Summary of Monitoring Studies Reported in December 1997 through December 1999

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INTRODUCTION

A total of 361 environmental samples and 153 quality assurance samples were analyzed and reported. In addition to scientific reports, these data also were reported electronically. The monitoring program focused on PCBs (i.e. 1248, 1254, 1260), eight metals of concern (Ag, Be, Cd, Cr, Cu, Ni, Pb, Zn), and mercury. Assays included water and sediment samples from the Bayou Creek system and animal tissues (i.e. fish, red-tailed hawk, mink, deer). The final report was delayed due to late responses from reviewers.

Study Area

Study areas are detailed in Figures 1, 2 and 3. Figure 1 shows the major collecting sites, as well as the intermittent (003, 013, 014, 015, 016, 017) and continuously flowing PGDP effluents. Figure 2 is an illustration of the Bayou Creek system diagramed over a topographical map of the area and Figure 3 is an enlargement of the PGDP sector of Figure 2. The collecting sites on Big Bayou Creek in downstream order, include BB1A, BB1, BB3, BB4, BB5, BB6, BB7, BB8, BB9, CF1, and CF3. Stations BB2 and BB2A are situated on the unnamed tributary that enters Big Bayou Creek just upstream of station BB3 (Figure 1). Stations CF1 and CF2 are upstream of the juncture of Big and Little Bayou Creeks and CF3 is below this confluence and near the Ohio River. Locations of these stations and the position of the continuously flowing effluents are given in Table 1 in stream kilometers (Km) measured upstream from the Ohio River. The intermittent 003 effluent and the north/south (N-S) ditch are illustrated in Figures 2 and 3. The N-S ditch enters Little Bayou Creek about 1 Km upstream of
station LB4. Figure 3 also shows intermittent effluents 013 on Little Bayou Creek, as well as 017 and 014 that enter Big Bayou Creek. Intermittent effluents 016 and 015 are not shown in Figures 2 and 3. They enter Big Bayou Creek just below station BB3 and upstream of BB4, respectively (Figure 1). The continuous effluents originate from plant operations, whereas the intermittent effluent primarily carry “runoff” from the plant during periods of moderate to high rainfall.

RESULTS

Metal Assays for Water

The first sampling under State support was conducted in July, 1997. Concentrations of metals in Big Bayou Creek water samples were consistently elevated in the effluent receiving zone, starting at BB3 for Cr, Cu and Zn and at BB6 for Ag, Be, Cd, Cr, Cu, Pb, Ni, and Zn. For the most part, metal concentrations remained elevated all the way downstream to and including station BB9. It is important to note that concentrations of metals, except for Cr, were generally higher than mean values given for the period from October 1987 through July 1991. This is based on a comparison with Tables 1 and 2 given by Birge and Price (1997a) in their report dated December 8, 1997. For example, mean values (µg/L) for Zn in the earlier study were 5.8, 5.9, 4.7, and 4.5 for stations BB6, BB7, BB8, and BB9, respectively. The July 1997 values, for the same stations, given in the same order were 15.1, 11.5, 23.0, and 8.46. Averaging all values for these four stations, there was an increase in Zn contamination of about 44% during the intervening years. Such comparisons also indicated substantial increases for Cd, Cu, Ni, and Pb. Water samples were again sampled in October of 1998 (Birge and
Metal concentrations in Big Bayou Creek were lower, possibly due in part to greater dilutions associated with increased stream discharge. The last water sampling event was in September, 1999 (Birge and Price, 1999b). Values for Cu and Pb at BB4 averaged 5.16 and 3.98 µg/L compared with mean values of 3.57 and 0.71 for the 1987-1991 period (Birge et al., 1992). Other metals also were elevated within and below the effluent receiving zone (i.e. BB3-BB6). In summary, PGDP effluents still contribute to metal pollution in the Bayou Creek system. Both in 1998 and 1999, concentrations of silver at stations BB4 through BB9 were considerably above the range of 0.1 to 0.2 µg/L considered to be the threshold for chronic effects on sensitive biota (Birge and Zuiderveen, 1995; Hogstrand and Wood, 1998; Wood et al., 2000). Silver values also were elevated at stations BB6-BB8 in 1997.

