzed (e.g., standard deviation; standard error; relative deviation). Chromatographs and bench records for all PCB assays will be maintained as given below under quality assurance.

### **Metal Determinations**

Eight metals of concern, silver (Ag), beryllium (Be), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), nickel (Ni), and zinc (Zn) were determined. Metal analysis was 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<sub>3</sub>) and check standards were processed with all samples. Sample concentrations were then corrected for deviations from the standards, and sample weights were factored into calculation of final values.

## **Mercury Methods**

EPA Method 7470A and Method 7471A (U.S. EPA, 1997) was followed for waters and solid matrices, respectively. Modifications made to the methods are described below. All acids used were TraceMetal grade and all chemicals were "Baker Analyzed" grade, or better. Water samples were preserved with approximately 5 mL nitric acid, and 100 mL of each sample was added to each BOD bottle. Then 2.5 mL concentrated nitric acid, 5 mL concentrated sulfuric acid, 15.0 mL 5% potassium permanganate solution, and 8 mL 10% potassium persulfate solution were added to each bottle which were heated at 90 °C for two hours. After allowing the bottles to cool, enough 12% hydroxylamine hydrochloride solution was added to each bottle to neutralize the potassium permanganate. Treating each sample individually, 5 mL 10% stannous chloride solution were added and the mercury analysis aerator was immediately put in place.

Mercury determinations were performed by cold vapor atomic absorption spectrophotometry (CVAAS) using a Coleman MAS-50B Mercury Analyzer System (Method 7471A, solids; Method 7470A, liquids, U.S. EPA, 1997). Calibration curves were based on eight standards. Check standards and reagent blanks also were analyzed with the samples.

## **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) replicate assays, 3) spiked and procedure recoveries, and 5) glassware solvent blanks.

## RESULTS

Metals detected in the water column of samples taken from Big and Little Bayou Creeks are reported in Tables 1 and 2 and Figures 1 through 5. The metal profiles in Big Bayou Creek were similar to those reported earlier (Birge and Price, 1997 and Birge, *et al.* 1998). Silver, beryllium, chromium, and zinc were sharply elevated in stream samples from station BB4, indicating contamination from effluent 008 (Figures 1,2,5). The predominant elevation in concentrations of copper, lead, and nickel occurred primarily at station BB5 or BB6, indicating possible contamination from effluents 006 and 001. It is important to note that elevations in silver, beryllium, and other metals persisted well downstream to the last monitoring station (BB9).

Concerning Little Bayou creek all metal except cadmium were elevated at and downstream of station LB2 (Table 2, Figures 1,2,4), indicating contamination from effluent 011 and/or other point sources upstream. Mercury was not detected at quantifiable concentrations in any of the water samples (Tables 3,4). No PCB contamination was detected in Big Bayou Creek. However, as in past studies (Birge and Price, 1998), Aroclor 1248 was observed at concentrations of 0.12 to 0.10  $\mu\text{g/L}$  at stations LB2 and LB2A on Little Bayou Creek (Tables 5,6). Results for glassware controls and procedure recoveries are given in Tables 7 and 8. The above results will be integrated into a final report after the remaining stream surveys have been completed. These results were reported by electronic format on January 21, 1999.



## REFERENCES

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Erickson, M.D. 1997. *Analytical Chemistry of PCBs*, 2<sup>nd</sup> edition. CRC Press, Boca Raton, FL. pp.667.

Federal Register. 1989. Good Laboratory Practice Standards. 40 CFR Part 160. August 17, 1989. Washington, DC.

Jensen, S., L. Renberg, and L. Reutergardh. 1977. Residue of sediment and sewage sludge for organochlorines in the presence of elemental sulfur. *Anal. Chem.* 49:316-318.

U.S. EPA. 1997. Test methods for evaluating solid wastes, SW-846, Final Update 3. Office of Solid Waste and Emergency Response, Washington, D.C.

Table 1. Metal concentrations in Stream Water from Big Bayou Creek Collected October 20, 1998.

