

**Analysis of Iron in Water and Sediments Samples Collected
September 9, 1999 and February 28 – March 1, 2000
from the Bayou Creek System**

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DRAFT REPORT

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INTRODUCTION

This report presents the results for iron (Fe) analyzed for 31 stream water and 21 stream sediment samples collected from Big and Little Bayou Creeks on September 9, 1999 and for 32 water samples collected February 28 and March 1, 2000. Sampling stations BB1 through BB9 on Big Bayou Creek and LB2 through LB4 on Little Bayou Creek 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. The locations of sampling stations within the Bayou Creek system are shown schematically in Figure 1. The new reference station BB1A (not shown), was located about 200 m upstream of BB1, the original reference site. Analyses of other metals of concern (MOC) in water column and sediment samples were presented previously (Birge and Price, December 3, 1999; Birge and Price, March 14, 2000).

METHODS

Digestions for Metal Assays

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. Sediment samples were restricted to the upper 5-10 cm of sediment soil, including depositional areas where found. All sediment samples were collected in acetone-rinsed 0.47L glass jars with Teflon-lined lids. Stainless steel spoons and scoops used for collections were acetone-rinsed between sampling

stations. Samples were maintained on ice (4 °C) from collection through storage at the UK laboratory. Formal chain of custody was maintained for all samples.

Sediment samples were digested and extracted according to procedures described by U.S. EPA 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. Sediment samples were wet-weighed and placed in 50-mL Hot-Block® digestion tubes. The samples were digested with 1:1 TraceMetal grade HNO₃ (10.0 mL) and heated to 95° C for 15 min in a Hot-Block® digestion unit. The samples were allowed to cool to room temperature and 5.0 mL of TraceMetal grade concentrated HNO₃ were then added and the sample was heated to 95° C for 30 min or until a volume of 5.0 mL was reached. Once complete digestion was achieved, 2.0 mL of nano-pure water and 3.0 mL of 30% H₂O₂ were added to each sample followed by heat-instilling. Thirty percent H₂O₂ was added followed by heating until no effervescence was observed. The samples were then heated to obtain a final volume of 5.0 mL and then filtered through a Gelman Sciences Type A/E glass fiber filter to remove suspended particulates. The filters were rinsed with 0.5% HNO₃ prior to use and filtrates were taken to a final volume of 100 mL.

Metal Determinations

Iron was analyzed by atomic absorption spectrophotometry (AAS), using either graphite furnace atomization or by flame atomization techniques. The instruments were a Varian AAS unit (Model Spectra AA-20) equipped with a GTA-96 graphite furnace and a Perkin-Elmers (Model 603) AAS unit equipped with an air-acetylene flame. All gases used were ultra pure carrier grade. Calibration curves were based on five standards. The instruments were 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 the calculation 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 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 the samples collected. Quality assurance included 1) assays for certified and prepared standards, 2) replicate assays, and 3) glassware solvent blanks.

RESULTS

The results for Fe assays of stream water samples collected in September 1999 are given in Tables 1 and 2 for Big and Little Bayou Creeks, respectively. Maximum concentrations in Big Bayou Creek were 3974 µg/L at station BB2 and 1423 µg/L at BB5, compared with 949 µg/L observed for Massac Creek and 200 µg/L for BB1A. The latter is a new upstream reference station on Big Bayou Creek. Compared to values obtained for station BB1A, Fe was elevated, at least to some extent, at all downstream monitoring sites. The contamination at BB2 may be related to PGDP rubble used in bridge construction (*pers. communication*, G. Brewer, 2000). The maximum value for Little Bayou Creek (Table 2) was 1268 µg/L for a sample from station LB2A, downstream of effluent 011.

