

**Analysis of Metals and Polychlorinated Biphenyl (PCB) Residues
in Water Samples Collected September 9, 1999
from the Bayou Creek System**

Wesley J. Birge

David J. Price

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Jon Maybriar

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INTRODUCTION

Samples were taken for metal and PCB analyses from the water column of Big and Little Bayou Creeks on September 9, 1999. Sampling stations BB1 through BB9 on Big Bayou Creek and LB2A through LB4 on Little Bayou Creek were included in this field survey. The new reference station, upstream of BB1 and designated BB1A, also was collected. In addition, Massac Creek (MC) was sampled and served as a reference station independent of the Bayou Creek system. Two samples were collected for PCB assays for each of the sampling stations. Two samples per station were collected for metal assays. Three Aroclors (*i.e.* 1248, 1254, and 1260) were determined for the samples and 8 metals (*i.e.* Ag, Be, Cd, Cr, Cu, Ni, Pb and Zn) were analyzed.

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 HNO₃ upon collection and analyzed for total recoverable (TR) metals.

Metal Determinations

Eight metals, including 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 % HNO₃) 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.

PCB Water Extractions

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 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, 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 μ L 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 (0.5 μ m 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.

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 assays are presented in Table 1 for two independent samples taken from each station on Big Bayou Creek. The most important findings for Big Bayou Creek include the origin of toxic metals from effluent 008 detected at the adjacent station, BB4. This included silver (Ag), beryllium (Be), copper (Cu), lead (Pb), nickel (Ni) and zinc (Zn). This source of contamination was traceable continuously all the way through the most downstream station (*i.e.* BB9) for Ag, Be, Cu and to a lesser extent for the other metals. Silver was detected at concentrations that clearly could affect aquatic life.

Concerning Little Bayou Creek (Table 2), Ag and Be were detected at and below station LB2A. Silver water column concentrations ranged from 0.25 to 0.40 µg/L. The chronic criterion likely to be proposed for Ag will be in the range of 0.10 to 0.20 µg/L.

Results for PCB analyses are given in Table 3. Aroclors 1254 and 1260 were detected at station LB2 on Little Bayou Creek and at station BB2 on Big Bayou Creek. The LB2 site is adjacent to the Ash Landfill. There was little or no flow at BB2 at the time of collection and a light oil sheen was observed on the persisting pools. This may have accounted for the presence of PCB. Quality assurance results for PCB included 30 assays and are given in Tables 5 through 7.

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

			Water Metal Conc. (µg/L)							
Sample Name			Ag	Be	Cd	Cr	Cu	Pb	Ni	Zn
MC	090999	MSU1	<0.25	<0.25	<0.25	<1.00	<1.00	<3.00	<0.50	<1.00
BB1	090999	MSU1	<0.25	0.38	<0.25	<1.00	<1.00	<3.00	<0.50	12.45
BB1	090999	MSU2	<0.25	0.32	<0.25	<1.00	<1.00	<3.00	<0.50	60.96
BB1A	090999	MSU1	<0.25	0.34	<0.25	<1.00	<1.00	<3.00	0.67	<1.00
BB1A	090999	MSU2	<0.25	0.33	<0.25	<1.00	<1.00	<3.00	<0.50	<1.00
BB2	090999	MSU1	<0.25	0.39	0.26	<1.00	<1.00	5.50	0.65	1.44
BB2	090999	MSU2	<0.25	0.33	0.27	5.36	<1.00	4.67	<0.50	<1.00
BB2A	090999	MSU1	<0.25	<0.25	<0.25	1.79	1.37	<3.00	1.52	1.84
BB2A	090999	MSU2	<0.25	0.50	<0.25	<1.00	<1.00	<3.00	<0.50	<1.00
BB3	090999	MSU1	<0.25	0.83	<0.25	<1.00	<1.00	<3.00	<0.50	<1.00
BB3	090999	MSU2	<0.25	0.84	<0.25	<1.00	<1.00	<3.00	<0.50	<1.00
BB4	090999	MSU1	0.33	0.42	<0.25	<1.00	5.22	3.81	0.51	2.82
BB4	090999	MSU2	0.45	0.94	<0.25	<1.00	5.10	4.15	<0.50	1.81
BB5	090999	MSU1	<0.25	0.28	<0.25	1.74	4.72	<3.00	0.53	5.15
BB5	090999	MSU2	<0.25	0.32	<0.25	1.14	2.50	<3.00	<0.50	2.05