In several instances, water column metal concentration observed in the three surveys were at or above values adopted as aquatic life standards by the State of Kentucky, depending in part on water hardness (i.e. mg CaCO₃ /L). For purposes of this review, water hardness was based on an extensive database established from January through August, 1991 (Birge et al., 1992). This involved more than 125 measurements for monitoring stations upstream of effluent 001. The mean value was 90 mg CaCO₃ /L and the mean of the lower 95% confidence values (HLCV) was 70 mg CaCO₃ /L. These values also approximated conditions in Little Bayou Creek. At station BB6, downstream of effluent 001, hardness averaged 148 mg CaCO₃ /L and the lower confidence values (LCV) was near 100 mg CaCO₃ /L. As present aquatic life standards do not take into account “trophic” uptake/exposure to metals nor include prospects for “additive” effects, it is recommended that metal hardness calculations be based on the HLCV. This is
further justified by the pervasive, wide-spread pollution from many metal-containing effluents that affect two small but important stream systems. In addition, the effects of suites of metals may prove more deleterious under stresses imposed by low dissolved oxygen or elevated stream temperatures as discussed below. Using 70 and 100 mg CaCO₃ /L, the chronic limits (µg/L) would be 0.86 and 1.1 for Cd; 8.7 and 12.0 for Cu; and 2.02 and 3.2 for Pb. Examples of metal exceedences include Pb at LB2A, LB2, LB3 and LB4 in 1997; Pb at LB2 and BB4 in 1999, and at BB3 and BB7 in 1997.

**Metal Assays for Sediments**

Analysis of metals in sediments from the Bayou system were performed in July, 1997 (Birge et al., February, 1998). Twenty six samples were analyzed for eight metals (Ag, Be, Cd, Cr, Cu, Ni, Pb, Zn) and BB1 was used as the reference site. By comparison, most metals increased in concentration in Big Bayou Creek within and below the effluent receiving zone (BB3-BB6). For example, maximum values for Ag were 0.09, 0.39, 0.82, 1.29, 1.03, 0.80, and 0.37 at stations BB1, BB3, BB4, BB5, B6, BB7, BB8, and BB9, respectively. Therefore, Ag has polluted Big Bayou Creek at toxic concentrations at least to the lowest downstream station (BB9), which is only 2.8 Km from the Ohio River confluence. Maximum values (mg/Kg) for other metals were 1.34 for Be at BB4; 1.56 for Cd at BB9; 107.6 for Cr at BB7; 26.6 for Cu at BB7; 38.4 for Ni at BB7; 8.78 for Pb at BB7, and 127.6 for Zn at BB7. Concerning Little Bayou Creek, maximum values (mg/Kg) were 0.78 for Ag at LB3; 1.24 for Be at LB2A; 2.8 for Cd at LB3; 93.4 for Cr at LB3; 10.9 for Cu at LB3; 14.9 for Ni at LB3; 8.35 for Pb at LB3; and 85.7 for Zn at LB3. In all instances these values were higher than maximum values
found at the reference stations (*i.e.* BB1, LB1). Stations LB3 and BB7 were the most impacted by metal pollution in the Bayou Creek system. In addition, the sediment metal contamination is in good agreement with data given for water column pollution and supports the conclusion that sources of water column metals are continuous and pervasive. A recent report (Birge and Price, 1999b) on sediment assays for samples collected in September, 1999, not included in this review, shows similar trends for sediment metal pollution in Big Bayou Creek. In addition, sediment metal in Little Bayou Creek were greatly increased at LB3 for certain metals (*i.e.* Be, Cu, Ni, Pb, Zn).

