Polychlorinated Biphenyls (PCB) and Metals in Water Samples Collected September 25, 2000 from the Bayou Creek System

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INTRODUCTION

This report presents the results for water samples collected during high water conditions from Big and Little Bayou Creeks on September 25, 2000. Samples were collected from 11 stations on Big Bayou Creek, 5 on Little Bayou Creek, and 1 on Massac Creek. Samples collected from Massac Creek and BB1A served as "qualified" references. Three water samples were collected at each sampling station. One sample was used for PCB assays, one for physical parameters (*i.e.* settleable solids, suspended solids, conductivity) and one for metal assays. Three Aroclors (*i.e.* 1248, 1254, 1260) were determined for the PCB samples and 8 metals of concern (MOC, *i.e*. Ag, Be, Cd, Cr, Cu, Ni, Pb and Zn) were analyzed. In all, 51 water samples were processed.

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®. 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_3 upon collection and analyzed for total recoverable (TR) metals.

Settleable Solids, Suspended Solids and Conductivity

Determinations of settleable and suspended solids were performed using methods specified by APHA (1995). Measurements of conductivity were performed with a conductivity meter (Amber Science Model 604).

Water Extraction

Liquid-liquid extractions of PCBs were performed in separatory funnels following SW-846 Method 3510C (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 and concentrated to near dryness in a Roto-evaporator (Buchi Model RE121). The reconstituted samples (2.0 mL in isooctane) 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 ^{o}C/24 h) with 10.0 mL hexanes and evaporated to 2.0 mL (Erickson, 1997; U.S. EPA, 1997, 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). Analyses 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.) using ultra-high purity helium and nitrogen as carrier and makeup gases, respectively. 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 were analyzed, including silver (Ag), beryllium (Be), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), nickel (Ni), and zinc (Zn). Metal analyses were performed by atomic absorption spectrophotometry (AAS), using graphite furnace

atomization techniques (U.S. EPA 1997). 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 and sample weights were factored into calculations of final values.

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. These bench records will be archived within two years after the close of the project. Chain of Custody was maintained for all samples collected.

RESULTS

As noted above, water samples were collected under wet conditions and stream discharge was elevated. U.S. Geological Survey (USGS) stream discharge values for the Bayou Creek system are not yet available for this collecting period, but will be incorporated into follow-up reports when they are forthcoming.

PCBs

Results for PCB assays are given in Tables 1 and 2 for Big and Little Bayou Creeks, respectively. Of 11 water samples taken from Big Bayou Creek, there were no detection of Aroclors 1248, 1254, or 1260 (Table 1). Similar results were obtained for Massac Creek (MC) and Little Bayou Creek (Tables 1, 2). However, PCB retention time in the water column is of short duration and negative results apply only to the specific collecting period. PCB contamination in water has been reported previously.

Physical Parameters

Analyses of settleable solids (SS) revealed no distinct trend among stations and values were at or below 0.1 mL/500 mL at most collecting sites. However, total suspended solids (TSS) were elevated at Big Bayou Creek stations, as compared with the Massac Creek reference site (Table 3). The values (mg/L) obtained for Big Bayou Creek water samples were variable but somewhat higher at upstream stations BB1A and BB1. Likewise, the highest value (138.2 mg/L) for Little Bayou Creek was for the upstream station (LB1). Downstream of LB1, values for TSS ranged only from 16.45 to

54.20 mg/L. Further reference to TSS is given below, together with the results for metal assays. Conductivity generally was higher at stations BB4 through BB9 and LB2A through LB3. These are the areas which usually are most affected by PGDP effluents.

Metals

The most distinctive results concerned the upstream collecting sites BB1A and BB1. Samples form these stations contained disproportionately higher metal concentrations than shown 1) for earlier surveys of these stations (*e.g.*, March 2000; Birge and Price) or 2) values for most metals obtained at the effluent-impacted stations given in Table 1 and collected on the same date (*i.e.* September 25, 2000). For example, the highest values for lead (Pb) were 10.77 µg/L obtained at BB1A and 13.24 µg/L observed for BB1. By comparison, the value for station BB6, which usually is most contaminated with PB, was 8.21 µg/L. The distinctive patterns, in which the highest metal concentrations are observed at and below the effluent receiving zone, was not apparent in these data. This unusual condition is attributed, at least in part, to the wet field conditions and higher stream discharge that occurred on and just prior to the collection made on September 25, 2000.