With respect to stream sediments, Fe was elevated at stations BB1 through BB7, as compared with values obtained for stations MC and BB1A (Table 3). The highest value was 23577 $\mu\text{g/g}$ at BB7. At station BB2A, located adjacent to the "ash landfill", the Fe concentration was 16302 $\mu\text{g/g}$. The high values ($\mu\text{g/g}$) for sediment Fe for Little Bayou Creek were 24322 and 37369 at stations LB2 and LB3, respectively (Table 4). These stations are downstream of effluent ditches 010 and 002. Some effluents that enter Little Bayou Creek have been consolidated and the pattern of continuous and intermittent outfalls should be updated. It also is important to note runoff conditions of the unused effluent ditches. Mean values for sediment Fe are plotted against stream water concentrations in Figures 2 and 3. The results indicate increased Fe contamination occurred primarily in stream sectors considered to be affected by PGDP activities.

The results for the collections made in February and March 2000 are given in Tables 5 and 6. The high values ($\mu\text{g/L}$) observed for Big Bayou Creek were 1193 at station BB3 and 1077 at BB5 (Table 5). The maximum value for MC was 269 $\mu\text{g/L}$ as shown in Table 6. The concentrations of Fe detected in water samples for Little Bayou Creek collected in this series were all below 1000 $\mu\text{g/L}$ (*i.e.* ppm). The mean values for Fe in water samples for each station and collection period are given in Figure 4.

DISCUSSION

The Commonwealth of Kentucky has established a chronic standard for Fe at 1 mg/L (*i.e.* 1000 µg/L), with an allowable variance up to 3.5 mg/L if it can be shown that no adverse effects occur (Water Quality Regulations, Commonwealth of Kentucky, 1999). In view of the record of pollution and environmental impact established for stream sectors near PGDP, this variance would not seem to be applicable. Thus, the Fe standard for warmwater aquatic life would remain at 1 mg/L (*i.e.* 1000 µg/L). Of 18 stream water samples collected from Big Bayou Creek at stations BB2 through BB5, seven exceeded the 1 mg/L standard for chronic effects of Fe. This amounts to a frequency of exceedences of about 39%. Only one value among Fe assays of water for Little Bayou Creek exceeded the 1 mg/L standard. However, for the two collections from the Bayou system in 1999 and 2000, there was a total of “eight” detections above the warmwater chronic standard.

Special efforts were devoted to Fe contamination in PGDP effluents and the Bayou Creek system in an earlier investigation (Birge, 1990). Concerning stream stations BB2 through BB5 on Big Bayou Creek, only five of 39 water samples (*i.e.* 13%) contained Fe above 1 mg/L for a “low-flow” period dating from October 1987 through August 1988. During the period from April 1989 through February 1990, when stream discharge was increased, only one exceedence occurred for Fe in 83 water samples analyzed for stations BB2-BB9.

Based on these results and those given in Tables cited above, it appears likely that Fe contamination has increased over the year. It also is clear from the earlier results that

any metal exposure scenario used in risk assessment of aquatic organisms should be based on low-flow conditions (*i.e.* 7Q10). In evaluating the environmental impact of Fe, it should be noted that appreciable fractions of Fe were found to pass through a 0.45 μ filter (Birge, 1990). Filtered fractions were as high as 39 % of total recoverable Fe for effluent 008 and about 47 % for stream water collected from station BB4. This information further supports the application of the 1 mg/L Fe standard, as recommended earlier (Birge *et al.*, 1985; U.S. EPA, 1976 *i.e.* Red Book). The bioreactivity of Fe, as shown for most other metals, may decrease with increasing residence time in stream water due to complexation with biotic ligands and other chemical reactions. However, the multiplicity of “active” outfalls from PGDP clearly put the Bayou Creek system at risk. The propensity for metal additivity further exacerbates the likelihood of impact on aquatic life (Birge *et al.*, 2000).

According to information received from the State of Kentucky, Division of Waste Management (*pers. communication*, L. Martin, 2000), Fe frequently has been reported to exceed State limits and, together with information included in this report, this metal appears problematic and deserving of further consideration.

Table 1. Iron concentrations in stream water from Big Bayou Creek collected September 9, 1999.