			Water Metal Conc. ( $\mu\text{g/L}$ )							
Sample Name			Ag	Be	Cd	Cr	Cu	Pb	Ni	Zn
MC	102098	MSU1	<0.25	<0.10	<0.25	<0.50	<1.00	<0.50	2.19	2.62
BB1A	102098	MSU1	<0.25	0.10	<0.25	<0.50	<1.00	<0.50	<2.00	3.05
BB1	102098	MSU1	<0.25	<0.10	0.45	<0.50	1.80	0.70	6.30	3.52
BB2	102098	MSU1	<0.25	0.12	<0.25	<0.50	<1.00	<0.50	2.20	1.86
BB2A	102098	MSU1	<0.25	<0.10	<0.25	<0.50	<1.00	0.84	<2.00	3.50
BB3	102098	MSU1	<0.25	<0.10	<0.25	<0.50	<1.00	0.85	<2.00	5.56
BB4	102098	MSU1	0.42	0.40	<0.25	0.62	1.74	<0.50	<2.00	10.60
BB5	102098	MSU1	0.38	0.35	<0.25	0.74	1.36	1.60	<2.00	6.63
BB6	102098	MSU1	0.35	0.34	<0.25	<0.50	7.91	<0.50	3.35	6.56
BB7	102098	MSU1	0.35	0.34	<0.25	<0.50	1.36	1.72	<2.00	5.11
BB8	102098	MSU1	0.34	0.39	<0.25	<0.50	3.35	0.93	<2.00	4.16
BB9	102098	MSU1	<0.25	0.20	<0.25	<0.50	<1.00	1.11	<2.00	2.63

Table 2. Metal concentrations in Stream Water from Little Bayou Creek Collected October 20, 1998.

Sample Name			Water Metal Conc. (µg/L)							
			Ag	Be	Cd	Cr	Cu	Pb	Ni	Zn
LB2	102098	MSU1	0.53	0.55	<0.25	1.28	2.18	1.81	2.09	17.52
LB2A	102098	MSU1	0.28	0.34	<0.25	0.87	<1.00	1.89	3.20	14.57
LB3	102098	MSU1	0.47	0.43	<0.25	0.89	1.46	1.41	2.25	14.76
LB4	102098	MSU1	0.28	0.21	<0.25	2.02	1.21	<0.50	<2.00	6.66

Table 3. Mercury Concentrations in Stream Water from Big Bayou Creek  
Collected October 20, 1998.

Sample Number	µg Hg/L
MC102098HWSU1 <sup>a</sup>	<1.00
BB1A102098HWSU1	<1.00
BB1102098HWSU1	<1.00
BB2102098HWSU1	<1.00
BB2A102098HWSU1 <sup>b</sup>	<0.25
BB3102098HWSU1	<1.00
BB4102098HWSU1	<1.00
BB5102098HWSU1	<1.00
BB6102098HWSU1	<1.00
BB7102098HWSU1	<1.00
BB8102098HWSU1	<1.00
BB9102098HWSU1	<1.00

<sup>a</sup> Reference sample collected from a nearby stream of similar characteristics.

<sup>b</sup> Sample run twice. The more precise value is reported here.

Table 4. Mercury Concentrations in Stream Water from Little Bayou Creek  
Collected October 20, 1998.

Sample Number	$\mu\text{g Hg/L}$
LB2102098HWSU1	<1.00
LB2A102098HWSU1	<1.00
LB3102098HWSU1	<1.00
LB4102098HWSU1	<1.00

Table 5. PCB results for PGDP surface water samples collected from Big Bayou Creek October 20, 1998.