However, it is not entirely clear as to why the upstream stations were disproportionately affected by the field conditions. It is expected that dissolved metals in some measure would adsorb to suspended particulates. Nevertheless, results obtained for settleable solids (SS) do not explain these phenomena. There was no close correlation between SS and metal concentrations. For example, Pb was 13.24 and 6.28

µg/L at BB1 and BB9, respectively. The values for SS were reversed. They were 0.1 and 0.3 mL/500 mL for stations BB1 and BB9. There was a somewhat closer fit between TSS and metal concentrations (Tables 1, 4). However, discrepancies occur when Pb or Zn values are compared with the corresponding TSS values for stations BB1A and BB1 versus stations BB3 and/or BB4. In addition, the preserved samples from upstream stations differed visually from the other samples. Therefore, further studies will be conducted, including spectrophotometric analysis.

As for Big Bayou Creek, highest values for most metals (*e.g.* Cr, Cu, Pb, Ni, Zn) in Little Bayou Creek were observed for the upstream reference station (*i.e.* LB1), but there was a stronger relationship with TSS. More study will be required to address the variations that occur between metal contamination and stream hydrology. These findings also bear on the question of the integrity of the upstream reference collecting stations and will require further investigation. Questions also should be addressed concerning soil erosion and downstream transport, as well as the possibility of other sources of metal contamination. Results of this survey are described further in Figures 1 through 12.

Table 1. PCB assays for water samples from Big Bayou Creek collected September 25, 2000.

	Aroclor Concentration (μg/L)		
Sampling Station	1248	1254	1260
MC[a]	<0.081	<0.081	<0.081
BB1A	<0.080	<0.080	<0.080
BB1	<0.082	<0.082	<0.082
BB2A	<0.081	<0.081	<0.081
BB2	<0.082	<0.082	<0.082
BB3	<0.082	<0.082	<0.082
BB4	<0.082	<0.082	<0.082
BB5	<0.082	<0.082	<0.082
BB6	<0.081	<0.081	<0.081
BB7	<0.082	<0.082	<0.082
BB8	<0.082	<0.082	<0.082
BB9	<0.082	<0.082	<0.082

[a]MC indicates the Massac Creek reference station.

Table 2. PCB assays for water samples from Little Bayou Creek collected September 25, 2000.

	Aroclor Concentration (μg/L)		
Sampling Station	1248	1254	1260
LB1	<0.082	<0.082	<0.082
LB2	<0.082	<0.082	<0.082
LB2A	<0.081	<0.081	<0.081
LB3	<0.082	<0.082	<0.082
LB4	<0.081	<0.081	<0.081

Table 3. Results for settleable solids, suspended solids, and conductivity for surface water samples collected from the Bayou Creek system September 25, 2000.

Station	Settleable Solids (mL/500 mL)	Suspended Solids (mg/L)	Conductivity (µMHOs/cm)
MC[a]	<0.1	40.40	107
BB1A	0.2	171.80	119
BB1	0.1	185.23	126
BB2A	0.1	137.00	116
BB2	0.2	78.04	90
BB3	0.25	172.55	122
BB4	0.1	149.02	159
BB5	0.1	104.18	189
BB6	0.1	141.20	188
BB7	0.2	121.96	189
BB8	0.2	120.78	181
BB9	0.3	114.65	149
LB1	0.05	138.20	215
LB2A	<0.1	22.32	338
LB2	<0.1	17.77	277
LB3	<0.1	16.45	253
LB4	0.1	54.20	158

[a]MC indicates Massac Creek reference station.

Table 4. Metal concentrations in water samples from Big Bayou Creek collected on September 25, 2000.

