Analysis of Polychlorinated Biphenyl Mixtures (PCB) in Water Samples Collected from the Bayou Creek System on June 3-4, 2002

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DRAFT REPORT

March 18, 2003

Submitted to

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Kentucky Department for Environmental Protection

INTRODUCTION

Water samples (36 samples) were taken from Big and Little Bayou Creeks on June 3-4, 2002 for PCB analyses. A total of 12 sites were sampled from Big Bayou Creek (stations BB1A through BB9) and 5 sites were included for Little Bayou Creek (stations LB1 through LB4). A new station, upstream of BB1A and designated BB1U, was added to this stream survey. In addition, Massac Creek (MC) was sampled and served as a possible reference station independent of the Bayou Creek system. The MC station was on the West Fork of Massac Creek. Water samples also were taken at each station for general water quality analyses which included pH, conductivity, alkalinity, and hardness. Two water samples per station were collected for PCB assays. Three Aroclors (*i.e.* 1248, 1254, and 1260) were analyzed for each sample.

METHODS

Water Collection

General Water Quality: On-site measurements were taken from stream water. These measurements included temperature, pH, and conductivity. Samples for dissolved oxygen, hardness and alkalinity measurements were collected in 1-L "Cubitainer" receptacles and were placed on ice until delivery to the laboratory.

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.

General Water Quality

On-site water quality measurements, which included temperature, pH, and conductivity, were taken with a YSI 650 MDS meter and a YSI 600 QS multi-parameter sonde. Dissolved oxygen was measured with a YSI Model 51A oxygen meter. Parameters of pH, conductivity, alkalinity and hardness were measured according to procedures described by APHA (1995). The measurements were performed with a pH meter (Orion Research EA920), a conductivity meter (Amber Science Model 604), the bromocresol green-methyl red titrimetric and EDTA titrimetric procedures, respectively.

PCB Water Extractions

Liquid-liquid extractions 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 iso-octane) were cleaned of interferences as described below and then analyzed by gas chromatography.

Sample Cleanup

Lipid and pesticide cleanup 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 hexane and evaporated to 2.0 mL (Erickson, 1997; U.S EPA, 1997 Method 3620B). Elemental sulfur was 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 Method 3660B). A 4 μL sub-sample was analyzed by gas chromatography.

PCB Determinations

Samples were analyzed for Aroclors 1248, 1254, and 1260 according to SW-846 Method 8082 (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.) with ultra-high purity helium and nitrogen as carrier and makeup gases, respectively. The temperature program was regulated at 160 °C to 235 °C at 10 °C/min, then 235 °C to 260 °C at 0.9 °C/min, and held for 10 min. Injector temperature was 280 °C and detector temperature was 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 for each Aroclor 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 was maintained for all samples collected.

RESULTS

Water Quality

The results for general water quality parameters are given in Table 1. Overall, all pH values were within the preferred range of 6.5-8.5. Conductivity ranged from 137.5 to 1011.0 µS/cm and was highest at BB6 and BB7. The latter was attributed to electrolytes contained in the 001 effluent. Alkalinity was in the "moderate" range and varied from 20 to 32 mg $CaCO_3$/L in Big Bayou Creek and 28 to 36 mg $CaCO_3$/L in Little Bayou Creek. Hardness ranged from 48 to 244 mg $CaCO_3$/L and 92 to 124 mg $CaCO_3$/L for Big and Little Bayou Creeks, respectively. Hardness levels were highest for stations BB6, BB7 and BB8.

PCB Contamination

Results for PCB analyses of water samples are given in Tables 2 and 3 for Big and Little Bayou Creeks, respectively. PCBs were detected at stations BB6, BB7, and BB8 on Big Bayou Creek, with Aroclor 1248 values of 0.11, 0.12, and 0.14 µg/L, respectively. No PCBs were detected in any of the other Big Bayou Creek water samples collected, observing detection limits of 0.08 to 0.09 µg PCB/L. Aroclor 1248 also was detected for stations LB2A and LB2 on Little Bayou Creek, with mean values of 0.12 ± 0.03 and 0.10 ± 0.01 µg/L, respectively.

In summary, PCB (*i.e*. Aroclor 1248) was detected in the water column in five collecting stations within the Bayou Creek system. Considering the short residence time of PCBs in stream water and that only Aroclor 1248 was detected, it was concluded that the contamination likely was of recent origin. At all five stations, the concentrations detected were above values considered acceptable by the Commonwealth of Kentucky for aquatic life and human health. Further studies will be undertaken.

