# Analysis of Mercury in Stream Water, Sediments and Fish from the Bayou Creek System

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**Final Report**

**May 28, 1998**

## INTRODUCTION

This report integrates results of mercury (Hg) assays for water, sediments, and fish collected from the Bayou drainage system in July (*i.e.* water samples) and September (*i.e.* sediments and fish) of 1997. A preliminary report on sediment Hg was submitted on April 30, 1998. The frequency and magnitude of Hg pollution to Big and Little Bayou Creeks are less well known than for other metals or PCBs. However, appreciable numbers of Hg action-level fish were reported in earlier studies (Birge *et al.*, 1992). The principal area affected by Hg was between stations BB4 and BB7 on Big Bayou Creek. The Hg action-level is 1 mg/Kg in fish fillet. The surface water standard is 0.012 µg/L for both the State of Kentucky (KDEP, 1990) and U.S. EPA (1986). Although no official limit has been established for sediment Hg, a concentration of 0.1 mg/Kg likely is significant. This is the level of concern for PCBs (Graham, 1997) and Hg has approximately the same potential for bioconcentration/biomagnification and for impact on environmental health.

## METHODS

EPA Method 7470A and Method 7471A (U.S. EPA, 1997) were 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

Water samples were preserved with approximately 5 mL nitric acid, and 100 mL of each sample were 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 was 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 concentrations were determined as described below.

### Sediment Samples

The sediment samples were returned to the lab and air-dried in a fume hood. The samples were then sieved (>250 µm) to obtain the clay/silt fraction. The digestion procedure used was EPA Method 7471A (U.S. EPA, 1997). In “Run One” a 0.2-g sample was extracted as recommended. Although Hg was detectable in some samples, the Hg concentrations and procedures did not permit reliable quantification. A second complete set of assays (Run Two) were performed using a modified procedure in which a larger sample of 2.00-g sediment was extracted. This greatly increased Hg detection and quantification. Sediment samples were analyzed as given above, except that potassium persulfate was not used. Each sediment sample was digested with 2.0 mL concentrated nitric acid and 5.0

mL concentrated sulfuric acid in a BOD bottle. Samples were heated in a water bath (70°C/3 min.) and allowed to cool to room temperature. Fifty mL of deionized water and 15.0 mL 5% potassium permanganate solution were added to each bottle and the bottles were heated to 95°C for 30 minutes, then allowed to cool. Deionized water was added to each bottle to obtain a total volume of 100 mL, followed by the addition of 6 mL 12% hydroxylamine hydrochloride solution, to reduce unused potassium permanganate. Five mL 10% stannous chloride solution were added and the mercury analyzer aerator was placed on the BOD bottle immediately thereafter. Mercury concentrations were determined as described below.

**Fish Samples**

From each station on Big Bayou Creek up to three stoneroller minnows were placed in each of two 125-mL Erlenmeyer flasks. Similarly, for each station on Little Bayou Creek, sunfish muscle fillets were placed individually in 125-mL flasks. Three mL concentrated nitric acid per gram fish body weight were added to each flask, the flasks were covered and the fish allowed to digest overnight. Digested samples were transferred to pre-weighed BOD bottles. Initially, 5 mL of concentrated sulfuric acid, 15 mL 5% potassium permanganate solution, and 8 mL 10% potassium persulfate solution were added to each bottle. To ensure complete digestion, another 8 mL 10% potassium persulfate solution and potassium permanganate crystals were added until a purple color persisted. The bottles were then heated (90° C/ 3h) in a water bath. Bottles were checked periodically and additional potassium permanganate crystals were added if necessary. After allowing the bottles to cool to room temperature, enough 12% hydroxylamine hydrochloride solution was added to each bottle to neutralize the potassium permanganate. An aliquot of 25 mL or greater was reserved from each sample and the final volume was taken to 100mL with 0.5 % nitric acid. Five mL 10% stannous chloride solution were added and the mercury analyzer aerator was placed on the BOD bottle immediately thereafter. Mercury concentrations were determined as described below.

**Mercury Analysis**

Mercury determinations were performed by cold vapor atomic absorption spectrophotometry (CVAAS) using a Coleman MAS-50B Mercury Analyzer System. Calibration curves were based on eight standards. Check standards and reagent blanks were also analyzed.