Sampling Station	Aroclor Concentration ( $\mu\text{g/L}$ )		
	1248	1254	1260
MC102098PWSU1	<0.080	<0.080	<0.080
MC102098PWSU2	<0.080	<0.080	<0.080
BB1A102098PWSU1	<0.080	<0.080	<0.080
BB1A102098PWSU2	<0.081	<0.081	<0.081
BB1102098PWSU1	<0.080	<0.080	<0.080
BB1102098PWSU2	<0.080	<0.080	<0.080
BB2102098PWSU1	<0.080	<0.080	<0.080
BB2102098PWSU2	<0.080	<0.080	<0.080
BB2A102098PWSU1	<0.080	<0.080	<0.080
BB2A102098PWSU2	<0.080	<0.080	<0.080
BB3102098PWSU1	<0.080	<0.080	<0.080
BB3102098PWSU2	<0.079	<0.079	<0.079
BB4102098PWSU1	<0.080	<0.080	<0.080
BB4102098PWSU2	<0.080	<0.080	<0.080
BB5102098PWSU1	<0.080	<0.080	<0.080
BB5102098PWSU2	<0.081	<0.081	<0.081
BB6102098PWSU1	<0.080	<0.080	<0.080
BB6102098PWSU2	<0.080	<0.080	<0.080
BB7102098PWSU1	<0.080	<0.080	<0.080
BB7102098PWSU2	<0.081	<0.081	<0.081
BB8102098PWSU1	<0.080	<0.080	<0.080
BB8102098PWSU2	<0.080	<0.080	<0.080
BB9102098PWSU1	<0.080	<0.080	<0.080
BB9102098PWSU2	<0.080	<0.080	<0.080

Table 6. PCB results for PGDP surface water samples collected from Little Bayou Creek October 20, 1998.

Sampling Station	Aroclor Concentration ( $\mu\text{g/L}$ )		
	1248	1254	1260
LB2102098PWSU1	<0.080	<0.080	<0.080
LB2102098PWSU2	0.116	<0.080	<0.080
LB2A102098PWSU1	0.107	<0.082	<0.082
LB2A102098PWSU2	0.101	<0.081	<0.081
LB3102098PWSU1	<0.080	<0.080	<0.080
LB3102098PWSU2	<0.080	<0.080	<0.080
LB4102098PWSU1	<0.080	<0.080	<0.080
LB4102098PWSU2	<0.080	<0.080	<0.080

Table 7. PCB Concentrations in Controls for Water Samples from Bayou Creek System Collected October 20, 1998.

Sampling Station	Aroclor Concentration ( $\mu\text{g/L}$ )		
	1248	1254	1260
CON102298PCON1W	<0.0003	<0.0003	<0.0003
CON102298PCON2W	<0.0003	<0.0003	<0.0003
CON102298PCON3W	<0.0003	<0.0003	<0.0003
CON102298PCON4W	<0.0003	<0.0003	<0.0003