REFERENCES

APHA-American Public Health Association, American Water Works Association and Water Pollution Control Federation. 1995. Standard Methods for the Examination of Water and Wastewater, 19th edition. American Public Health Association, Washington, DC.

Erickson, M.D. 1997. *Analytical Chemistry of PCBs*, 2nd 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. Water quality results for stream water samples from the Bayou Creek system collected June 3-4, 2002.

Station	Temperature (^{o}C)	pH	Conductivity (µS/cm)	D.O. (mg/L)	Alkalinity (mg $CaCO_3$/L)	Hardness (mg $CaCO_3$/L)
MC	25.69	6.79	137.5	8.8	20	48
BB1A	25.24	7.34	241.4	7.7	32	60
BB1	24.28	7.45	242.5	8.2	28	56
BB2	23.50	7.13	230.0	7.8	28	60
BB2A	28.74	7.44	273.8	9.0	28	72
BB3	29.68	7.53	276.0	8.6	28	80
BB4	28.89	7.49	308.0	8.0	24	80
BB5	29.74	7.57	279.1	7.6	28	96
BB6	30.07	7.54	1007.0	8.6	24	240
BB7	29.87	7.40	1011.0	8.4	28	232
BB8	29.26	7.40	289.0	8.5	28	244
BB9	27.01	7.12	690.8	8.4	28	172
LB1	23.17	7.52	269.0	8.7	36	124
LB2	26.38	7.34	360.8	8.8	28	96
LB3	25.24	7.53	377.3	8.0	32	104
LB4	27.33	7.47	373.1	8.4	32	92

Table 2. PCB results for water samples from Big Bayou Creek collected June 3-4, 2002.

Station	Date	Sample	Aroclor Concentration (μg/L) 1248	1254	1260
MC	06/03/02	PWS1	<0.08	<0.08	<0.08
MC	06/03/02	PWS2	<0.08	<0.08	<0.08
BB1U[1]	06/03/02	PWS1	<0.08	<0.08	<0.08
BB1A	06/03/02	PWS1	<0.08	<0.08	<0.08
BB1A	06/03/02	PWS2	<0.09	<0.09	<0.09
BB1	06/03/02	PWS1	<0.08	<0.08	<0.08
BB1	06/03/02	PWS2	<0.08	<0.08	<0.08
BB2	06/03/02	PWS1	<0.09	<0.09	<0.09
BB2	06/03/02	PWS2	<0.09	<0.09	<0.09
BB2A	06/03/02	PWS1	<0.08	<0.08	<0.08
BB2A	06/03/02	PWS2	<0.08	<0.08	<0.08
BB3	06/03/02	PWS1	<0.08	<0.08	<0.08
BB3	06/03/02	PWS2	<0.08	<0.08	<0.08
BB4	06/03/02	PWS1	<0.08	<0.08	<0.08
BB4	06/03/02	PWS2	<0.08	<0.08	<0.08
BB5	06/03/02	PWS1	<0.08	<0.08	<0.08
BB5	06/03/02	PWS2	<0.08	<0.08	<0.08
BB6	06/03/02	PWS1	<0.08	<0.08	<0.08
BB6	06/03/02	PWS2	0.11	<0.08	<0.08
BB7	06/03/02	PWS1	<0.08	<0.08	<0.08
BB7	06/03/02	PWS2	0.12	<0.08	<0.08
BB8	06/03/02	PWS1	<0.08	<0.08	<0.08
BB8	06/03/02	PWS2	0.14	<0.08	<0.08
BB9	06/03/02	PWS1	<0.08	<0.08	<0.08
BB9	06/03/02	PWS2	<0.09	<0.09	<0.09

[1] BB1U was sampled upstream of BB1A at Woodville road.

Table 3. PCB results for water samples from Little Bayou Creek collected June 3-4, 2002.

			Aroclor Concentration (μg/L)		
Station	Date	Sample	1248	1254	1260
LB1	06/03/02	PWS1	<0.08	<0.08	<0.08
LB1	06/03/02	PWS2	<0.08	<0.08	<0.08
LB2A	06/04/02	PWS1	0.09	<0.08	<0.08
LB2A	06/04/02	PWS2	0.14	<0.08	<0.08
LB2	06/04/02	PWS1	0.10	<0.08	<0.08
LB2	06/04/02	PWS2	0.09	<0.08	<0.08
LB3	06/04/02	PWS1	<0.08	<0.08	<0.08
LB3	06/04/02	PWS2	<0.08	<0.08	<0.08
LB4	06/03/02	PWS1	<0.08	<0.08	<0.08
LB4	06/03/02	PWS2	<0.08	<0.08	<0.08
010+011	06/04/02	PWS1	<0.08	<0.08	<0.08