Sample Name			Water Metal Conc. (µg/L)							
			Ag	Be	Cd	Cr	Cu	Pb	Ni	Zn
MC	092500	MSU1	0.18*	0.28	<0.25	2.67	3.58	6.44	<1.00	5.38
BB1A	092500	MSU1	0.14*	0.77	<0.25	6.34	6.23	10.77	3.74	19.29
BB1	092500	MSU1	0.10*	0.79	<0.25	7.51	7.55	13.24	4.56	11.57
BB2A	092500	MSU1	0.05*	0.45	<0.25	4.64	3.79	6.45	2.12	14.92
BB2	092500	MSU1	0.04*	0.28	<0.25	3.42	2.87	4.16	1.07	10.32
BB3	092500	MSU1	0.11*	0.54	<0.25	6.19	5.33	8.47	3.46	14.70
BB4	092500	MSU1	0.15*	0.55	<0.25	6.72	5.97	7.51	2.31	14.56
BB5	092500	MSU1	0.20*	0.37	<0.25	4.64	3.92	5.35	1.19	10.09
BB6	092500	MSU1	0.16*	0.50	<0.25	7.07	6.47	8.21	1.80	13.63
BB7	092500	MSU1	0.20*	0.51	<0.25	5.01	8.99	8.25	1.64	12.63
BB8	092500	MSU1	0.16*	0.55	<0.25	4.42	5.80	6.18	2.23	11.59
BB9	092500	MSU1	0.16*	0.38	<0.25	4.52	4.88	6.28	1.48	8.06

* Values below Minimum Quantitation Limit (MQL). For qualitative purposes only.

Table 5. Metal concentrations in water samples from Little Bayou Creek collected on September 25, 2000.

Sample Name			Water Metal Conc. (µg/L)							
			Ag	Be	Cd	Cr	Cu	Pb	Ni	Zn
LB1	092500	MSU1	0.19*	0.58	<0.25	6.39	4.80	6.53	1.63	56.28
LB2A	092500	MSU1	0.27	0.34	<0.25	3.41	1.71	<3.00	<1.00	9.85
LB2	092500	MSU1	0.25	<0.25	<0.25	3.08	1.89	<3.00	<1.00	9.93
LB3	092500	MSU1	0.20*	<0.25	<0.25	2.99	2.10	<3.00	<1.00	6.50
LB4	092500	MSU1	0.12*	0.25	<0.25	5.04	3.17	<3.00	<1.00	10.43

* Values below Minimum Quantitation Limit (MQL). For qualitative purposes only.

Figure 1. Silver Concentrations in Stream Surface Water from Big Bayou Creek Collected September 25, 2000.

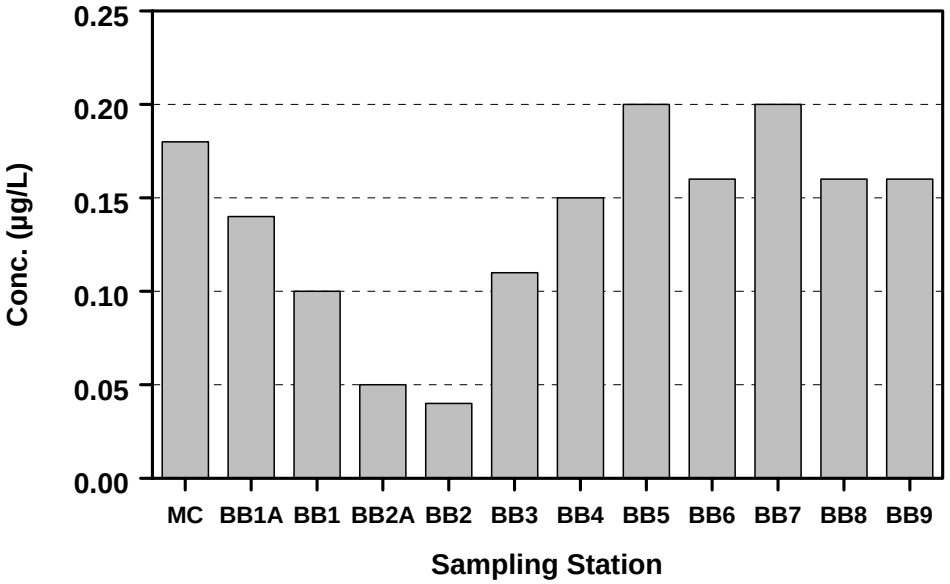


Figure 2. Beryllium Concentrations in Stream Surface Water from Big Bayou Creek Collected September 25, 2000.