**Metal Accumulation in Stoneroller Minnows**

Based on past studies (Birge *et al.*, 1992), the stoneroller minnow was selected as an *in situ* “sentinel” for assessing metal body burden relative to water column metal concentrations. The results supported this approach for determining bioavailable fractions of total recoverable metal concentrations, and this study was published last year (Birge *et al.*, 2000). Briefly, this information has been reviewed in a report by Birge *et al.* (1998).

This report was based on analysis of 32 stoneroller minnows collected in September, 1997. The primary objectives were 1) use whole-body metal residues to identify sources, magnitude, and spatial distribution of bioavailable metals within the Bayou Creek system; 2) estimate downstream movement of metal contamination in Big Bayou Creek resulting from upstream point-source discharges; and 3) identify stream sectors where metal stressors potentially may produce biological and/or ecological effects. The major conclusions were as follows:
• **Metal residues** in stoneroller minnows collected from Big Bayou Creek in 1997 generally were higher, especially downstream, than reported in 1988. For example, whole body residues of Pb, an important contaminant affecting aquatic life and human health, were about 50 to 100 times higher than found in 1988. This is particularly important due to the fact that Pb has a rather low potential for bioconcentration in fish.

• **Bioavailable metal fractions** were as high or higher at one or more downstream stations (e.g. BB7-BB9) than in the effluent receiving zone and they most always were higher than values recorded for the upstream reference station.

• **Sediment metal** concentrations often were as high or higher at downstream stations (BB7-BB9) as for effluent receiving stations (BB3-BB6).

• These and other findings indicated a progressive downstream spread of metal pollution.

In summary, these data reflect increased metal pollution in Big Bayou Creek since the earlier studies (Birge *et al.*, 1992) were performed. In addition, the metal body burden results correlate closely with water column and sediment findings for metal and conductivity. Ecological impact also has been observed to correlate inversely with metal body burden in stoneroller minnows (Birge *et al.*, 2000).

**PCBs in Stream Water**

The first collections for PCB water assays were made in July of 1997 (Birge and Price, 1997a). Out of ten water samples from Little Bayou Creek, PCBs were detected in 6 samples collected from stations LB2A, LB2, and LB3. The concentrations (µg/L) for
Aroclor 1248 were 1.08 and 0.16 at LB2A; 0.14 and 0.26 at LB2; and 0.85 and 0.11 at LB3. Aroclor 1260 also was detected at each of these stations but the concentrations were below the minimum quantitation limit (MQL). PCBs were not detected in six water samples taken from stations BB4, BB5 and BB9 on Big Bayou Creek.

Water samples for PCB assays were again taken from Little Bayou Creek in September, 1997 (Birge and Price, 1997b). There were no PCB detection in eight samples from stations LB2A through LB4. The next collection was in October, 1998 (Birge and Price, 1999a). PCBs were not detected in 24 water samples taken from Big Bayou Creek and Massac Creek. However, Aroclor 1248 again was found in water samples from station LB2A on Little Bayou Creek. The concentrations were 0.10 and 0.11 in two different water samples. Aroclor 1248 also was found in one of two samples at 0.12 µg/L for station LB2. The last collection of water samples for PCB assays was taken in September, 1999 (Birge and Price, 1999b). PCB was detected in two of eight water samples from Little Bayou Creek and one of 22 samples from the Big Bayou Creek system. Over the course of the study, PCBs were detected in 12 water samples which amounted to 14.3% of the total. This represents a substantial frequency of exceedence of the Kentucky Water Quality Standards for PCB, as well as for the U.S. EPA chronic criterion of 0.014 µg/L.