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

			Water Metal Conc. (µg/L)							
Sample Name			Ag	Be	Cd	Cr	Cu	Pb	Ni	Zn
BB6	090999	MSU1	0.34	0.46	<0.25	1.05	3.58	3.28	<0.50	<1.00
BB6	090999	MSU2	0.28	0.36	<0.25	1.05	2.87	<3.00	<0.50	<1.00
BB7	090999	MSU1	0.27	0.34	<0.25	1.55	2.37	<3.00	0.76	<1.00
BB7	090999	MSU2	0.31	0.36	<0.25	1.00	1.53	<3.00	0.59	<1.00
BB8	090999	MSU1	0.28	0.46	<0.25	<1.00	1.08	<3.00	0.75	2.66
BB8	090999	MSU2	0.29	0.41	<0.25	1.74	1.44	<3.00	<0.50	<1.00
BB9	090999	MSU1	0.33	0.33	<0.25	<1.00	<1.00	<3.00	<0.50	<1.00
BB9	090999	MSU2	<0.25	0.41	<0.25	<1.00	<1.00	<3.00	0.51	<1.00

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

			Water Metal Conc. (µg/L)							
Sample Name			Ag	Be	Cd	Cr	Cu	Pb	Ni	Zn
LB2A	090999	MSU1	<0.25	0.56	<0.25	1.80	<1.00	<3.00	1.08	1.99
LB2A	090999	MSU2	<0.25	0.47	<0.25	2.66	<1.00	<3.00	1.24	4.10
LB2	090999	MSU1	0.40	0.76	<0.25	1.44	<1.00	3.15	<0.50	4.83
LB2	090999	MSU2	0.39	0.73	<0.25	1.44	<1.00	<3.00	<0.50	2.60
LB3	090999	MSU1	0.30	0.68	<0.25	<1.00	<1.00	<3.00	<0.50	3.35
LB3	090999	MSU2	0.29	0.81	<0.25	<1.00	<1.00	<3.00	<0.50	<1.00
LB4	090999	MSU1	0.25	0.42	<0.25	1.57	<1.00	<3.00	<0.50	<1.00
LB4	090999	MSU2	<0.25	0.96	<0.25	1.59	<1.00	<3.00	<0.50	<1.00

Table 3. PCB results for PGDP surface water samples collected from Big Bayou Creek September 9, 1999.

Sampling Station	Aroclor Concentration ($\mu\text{g/L}$)		
	1248	1254	1260
MC-090999-PWSU1	<0.081	<0.081	<0.081
BB1A-090999-PWSU1	<0.080	<0.080	<0.080
BB1A-090999-PWSU2	<0.080	<0.080	<0.080
BB1-090999-PWSU1	<0.095	<0.095	<0.095
BB1-090999-PWSU2	<0.096	<0.096	<0.096
BB2-090999-PWSU1	<0.080	<0.080	<0.080
BB2-090999-PWSU2	<0.080	0.067*	<0.080
BB2A-090999-PWSU1	<0.080	<0.080	<0.080
BB2A-090999-PWSU2	<0.082	<0.082	<0.082
BB3-090999-PWSU1	<0.080	<0.080	<0.080
BB3-090999-PWSU2	<0.081	<0.081	<0.081
BB4-090999-PWSU1	<0.081	<0.081	<0.081
BB4-090999-PWSU2	<0.081	<0.081	<0.081
BB5-090999-PWSU1	<0.080	<0.080	<0.080
BB5-090999-PWSU2	<0.080	<0.080	<0.080
BB6-090999-PWSU1	<0.082	<0.082	<0.082
BB6-090999-PWSU2	<0.084	<0.084	<0.084
BB7-090999-PWSU1	<0.082	<0.082	<0.082
BB7-090999-PWSU2	<0.083	<0.083	<0.083
BB8-090999-PWSU1	<0.080	<0.080	<0.080
BB8-090999-PWSU2	<0.081	<0.081	<0.081
BB9-090999-PWSU1	<0.080	<0.080	<0.080
BB9-090999-PWSU2	<0.080	<0.080	0.088

* Values detected, but below minimum quantitation limit (MQL).