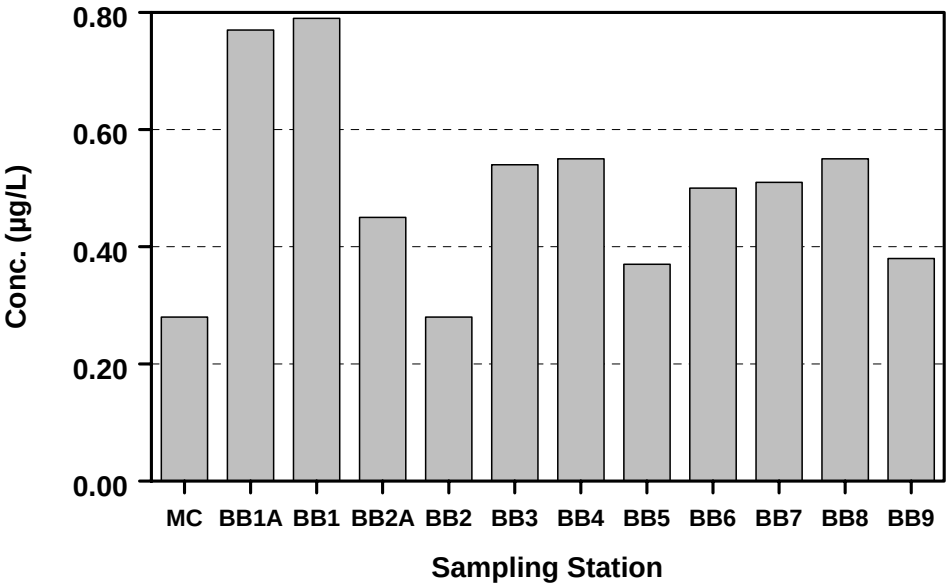


Figure 3. Chromium Concentrations in Stream Surface Water from Big Bayou Creek Collected September 25, 2000.

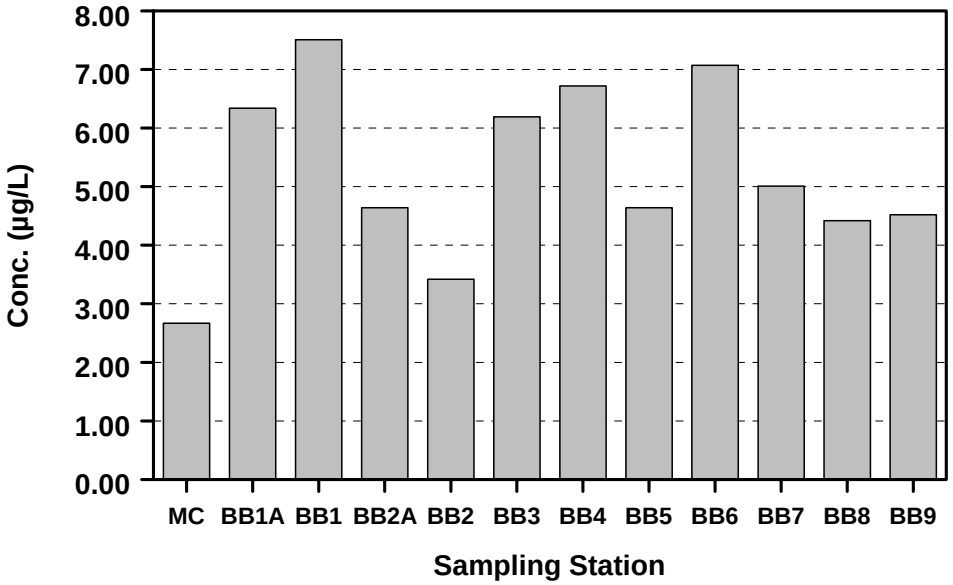


Figure 4. Copper Concentrations in Stream Surface Water from Big Bayou Creek Collected September 25, 2000.