Sample Name			Metal Conc. (µg/L)
MC	90999	MWS1	949.0
BB1A	90999	MWS1	200.2
BB1A	90999	MWS2	144.6
BB1	90999	MWS1	266.3
BB1	90999	MWS2	953.0
BB2	90999	MWS1	3974.2
BB2	90999	MWS2	3174.2
BB2A	90999	MWS1	249.6
BB2A	90999	MWS2	130.5
BB3	90999	MWS1	131.2
BB3	90999	MWS2	853.6
BB4	90999	MWS1	<130.0
BB4	90999	MWS2	<130.0
BB5	90999	MWS1	1423.1
BB5	90999	MWS2	609.9
BB6	90999	MWS1	353.3
BB6	90999	MWS2	400.5
BB7	90999	MWS1	304.8
BB7	90999	MWS2	253.8
BB8	90999	MWS1	195.4
BB8	90999	MWS2	192.1
BB9	90999	MWS1	426.3
BB9	90999	MWS2	411.0

iron teen swim =
 1910 ug/L
 1000 ug/L Ky WW
 3500 ug/L chronic
 "not to exceed"
 high end when no
 impact observed

Table 2. Iron concentrations in stream water from Little Bayou Creek collected September 9, 1999.

Sample Name			Metal Conc. ($\mu\text{g/L}$)
LB2	90999	MWS1	210.5
LB2	90999	MWS2	232.5
LB2A	90999	MWS1	601.0
LB2A	90999	MWS2	1267.9
LB3	90999	MWS1	214.2
LB3	90999	MWS2	245.4
LB4	90999	MWS1	315.9
LB4	90999	MWS2	324.0

Table 3. Iron concentrations in stream sediments from Big Bayou Creek collected September 9, 1999.

Sample Name		Sediment Weight (g)	Metal Conc. ($\mu\text{g/g}$)
MC	MS1A	2.801	4174.0
MC	MS1B	2.604	<100.0
BB1A	MS1A	3.904	4894.0
BB1	MS1A	2.584	9443.8
BB1	MS1B	2.309	18826.1
BB2	MS1A	3.245	9863.2
BB2A	MS1A	4.229	16302.3
BB3	MS1A	3.804	6228.2
BB4	MS1A	3.576	8350.8
BB4	MS1B	2.517	9821.4
BB5	MS1A	3.449	4483.8
BB5	MS1B	2.806	6610.8
BB6	MS1A	3.741	6882.9
BB6	MS1B	2.938	8064.0
BB7	MS1A	3.404	23576.7
BB8	MS1A	3.115	5624.9
BB9	MS1A	3.947	4699.8

Ky NFA Iron = 200 mg/kg (200 $\mu\text{g/g}$)

Table 4. Iron concentrations in stream sediments from Little Bayou Creek collected September 9, 1999.

Sample Name		Sediment Weight (g)	Metal Conc. ($\mu\text{g/g}$)
LB2	MS1A	2.466	24322.3
LB2A	MS1A	4.032	5955.9
LB3	MS1A	4.626	37369.0
LB4	MS1A	2.740	3659.7