**PCBs in Stream Sediments**

Three Aroclors (*i.e.* 1248, 1254, 1260) were present in each of 20 sediment samples collected in July, 1997 (Birge and Price, 1997a) from Big Bayou Creek, including station BB1. PCB contamination increased perceptively at station BB5, where total PCB concentrations ranged from 0.17 to 0.44 mg/Kg (*i.e.* ppm). However, PCB
contamination peaked at BB7, where the maximum concentration was 2.01 mg/Kg. PCB pollution was observed all the way downstream to the last station monitored (i.e. BB9). All but two of the 20 samples contained PCB above the 0.10 mg/Kg standard litigated by the State of Kentucky for PCB cleanup in the Town Branch/Mud River system. Sediment PCB concentrations for 8 samples from stations LB2A through LB4 on Little Bayou Creek averaged 0.93 mg/Kg, with a peak of 2.8 mg/Kg at LB2A. The average for LB1, the upstream reference, was 0.04 mg/Kg.

Although not included in this review, sediments collected in September, 1999 were analyzed for PCB and these data were reported in March of 2000 (Birge and Price, 2000). Analysis of “wet” sediment samples revealed PCB detection at only five stations (BB3, BB4, BB7, BB8, BB9) on Big Bayou Creek. Contamination was reduced or obscured by the extraction from “wet” sediments. PCBs were detected in “wet” sediment assays for all four stations on Little Bayou Creek but, as for Big Bayou Creek, the level of contamination appeared decreased. Therefore, sediment sub-samples were dried and sieved for analysis of the clay/silt fractions. PCB contamination was about one order of magnitude higher as compared to wet assays, and the maximum values for Little Bayou Creek (µg/g) were 0.29, 0.14 and 0.14 at stations LB2A, LB2 and LB3, respectively.

**PCB Residues in Fish Fillets**

In September of 1997, fillet samples from 20 sunfish collected from Little Bayou Creek were analyzed for Aroclors 1248, 1254, and 1260. All but 2 fish collected from stations LB2A, LB2, LB3 and LB4 contained 2 to 3 different Aroclors. Total PCB values
(mg/Kg) averaged 0.57, 1.12, 0.49, and 0.14 for stations LB2A, LB2, LB3 and LB4. Given in the same order, the maximum values (mg/Kg) were 0.94, 2.50, 0.60, and 0.20. Station LB4 is located 5.1 Km downstream of effluent 011 which historically has been the greatest source of PCBs. The highest value given above clearly exceeds the FDA action level of 2.0 mg/Kg and all but 2 of the 20 fish were found to contain PCBs in excess of the 0.05 mg/Kg limit using the Great Lakes Sport Fish Advisory Task Force (1993) recommendation for unlimited consumption. Eleven of 15 fish from stations LB2A, LB2 and LB3 exceeded the limit for fish consumption of one meal per week (0.22 mg/Kg).

**PCB Contamination in Terrestrial Animals**

As reported in 1998, analysis of 3 deer liver samples revealed no detectable PCB, observing detection limits of 0.021-0.027. However, Aroclor 1260 was found in two samples of mink kidney and liver at 0.53 and 1.10 mg/Kg, respectively. Other studies by Murry and Smith (1997) have reported widespread PCB contamination of rodents. Their assays focused on PCB congeners (e.g. 138, 153, 170, 180) and these data were reviewed in a raccoon proposal by Birge and Maybriar (1998).

In addition to the above work, Assays were performed on blood of four red-tailed hawks. Aroclor 1260 was detected in 3 specimens at concentrations ranging from 0.06 to 0.76 µg/L. This range of values is close to that found for bald eagles from threatened or endangered populations in Oregon and Washington (Price and Birge, 1998). The hawks were collected in 1997 by Matt Vick.
General Water Quality Parameters

In July of 1997, certain general water quality parameters were monitored, including conductivity, pH, dissolved oxygen, and temperature. Conductivity was consistently elevated on Big Bayou Creek at and downstream of station BB6, indicating increased stream water concentrations of electrolytes originating from effluent 001. The values ($\mu$S) ranged from 1048 at BB6 to 852 at BB9, compared to a value of 206 at the upstream reference (i.e. BB1).