Table 3, continued. PCB results for PGDP surface water samples collected from Little Bayou Creek September 9, 1999.

Sampling Station	Aroclor Concentration ($\mu\text{g/L}$)		
	1248	1254	1260
LB2-090999-PWSU1	<0.080	0.085	0.041*
LB2-090999-PWSU2	<0.080	0.062*	0.052*
LB2A-090999-PWSU1	<0.080	<0.080	<0.080
LB2A-090999-PWSU2	<0.080	<0.080	<0.080
LB3-090999-PWSU1	<0.080	<0.080	<0.080
LB3-090999-PWSU2	<0.080	<0.080	<0.080
LB4-090999-PWSU1	<0.083	<0.083	<0.083
LB4-090999-PWSU2	<0.080	<0.080	<0.080

* Values detected, but below minimum quantitation limit (MQL).

Table 4. PCB Concentrations in Controls^a for Water Samples from Bayou Creek System Collected September 9, 1999.

Sample Name	Aroclor Conc. ($\mu\text{g/L}$) ^b		
	1248	1254	1260
CON-091499-PCON1W	<0.080 <0.080	<0.080 <0.080	<0.080 <0.080
CON-091499-PCON2W	<0.080	<0.080	<0.080
CON-091599-PCON3W	<0.080	<0.080	<0.080
CON-091699-PCON4W	<0.080 <0.080	<0.080 <0.080	<0.080 <0.080

^a 1.0 L deionized water extracted as a regular sample.

^b Second number corresponds to confirmatory analysis on separate GC.

Table 5. PCB Concentrations in Procedure Recoveries ^A for Water Samples from Bayou Creek System Collected September 9, 1999.

Sample Name	Aroclor	µg Spike	Aroclor Conc. (µg)		Percent Recovery
			Expected Conc.	Measured Conc.	
RECO-091699-PPRR1	1248	1.0	1.000	0.847	85
RECO-091699-PPRR2	1254	1.0	1.000	0.764	76
RECO-091699-PPRR3	1260	1.0	1.000	0.714	71
RECO-091699-PPRR4	1248	1.0	1.000	1.057	106
RECO-091699-PPRR5	1254	1.0	1.000	0.771	77
RECO-091699-PPRR6	1260	1.0	1.000	0.788	79

^A 300 mL of solvent were spiked with the respective Aroclor, extracted and analyzed as a regular sample.

Table 6. Confirmatory PCB Concentrations in Procedure Recoveries ^A for Water Samples from Bayou Creek System Collected September 9, 1999.

Sample Name	Aroclor	µg Spike	Aroclor Conc. (µg)		Percent Recovery
			Expected Conc.	Measured Conc.	
RECO-091699-PPRR1	1248	1.0	1.000	1.179	118
RECO-091699-PPRR2	1254	1.0	1.000	1.211	121
RECO-091699-PPRR3	1260	1.0	1.000	0.912	91
RECO-091699-PPRR4	1248	1.0	1.000	1.085	109
RECO-091699-PPRR5	1254	1.0	1.000	1.194	119
RECO-091699-PPRR6	1260	1.0	1.000	0.987	99

^A 300 mL of solvent were spiked with the respective Aroclor, extracted and analyzed as a regular sample.

Table 7. Confirmatory PCB results for PGDP surface water samples collected from Bayou Creek September 9, 1999.

Sampling Station	Aroclor Concentration ($\mu\text{g/L}$)		
	1248	1254	1260
BB2A-090999-PWSU1	<0.080	<0.080	<0.080
BB3-090999-PWSU1	<0.080	<0.080	<0.080
BB4-090999-PWSU2	<0.081	<0.081	<0.081
BB5-090999-PWSU2	<0.080	<0.080	<0.080
BB6-090999-PWSU2	<0.084	<0.084	<0.084
BB7-090999-PWSU1	<0.082	<0.082	<0.082
BB8-090999-PWSU1	<0.080	<0.080	<0.080
BB9-090999-PWSU1	<0.080	<0.080	0.069*
LB2-090999-PWSU2	<0.080	<0.080	0.069*
LB2A-090999-PWSU1	<0.080	<0.080	0.067*
LB3-090999-PWSU2	<0.080	<0.080	<0.080
LB4-090999-PWSU2	<0.080	<0.080	<0.080

* Values detected, but below minimum quantitation limit (MQL).

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