**Quality Assurance**

Copies of all chain of custody forms and permanent records are maintained in active files and are available for review by FFOU or the Cabinet for Natural Resources and Environmental Protection. Quality assurance for mercury assays included blanks and check standards (U.S. EPA 1997).

## RESULTS

Assays of 27 water samples revealed no mercury (Hg) at a detection limit of 20 µg Hg/L (Tables 1,2) using the standard cold vapor atomic absorption procedure (U.S. EPA, 1997). In future studies of water column Hg, it is suggested that 200-300 mL of water be extracted, rather than the specified 100 mL sample. This modification should enhance detection.

In the first set of 16 sediment samples (*i.e.* Run One), Hg was detectable but not quantifiable. The original sediment samples were completely reanalyzed using a modification of Method 7471A. This essentially involved extracting 2.0-g sediment rather than the specified 0.2-g sample. Results for Run One and Run Two for Big Bayou Creek are given in Tables 3 and 4. Results for Run Two revealed detection of Hg in each of the 16 stream sediment samples. As for metals (Birge *et al.*, February, 1998), some contamination was evident at the upstream reference station (*i.e.* BB1) and, for the purpose of this study, station BB3 was selected as a tentative reference station. As recommended in previous reports, a new reference site should be relocated upstream of BB1 on Big Bayou Creek. Average concentrations of sediment Hg (*i.e.* Run Two) were 11.9, 57.6, 51.0, 143.9, 35.1, 38.6 µg Hg/Kg at stations BB3, BB4, BB5, BB7, BB8, and BB9, respectively (Table 4; Figure 1). Less Hg was observed at BB6 but this could have resulted from variations in the selection of sampling sites. An additional round of Hg sampling will be required to provide a more accurate profile of Hg contamination. However, Hg contamination in sediments from Big Bayou Creek generally increased within and downstream of the effluent receiving zone (*i.e.* effluents 008, 006, 001). The highest sediment Hg concentrations, which averaged 144 µg Hg/Kg, were observed at BB7 but elevations in Hg sediment contamination also were evident at stations BB8 and BB9. Possible downstream extension of Hg pollution, similar to that suggested for other metals (Birge *et al.*, February; April, 1998) should be considered (Figure 1). Further study will be necessary to clarify the downstream expanse of Hg pollution. No Hg was observed in the sediments from Little Bayou Creek in Run One (Table 5). However, when the procedure was modified as given above, Hg was detected in each of the 10 samples collected (Table 6). Hg concentrations observed in Run Two were below 25 µg Hg/Kg, except at LB4, and these preliminary results indicate less concern for sediment Hg than reported for Big Bayou Creek.

The results for Hg in 13 fish tissue samples are given in Table 7 for Big Bayou Creek, and those for 10 fish samples are given in Table 8 for Little Bayou Creek. The Hg concentrations given for Big Bayou Creek were based on whole body residues in composite samples of up to 3 stoneroller minnows. Tissue Hg averaged 13.2 and 29.0 µg Hg/Kg at stations BB1 and BB3, respectively. However, tissue residues were elevated perceptibly at BB4, averaging 115.9 µg Hg/Kg, and ranged from 35.9 to 64.9 at stations BB5–BB9. The pattern of Hg contamination in stoneroller minnows is illustrated in Figure 2. Although alternative sources of Hg have not been adequately studied, the results suggest that Hg from the effluent outfalls, particularly 008, have affected the downstream reaches of the stream system (Figures 1,2). Assays of fillet from game species of fish should be included in the next survey.

As was done in the study of PCBs (Birge *et al.*, January, 1998), Hg assays were performed on edible fillet of individual sunfish species taken from Little Bayou Creek (Table 8). The tissue concentrations of Hg ranged from 31.4 to 200 µg Hg/Kg and no action-level fish were observed. The greatest extent of Hg contamination in fish from Little Bayou Creek occurred at station LB2, located below effluents 010, 011, and 012. Overall, bluegill were found to contain higher fillet Hg than longear sunfish or green sunfish.