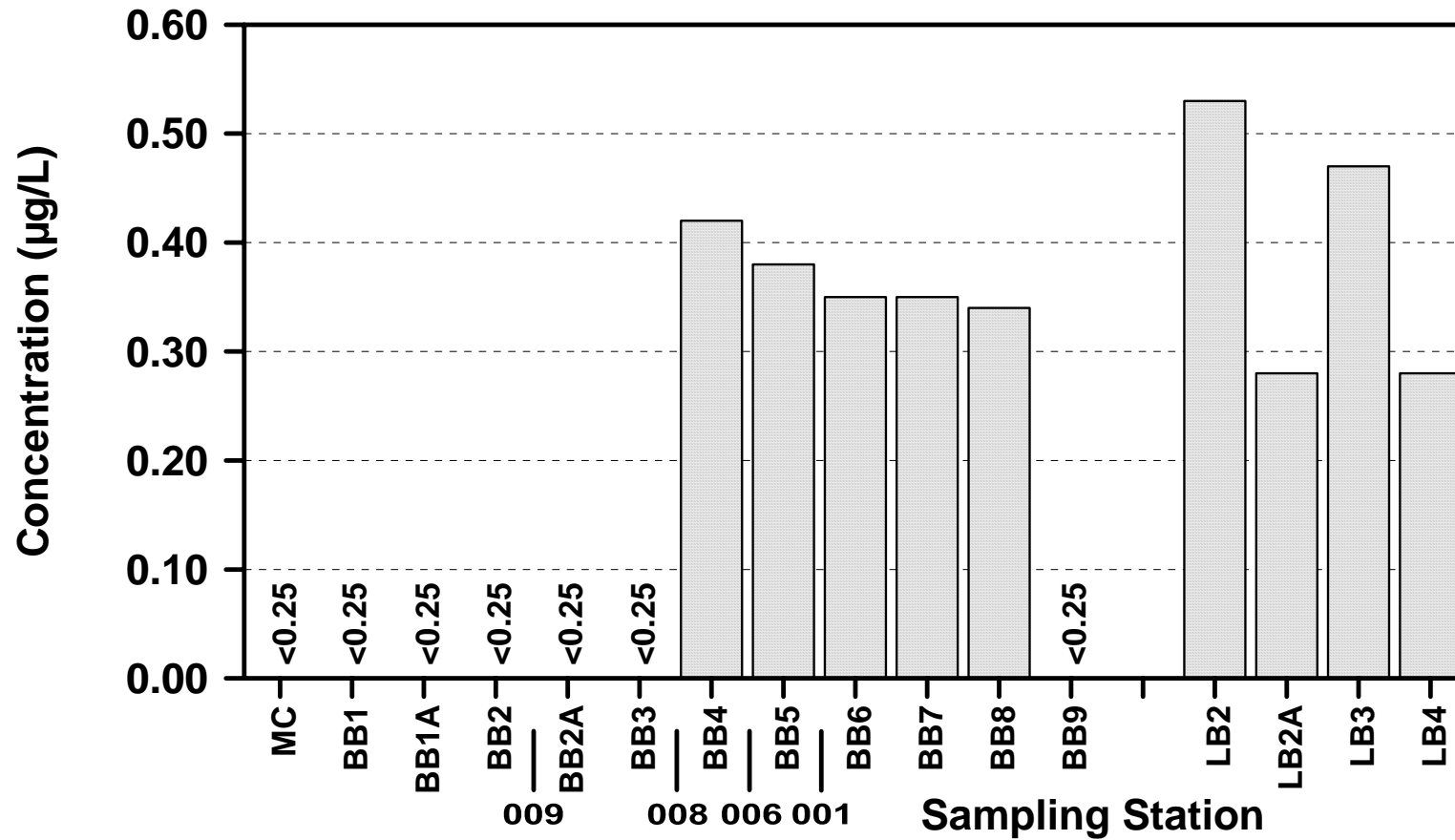


Table 8. PCB Concentrations in Procedure Recoveries <sup>a</sup> for Water Samples from Bayou Creek System Collected October 20, 1998.