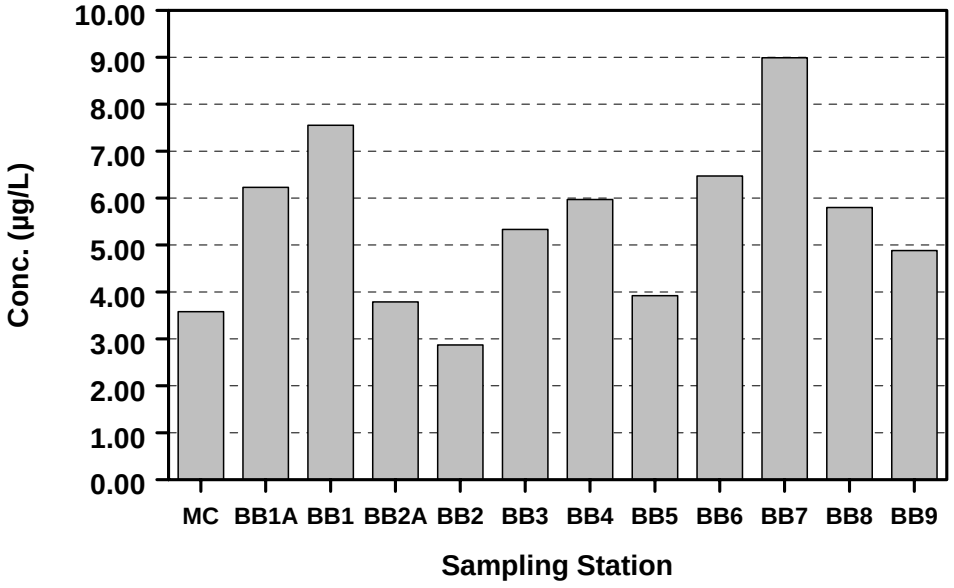


Figure 5. Nickel Concentrations in Stream Surface Water from Big Bayou Creek Collected September 25, 2000.

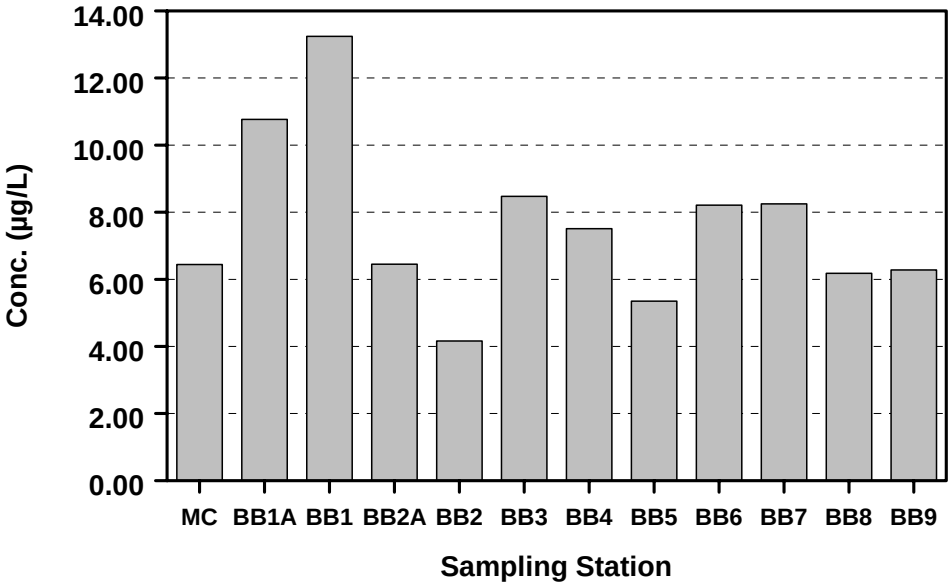


Figure 6. Lead Concentrations in Stream Surface Water from Big Bayou Creek Collected September 25, 2000.