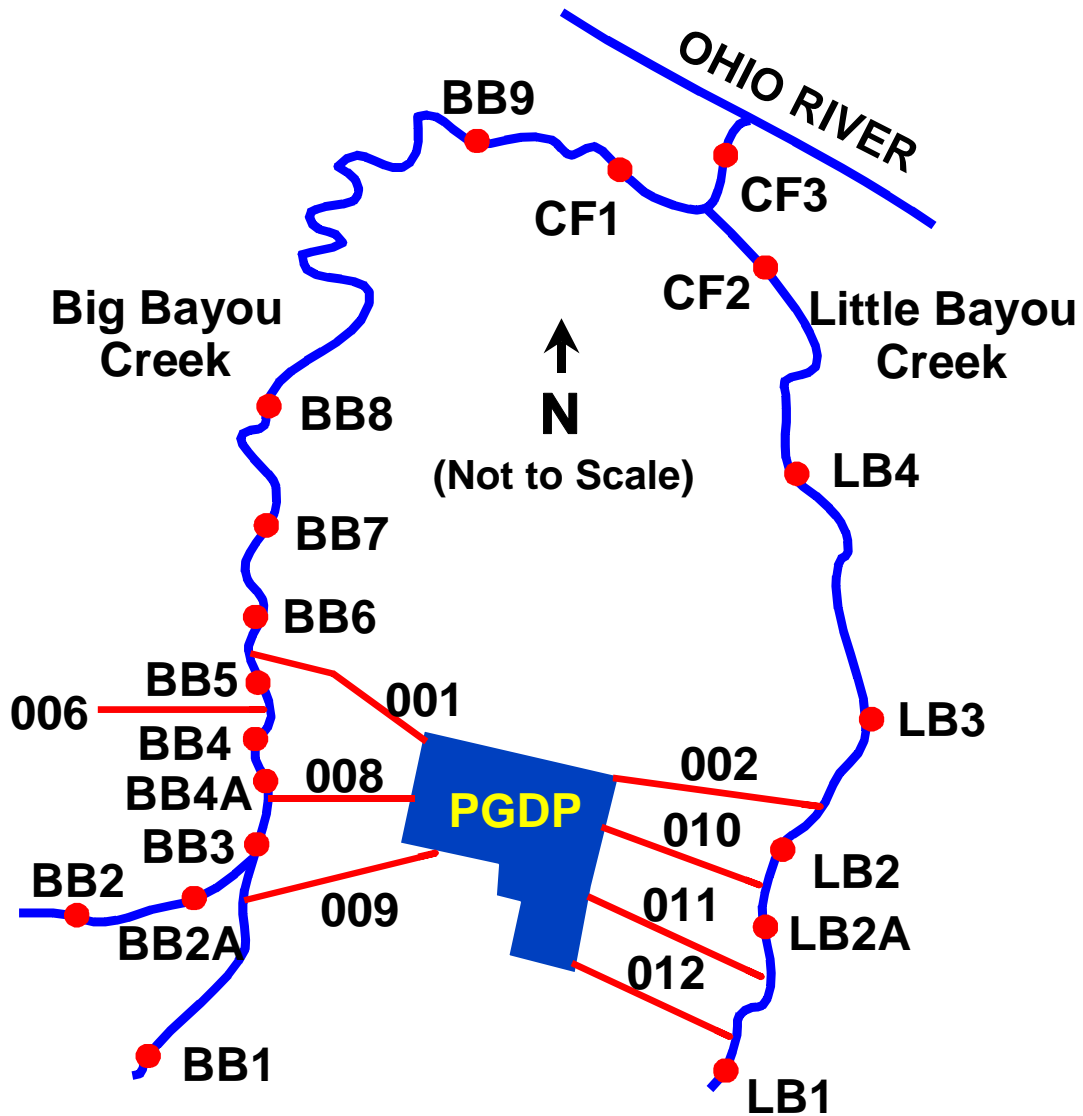
Table 5. Iron concentrations in stream water from Big Bayou Creek collected February 28 and March 1, 2000.

Sample Name			Metal Conc. ($\mu\text{g/L}$)
MC	30100	MWS1	<200.0
MC	30100	MWS2	268.8
BB1A	22900	MWS1	981.1
BB1A	22900	MWS2	751.2
BB1	22900	MWS1	<200.0
BB1	22900	MWS2	405.9
BB2	30100	MWS1	858.2
BB2	30100	MWS2	930.7
BB3	30100	MWS1	1171.1
BB3	30100	MWS2	1192.8
BB4	30100	MWS1	856.4
BB4	30100	MWS2	704.5
BB5	30100	MWS1	1076.8
BB5	30100	MWS2	1018.9
BB6	30100	MWS1	552.3
BB6	30100	MWS2	519.3
BB7	22900	MWS1	278.9
BB7	22900	MWS2	274.2
BB8	22900	MWS1	997.4
BB8	22900	MWS2	589.1
BB9	30100	MWS1	768.6
BB9	30100	MWS2	374.0

Table 6. Iron concentrations in stream water from Little Bayou Creek collected February 28 and March 1, 2000.