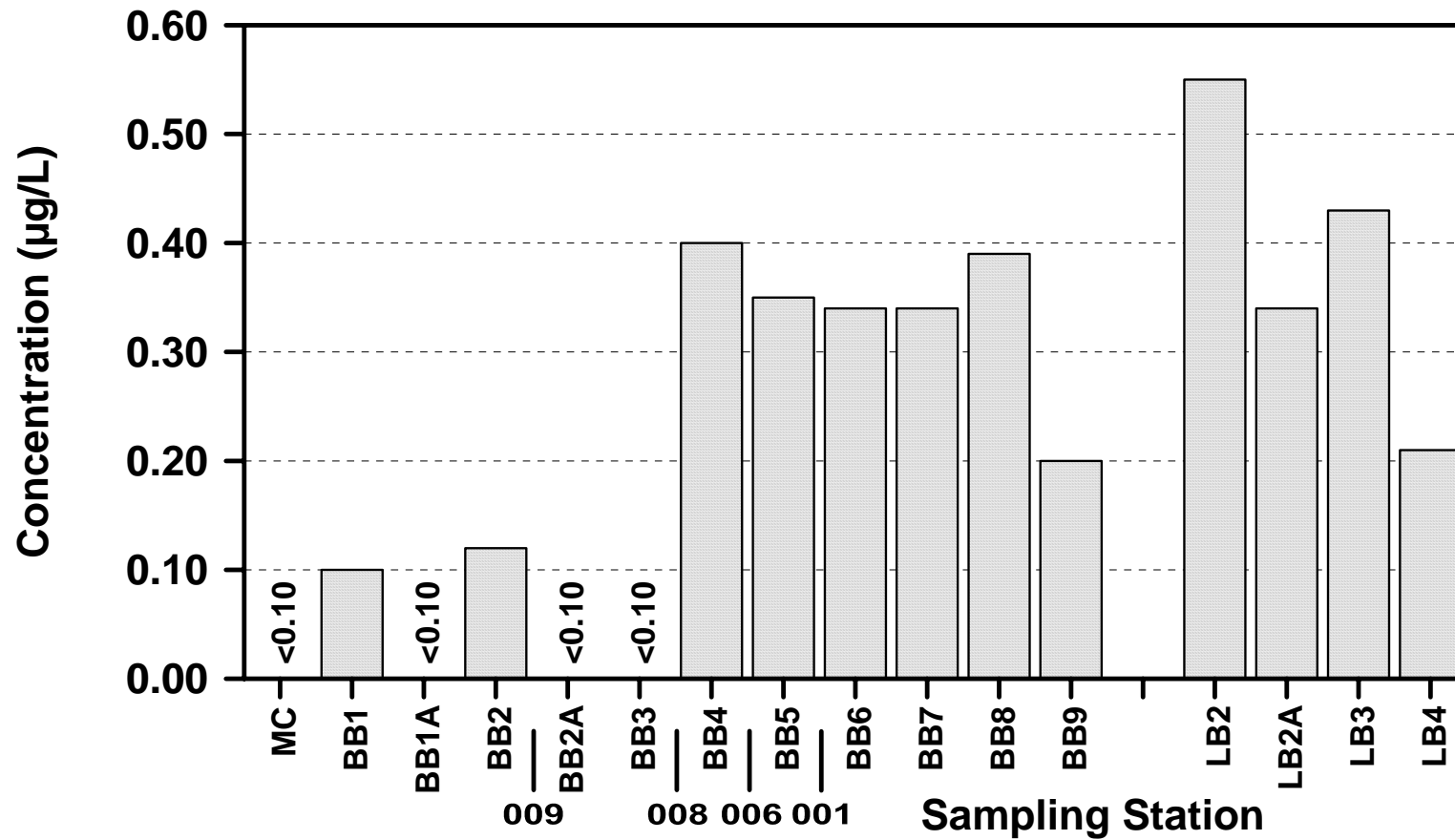
Sample Name	Aroclor	µg Spike	Aroclor Conc.(µg)		Percent Recovery
			Expected Conc.	Measured Conc.	
RECO102798PPRR1	1248	1.0	1.000	0.862	86.2
RECO102798PPRR2	1254	1.0	1.000	0.930	93.0
RECO102798PPRR3	1260	1.0	1.000	0.932	93.2
RECO102798PPRR4	1248	1.0	1.000	0.914	91.4
RECO102798PPRR5	1260	1.0	1.000	0.888	88.8

<sup>a</sup> 300 mL of solvent were spiked with the respective Aroclor, extracted and analyzed as a regular sample.