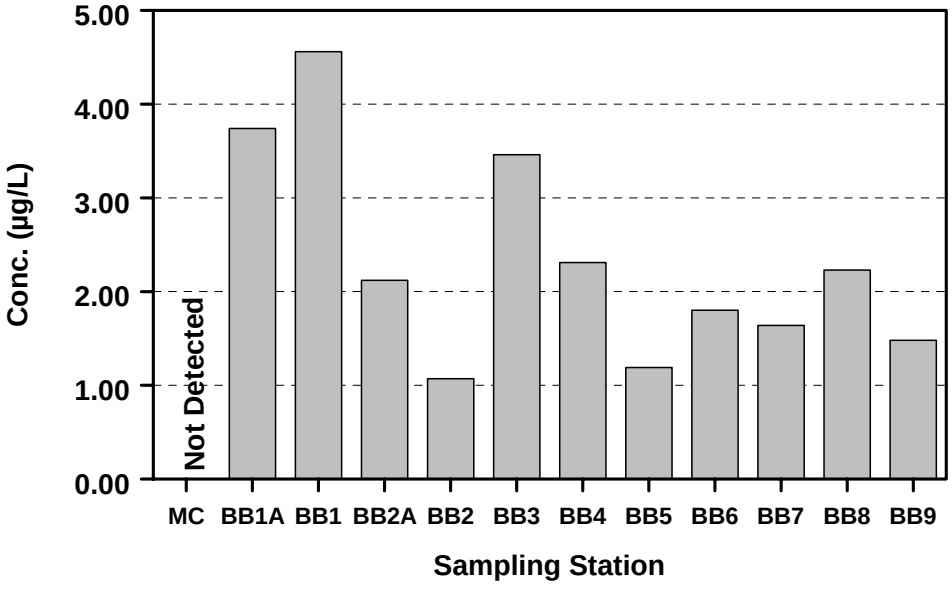


Figure 7. Zinc Concentrations in Stream Surface Water from Big Bayou Creek Collected September 25, 2000.

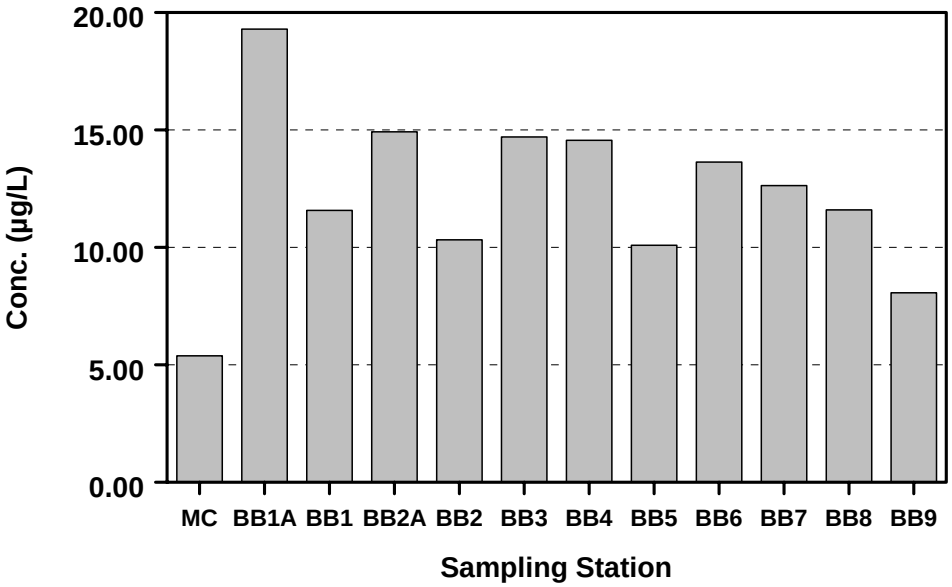


Figure 8. Silver Concentrations in Stream Surface Water from Little Bayou Creek Collected September 25, 2000.