A total of 102 Hg assays on water, sediments and fish were included in this study. The results provide an initial survey of Hg in the Bayou Creek system that should be useful in 1) gauging extent and magnitude of Hg pollution and 2) prioritizing further studies. Although further study will be required to provide a more accurate profile of current Hg pollution in the Bayou Creek systems, these preliminary results are suggestive of reduced Hg contamination as compared with earlier findings (Birge *et al.*, 1992).

Figure 1. Mean Mercury Concentrations in Stream Sediments from Bayou Creek Collected July 15-16, 1997.

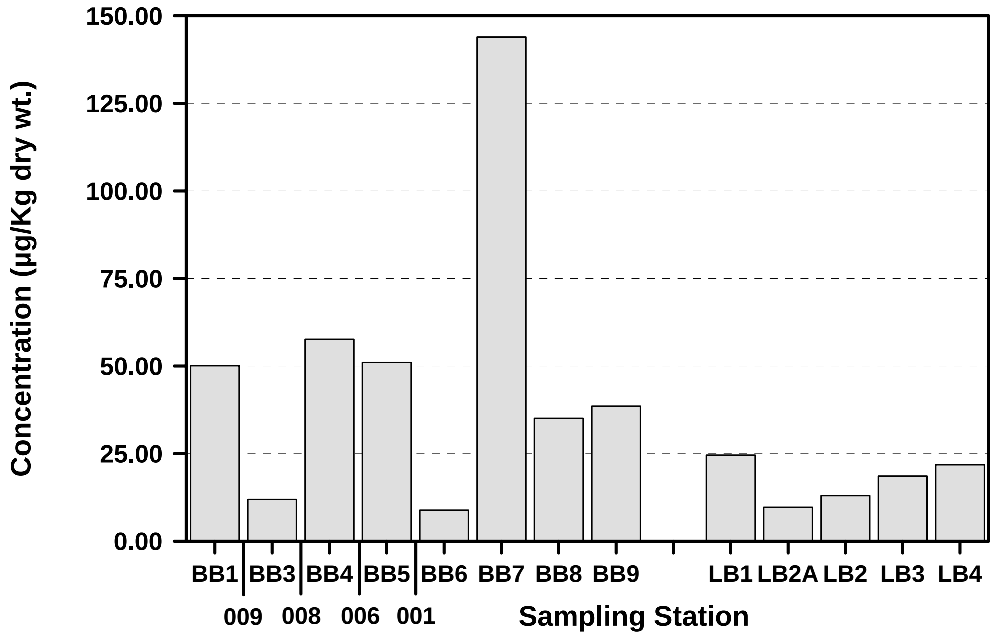


Figure 2. Mean Mercury Concentrations in Stoneroller Minnows from Big Bayou Creek Collected September 30, 1997.

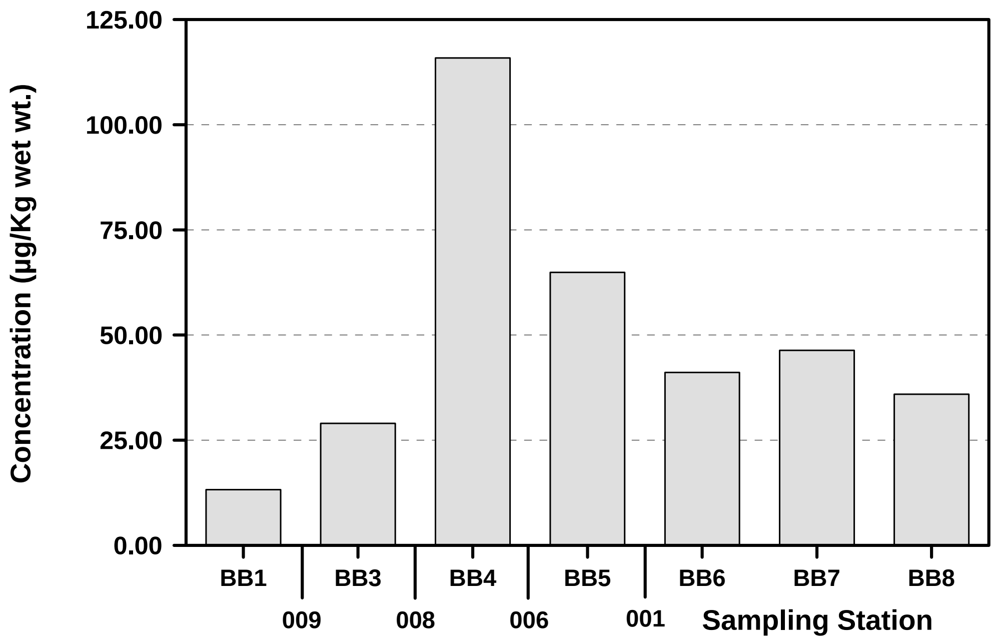

Table 1. Mercury concentrations in stream water from Big Bayou Creek.