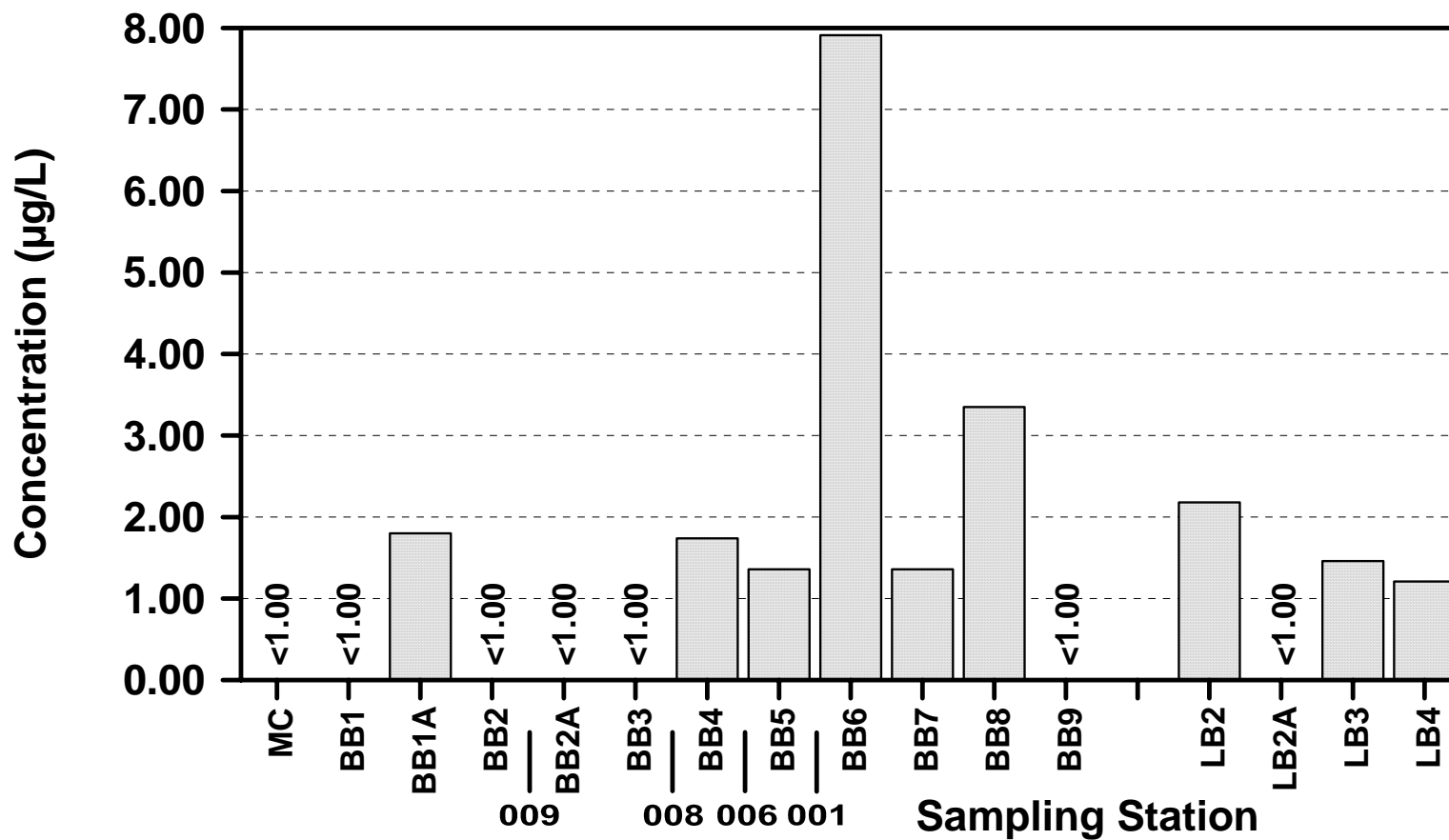
**Figure 1. Mean Silver Concentrations in Stream Surface Water from Bayou Creek Collected October 20, 1998.**