Dissolved oxygen values were below the State of Kentucky minimum (4.0 mg/L) at stations BB5 (3.9 mg/L) and BB6 (2.4 mg/L) and water temperature at stations BB3 and BB4 exceeded the upper State limit of 31.7 °C. Moreover, temperature at stations BB3 through BB6 exceeded the period average for the month of July given by the State of Kentucky for warm water habitat (29.9 °C). Values for pH, ranged from 6.7 at LB1 to 8.24 at BB5, and were within State of Kentucky guidelines. However, the value obtained at BB5 was close to the desirable upper limit of 8.5. Exceedences of the pH 9.0 limit were observed in earlier studies during the summer months (Birge and Short, 1990).

Periphyton Monitoring

In September of 1996 and 1997, analyses were conducted on periphyton obtained from natural substrates. Results were compared to periphyton studies performed in 1989 in which artificial substrates and floating rack samplers were used. Results were based on biomass, chlorophyll a and the autotrophic index of green algae (Birge et al., 1989; Price et al., 1998).
Results are summarized as follows:

- Periphyton studies in 1989, 1996, and 1997 all indicated some degree of impact in the effluent receiving zone of Big Bayou Creek and, occasionally, the more downstream stations.
- The most impacted station monitored was LB4 on Little Bayou Creek. This did not appear to be related to the discharge of upstream effluents (i.e. 002, 012, 011, 010).
- The impact at LB4 was observed over a period of ten years, suggesting the need for a focused study upon this area of the Bayou drainage, as well as the North-South Ditch which enters Little Bayou Creek upstream of the LB4 monitoring station.
- The periphyton assays, while useful in assessing and localizing magnitude of impact of PGDP effluents, were less sensitive than 1) species richness and other parameters as measured in macroinvertebrate communities or 2) tissue residues analyzed in fish sentinel monitors (e.g. stoneroller minnow, longear sunfish, green sunfish; Birge et al. 1992).

**CONCLUSIONS**

It is clear that PGDP operations have polluted the surrounding environment, contaminating terrestrial wildlife, aquatic life, biotic habitat and important surface water systems. Water quality has been affected 1) by fluctuations in general water quality parameters (i.e. pH, dissolved oxygen, temperature, suspended solids), 2) metal...
pollution (e.g. Ag, Cd, Cr, Cu, Fe, Ni, Pb, Zn) and 3) widespread occurrence of PCBs.

We recommend that an integrated and conservative approach to water quality and ecological risk assessment and risk management be undertaken jointly by the State of Kentucky and others concerned with CERCLA, RCRA or environmental quality issues. In addition, the database developed and conclusions reached will be useful in determining need and scope of a National Resource Damage Assessment and/or determining best-case remedial strategies. This takes into account the close proximity of PGDP to the Western Kentucky Wildlife Management Area and other important natural resources.
Some preliminary suggestions concerning the surface water systems are as follows:

- Base more critical assessments insofar as possible on low-flow conditions (*i.e.* 7Q10). It is during the “dry” years that impact on aquatic biota has been demonstrated most clearly.

- Increase monitoring of water quality parameters given above. This will help to compensate for considerable variability within the system.

- Temperature, dissolved oxygen and suspended solids are most critical during July and August at stations BB3-BB7 on Big Bayou Creek and LB2A-LB4 on Little Bayou Creek.

- pH fluctuations occur mostly between effluent 006 and station BB5 and between effluent 001 and station BB6 during the summer months.

- Metal monitoring should continue to focus on stations BB1-BB9 on Big Bayou Creek and LB2A-LB4 on Little Bayou Creek.

- PCB monitoring should continue to focus on Little Bayou Creek at stations LB2A-LB4 and more intense study should be conducted on Big Bayou Creek at stations BB1 through BB9.

- More attention should be given to those coplanar PCB congeners that have higher dioxin equivalent values, as well as to ratios of Aroclor 1248 vs. 1260 that bear on whether PCB contamination is current or historic. Equal or higher proportions of Aroclor 1248 suggest active pollution of PCBs in bioavailable form.