| Sample Number | µg Hg/L |
|---|---|
| BB1071597HWSU1A | <20.0 |
| BB1071597HWSU2A | <20.0 |
| BB3071597HWSU1A | <20.0 |
| BB3071597HWSU2A | <20.0 |
| BB3T071597HWSU1A[a] | <20.0 |
| BB4071597HWSU1A | <20.0 |
| BB4071597HWSU2A | <20.0 |
| BB5071597HWSU1A | <20.0 |
| BB5071597HWSU2A | <20.0 |
| BB6071597HWSU1A | <20.0 |
| BB6071597HWSU2A | <20.0 |
| BB7071597HWSU1A | <20.0 |
| BB7071597HWSU2A | <20.0 |
| BB8071597HWSU1A | <20.0 |
| BB8071597HWSU2A | <20.0 |
| BB9093097HWSU1A | <20.0 |
| BB9093097HWSU2A | <20.0 |

[a] Sample collected at BB3 near unnamed tributary.

Table 2. Mercury concentrations in stream water from Little Bayou Creek.

| Sample Number | µg Hg/L |
|---|---|
| LB1071697HWSU1A | <20.0 |
| LB1071697HWSU2A | <20.0 |
| LB2071697HWSU1A | <20.0 |
| LB2071697HWSU2A | <20.0 |
| LB2A071697HWSU1A | <20.0 |
| LB2A071697HWSU2A | <20.0 |
| LB3071697HWSU1A | <20.0 |
| LB3071697HWSU2A | <20.0 |
| LB4071697HWSU1A | <20.0 |
| LB4071697HWSU2A | <20.0 |

Table 3. Mercury Concentrations in Stream Sediments from Big Bayou Creek Collected July 15, 1997.

**RUN ONE**

| Sample Number | µg Hg/Kg dry wt. |
|---|---|
| BB1071597HSED1A | <50.0 |
| BB1071597HSED2A | <50.0 |
| BB3071597HSED1A | <50.0 |
| BB3071597HSED2A | <50.0 |
| BB4071597HSED1A | <50.0 |
| BB4071597HSED2A | <50.0 |
| BB5071597HSED1A | <50.0 |
| BB5071597HSED2A | <50.0 |
| BB6071597HSED1A | <50.0 |
| BB6071597HSED2A | <50.0 |
| BB7071597HSED1A | <50.0 |
| BB7071597HSED2A | <50.0 |
| BB8071597HSED1A | <50.0 |
| BB8071597HSED2A | <50.0 |
| BB9071597HSED1A | <50.0 |
| BB9071597HSED2A | <50.0 |

Table 4. Mercury Concentrations in Stream Sediments
from Big Bayou Creek Collected July 15, 1997.

**RUN TWO**

| Sample Number | µg Hg/ Kg dry wt. | Average | Standard Deviation |
|---|---|---|---|
| BB1071597HSED1A | 18.96 | | |
| BB1071597HSED2A | 81.24 | 50.10 | 31.14 |
| BB3071597HSED1A | 6.13 | | |
| BB3071597HSED2A | 17.71 | 11.92 | 5.79 |
| BB4071597HSED1A | 8.06 | | |
| BB4071597HSED2A | 107.18 | 57.62 | 49.56 |
| BB5071597HSED1A | 69.19 | | |
| BB5071597HSED2A | 32.84 | 51.01 | 18.17 |
| BB6071597HSED1A | 3.11 | | |
| BB6071597HSED2A | 14.60 | 8.85 | 5.75 |
| BB7071597HSED1A | 206.30 | | |
| BB7071597HSED2A | 81.57 | 143.94 | 62.37 |
| BB8071597HSED1A | 27.61 | | |
| BB8071597HSED2A | 42.54 | 35.08 | 7.47 |
| BB9071597HSED1A | 49.36 | | |
| BB9071597HSED2A | 27.75 | 38.55 | 10.81 |

Table 5. Mercury Concentrations in Stream Sediments from Little Bayou Creek Collected July 16, 1997.