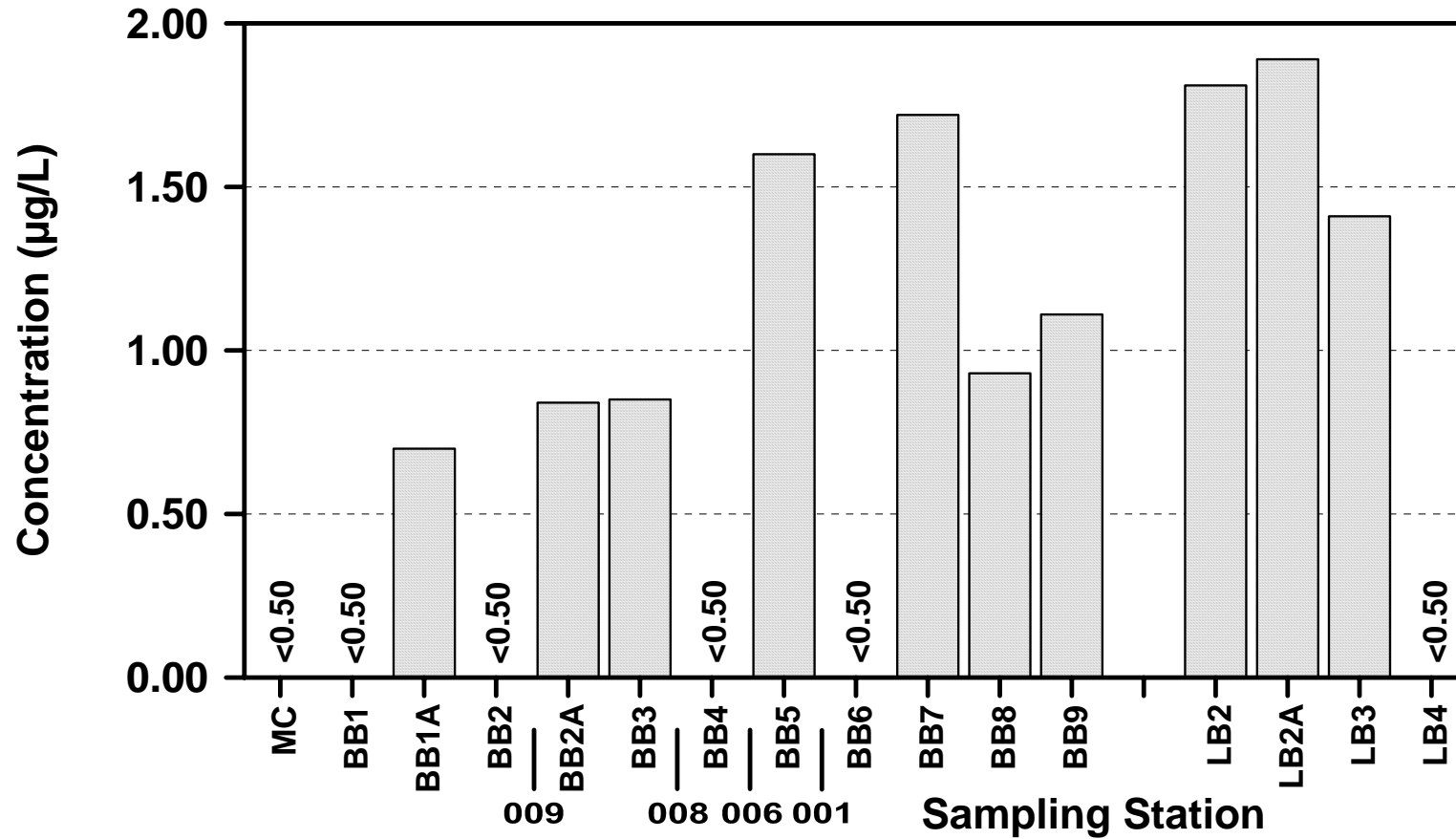
**Figure 2. Mean Beryllium Concentrations in Stream Surface Water from Bayou Creek Collected October 20, 1998.**



**Figure 3. Mean Copper Concentrations in Stream Surface Water from Bayou Creek Collected October 20, 1998.**



**Figure 4. Mean Lead Concentrations in Stream Surface Water from Bayou Creek Collected October 20, 1998.**



**Figure 5. Mean Zinc Concentrations in Stream Surface Water from Bayou Creek Collected October 20, 1998.**