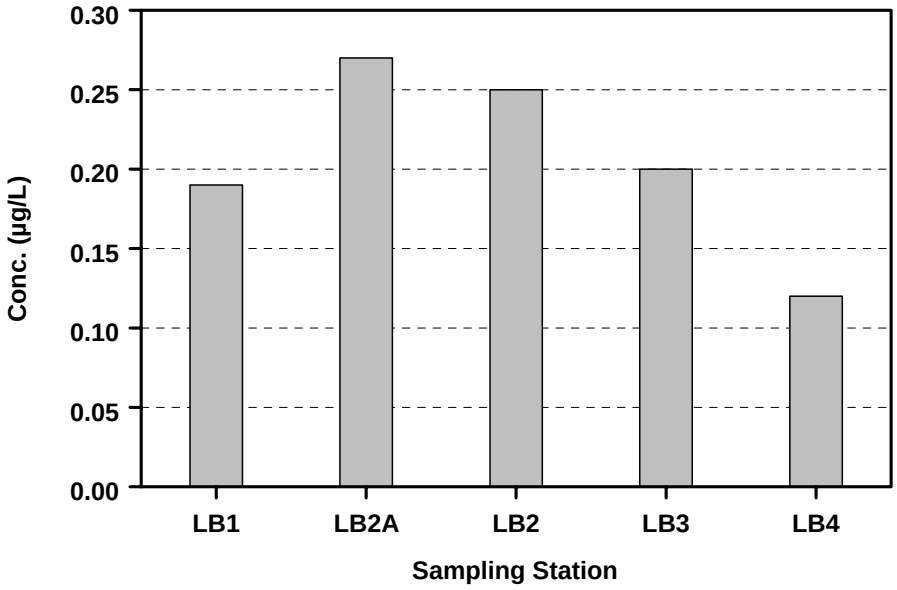


Figure 9. Beryllium Concentrations in Stream Surface Water from Little Bayou Creek Collected September 25, 2000.

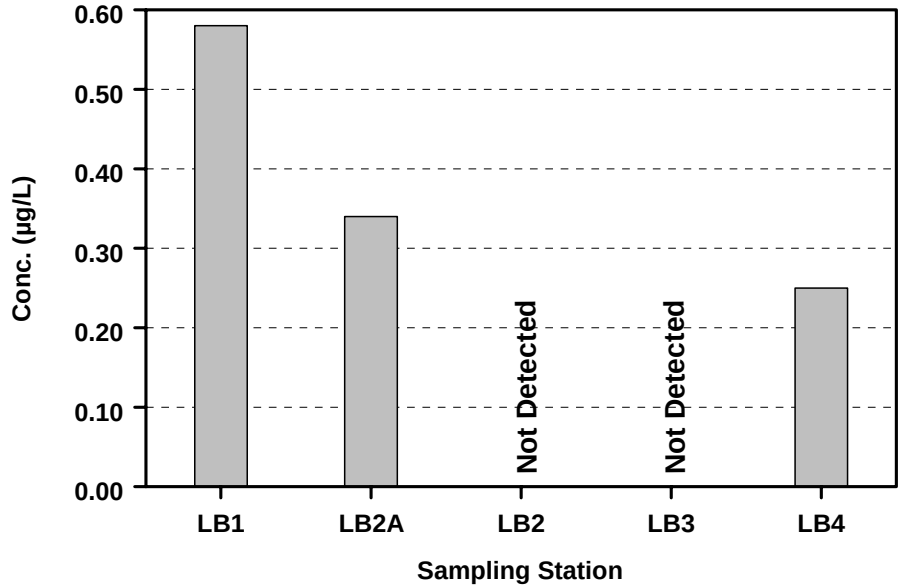


Figure 10. Chromium Concentrations in Stream Surface Water from Little Bayou Creek Collected September 25, 2000.

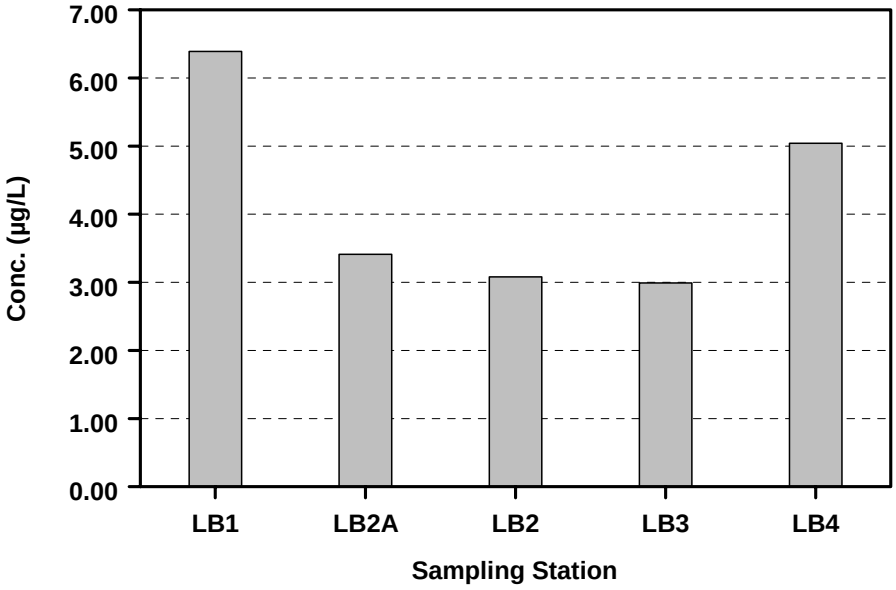


Figure 11. Copper Concentrations in Stream Surface Water from Little Bayou Creek Collected September 25, 2000.