**RUN ONE**

| Sample Number | µg Hg/Kg dry wt. |
|---|---|
| LB1071697HSED1A | <50.0 |
| LB1071697HSED2A | <50.0 |
| LB2071697HSED1A | <50.0 |
| LB2071697HSED2A | <50.0 |
| LB2A071697HSED1A | <50.0 |
| LB2A071697HSED2A | <50.0 |
| LB3071697HSED1A | <50.0 |
| LB3071697HSED2A | <50.0 |
| LB4071697HSED1A | <50.0 |
| LB4071697HSED2A | <50.0 |

Table 6. Mercury Concentrations in Stream Sediments from Little Bayou Creek Collected July 16, 1997.

**RUN TWO**

| Sample Number | µg Hg/ Kg dry wt. | Average | Standard Deviation |
|---|---|---|---|
| LB1071697HSED1A | 21.28 | | |
| LB1071697HSED2A | 27.89 | 24.58 | 3.30 |
| LB2071697HSED1A | 11.37 | | |
| LB2071697HSED2A | 8.02 | 9.69 | 1.67 |
| LB2A071697HSED1A | 13.02 | | |
| LB2A071697HSED2A | 13.02 | 13.02. | 0.00 |
| LB3071697HSED1A | 20.86 | | |
| LB3071697HSED2A | 16.32 | 18.59 | 2.27 |
| LB4071697HSED1A | 13.02 | | |
| LB4071697HSED2A | 30.58 | 21.80 | 8.78 |

Table 7. Mercury concentrations in stoneroller minnow tissues from Big Bayou Creek collected September 30, 1997.

| Sample Number | µg Hg/ Kg dry wt. | Average | Standard Deviation |
|---|---|---|---|
| BB1093097HFSR1A | 13.24 | | |
| BB3093097HFSR1A | 32.52 | | |
| BB3093097HFSR2A | 25.47[b] | 28.99 | 3.52 |
| BB4093097HFSR1A | 131.46 | | |
| BB4093097HFSR2A | 100.30 | 115.88 | 15.58 |
| BB5093097HFSR1A | 53.19 | | |
| BB5093097HFSR2A | 76.61 | 64.90 | 11.71 |
| BB6093097HFSR1A | 47.60 | | |
| BB6093097HFSR2A | 34.58[c] | 41.09 | 6.51 |
| BB7093097HFSR1A | 37.48 | | |
| BB7093097HFSR2A | 55.22 | 46.35 | 8.87 |
| BB8093097HFSR1A | 31.66 | | |
| BB8093097HFSR2A | 40.21 | 35.93 | 4.27 |

[a] Whole body samples were composites of three fish.
[b] One fish was analyzed.
[c] Whole body samples were composites of two fish.

Table 8. Mercury concentrations in sunfish muscle fillet from Little Bayou Creek collected September 30, 1997.

| Sample Number | Sunfish Type | µg Hg/Kg dry wt. | Average | Standard Deviation |
|---|---|---|---|---|
| LB2A093097HFBG1A | Bluegill | 199.96 | | |
| LB2A093097HFBG2A | Bluegill | 42.46 | 121.06 | 78.60 |
| LB2A093097HFLS1A | Longear sunfish | 44.13 | | |
| LB2A093097HFLS2A | Longear sunfish | 53.56 | 48.89 | 4.76 |
| LB2093097HFGS1A | Green sunfish | 145.56 | | |
| LB2093097HFGS2A | Green sunfish | 31.37 | 88.46 | 57.09 |
| LB2093097HFBG1A | Bluegill | 167.67 | | |
| LB2093097HFLS1A | Longear sunfish | 118.75 | | |
| LB3093097HFBG1A | Bluegill | 112.51 | | |
| LB3093097HFBG2A | Bluegill | 97.05 | 104.78 | 7.73 |

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