Sample Name			Metal Conc. ($\mu\text{g/L}$)
LB1	30100	MWS1	843.1
LB1	30100	MWS2	511.9
LB2	30100	MWS1	285.2
LB2	30100	MWS2	250.0
LB2A	30100	MWS1	677.8
LB2A	30100	MWS2	720.4
LB3	30100	MWS1	537.0
LB3	30100	MWS2	370.3
LB4	30100	MWS1	442.2
LB4	30100	MWS2	524.6

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

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

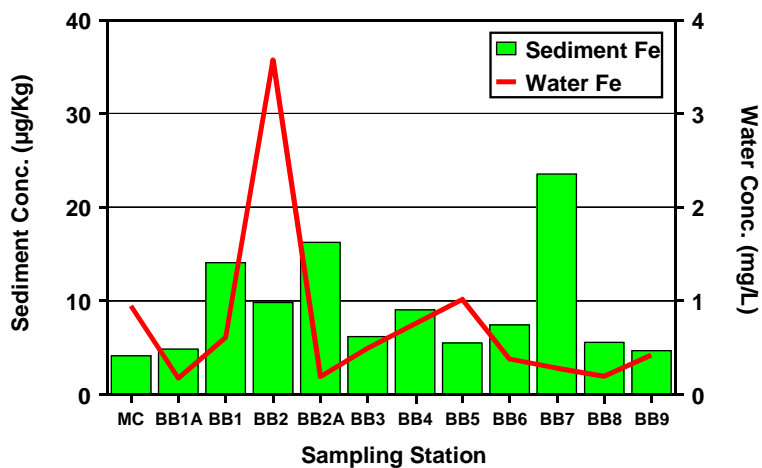


Figure 3. Iron concentrations in sediment and water samples from Little Bayou Creek collected September 9, 1999.

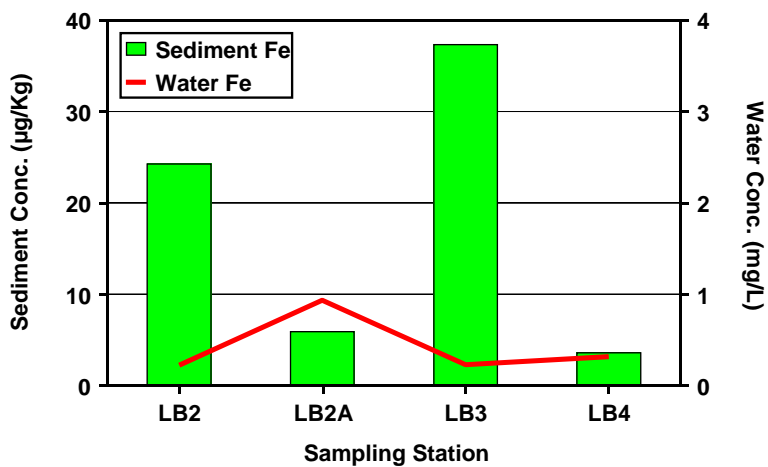
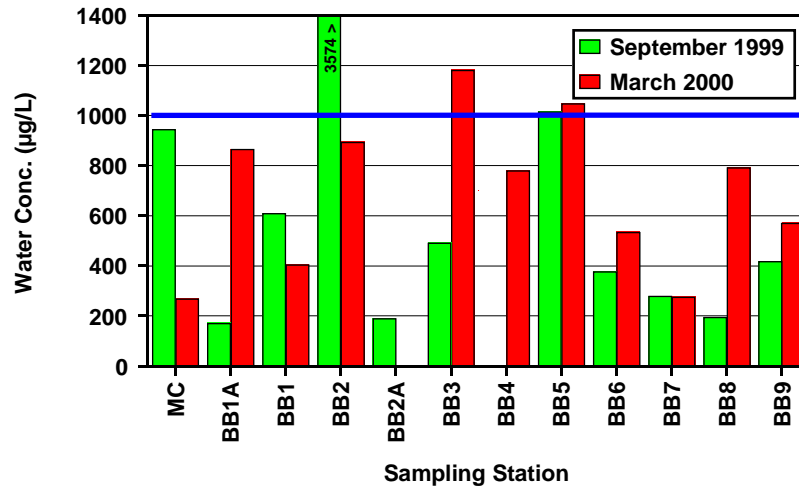


Figure 4. Iron concentrations in water samples from Big Bayou Creek collected September 9, 1999 and March 1, 2000.



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