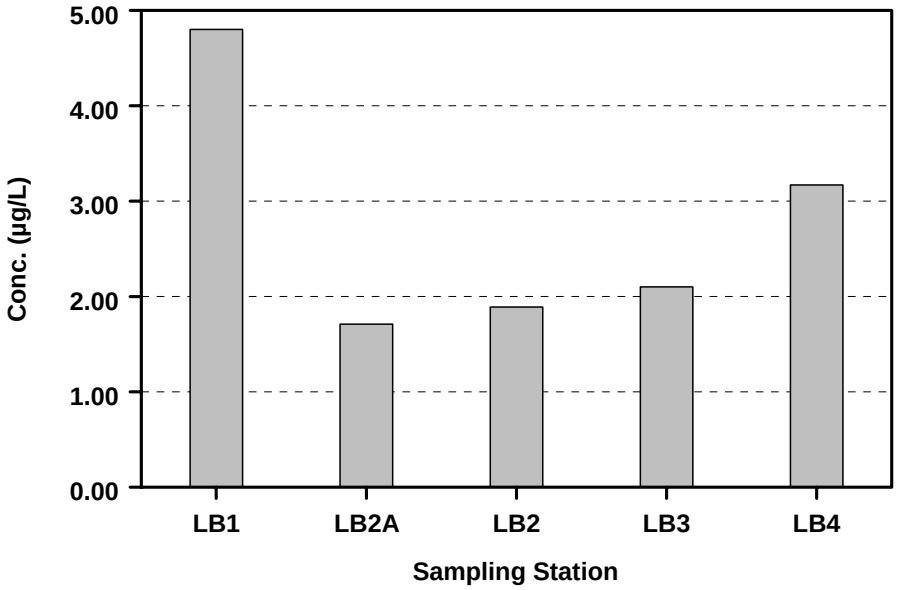
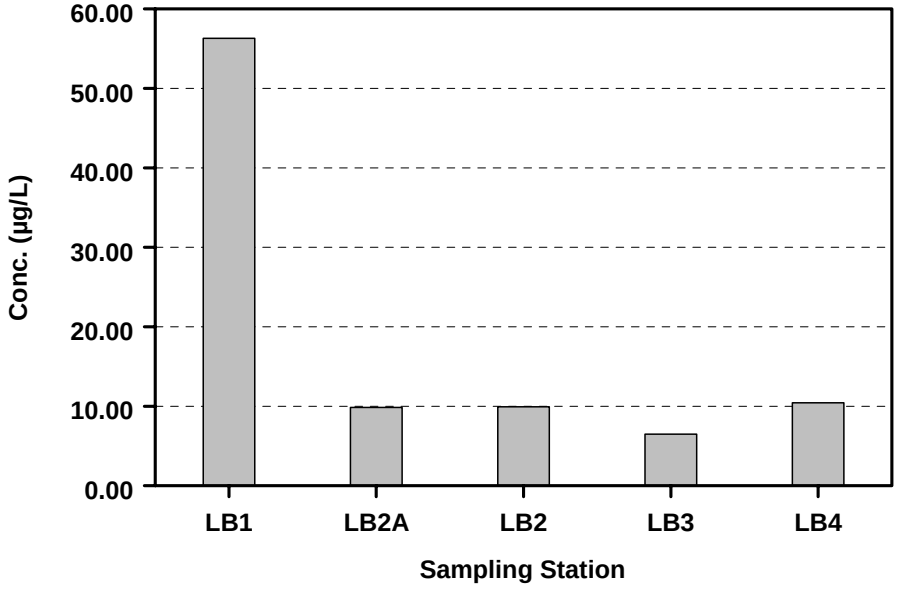


Figure 12. Zinc Concentrations in Stream Surface Water from Little Bayou Creek Collected September 25, 2000.



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