- Pollutant influx into the Ohio River should be characterized. This should include
monitoring of radionuclides, metals and PCB at stream stations CF1, CF2, CF3, and in the Ohio River up and downstream of the Bayou Creek confluence.

- All effluent ditches between receiving streams and plant sources should be included in at least one comprehensive survey of radionuclides, metals and PCBs.
- Independent effluent biomonitoring for chronic toxicity should be undertaken periodically, without prior notice to PGDP.
- There is a need to reassess reference sites and establish more reliable background concentrations of contaminants.

Of greater importance, pollution limits should be conservative and supported by overall weight of evidence. This approach is justified 1) by the efflux of many pollutants from many different sources originating in close proximity 2) by the occurrence of suites of pollutants (e.g. radionuclides, PCBs and metals) 3) sensitivity and importance of the first to third order stream systems and other natural resources and 4) the longstanding dilemma of unresolved issues between U.S. EPA, DOE, PGDP, and the Commonwealth of Kentucky. Other recommendations are as follows.

Concerning PCBs, limits on fish contamination should be based on the recommendation of the Great Lakes Sport Fish Task Force for unlimited consumption (i.e. 0.05 mg PCB/Kg. Guidelines for PCBs in sediments should be based on values somewhere in the range of 0.05 to 0.10 mg PCB/Kg, as documented in the attached summary on PCB sediment criteria.

Concerning metals, stream assessments should be based on the combined outfall from all effluents, stressing upper range metal values and considering use of the
metal additivity model developed for the Bayou Creek System (Birge et al., 2000; Birge et al. 1992). For those metals where toxicity is hardness related, we recommend using the lower 95% confidence value in calculations. These would be 70 mgCaCO₃/L for Little Bayou Creek and upper Big Bayou Creek (i.e. BB1-BB5) and 100 mgCaCO₃/L for stations BB6-BB9 on Big Bayou Creek. The low to moderate stream alkalinity should also be taken into account. Seasonal fluctuations and high rain events (i.e. high stream discharge) justify more frequent monitoring of all parameters. These suggestions, and comments from other concerned parties, possibly could form the basis for site specific risk assessment and risk management strategies for PGDP.
REFERENCES


Table 1. Location of Stream Sampling Stations and Effluent Discharge Points to Big Bayou (BB) and Little Bayou (LB) Creeks.

<table>
<thead>
<tr>
<th>Effluent Stream Location</th>
<th>Stream Kilometer&lt;sup&gt;1&lt;/sup&gt;</th>
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<tbody>
<tr>
<td>BB1 (upstream reference)</td>
<td>13.5</td>
</tr>
<tr>
<td>BB2 (tributary)&lt;sup&gt;2&lt;/sup&gt;, BB2A</td>
<td>12.1</td>
</tr>
<tr>
<td>BB3</td>
<td>11.7</td>
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<tr>
<td>BB4A</td>
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<td>8.6</td>
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<tr>
<td>LB1 (upstream reference)</td>
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<tr>
<td>LB2</td>
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<sup>1</sup> Measured as upstream distance from confluence with the Ohio River.

<sup>2</sup> Collecting stations BB2 located on a tributary 1.5 Km upstream of its confluence with Big Bayou Creek and BB2A located near the confluence.

<sup>3</sup> Collecting stations BB1A and BB1AA (not shown) are located 200 and 400 m upstream of station BB1.

<sup>4</sup> Eight or more additional collecting stations will be added in the Ohio River, four downstream of the Bayou Creek confluence and four upstream and will be sampled simultaneously with Bayou sites CF1, CF2, and CF3.
Figure 1. Map of PGDP Study Area (Schematic).

* Intermittent Flow

Distance:
BB1 to BB8 6.1 km
BB8 to OHIO RIVER 7.4 km
Figure 3. Monitoring stations on topographical map.