



Investigation of Petroleum Products in Black Lake Sediment and Surface Water Adjacent to an Underground Storage Tank Site

Abstract

In 1989, soil and groundwater beneath the Black Lake Grocery was found to be contaminated with petroleum products from leaking underground tanks. The grocery store is located at 4409 Black Lake Boulevard SW, west of Tumwater, Washington.

In November 2004, remediation of the site (treatment wall) was implemented. Sediments and water in Black Lake adjacent to the site were never evaluated for the presence of petroleum products or impacts to benthic communities.

In response, the Department of Ecology conducted a study to evaluate sediments and water from Black Lake downgradient of the site. In March 2005, sediment and water samples were collected and analyzed for total petroleum hydrocarbons (TPH-gasoline), benzene, toluene, ethylbenzene, xylenes (BTEX), polynuclear aromatic hydrocarbons (PAHs), and lead. Ancillary water quality parameters included temperature and conductivity.

Analysis of sediments and surface water in Black Lake adjacent to the site showed no significant levels of contamination. Only low concentrations of PAHs and lead were detected in sediments. Concentrations of total PAHs ranged from 12 to 218 $\mu\text{g}/\text{Kg}$ with a mean of 140 $\mu\text{g}/\text{Kg}$, dry weight. Concentrations of individual and total PAHs did not approach recommended sediment quality values, and were typically two to three orders of magnitude below levels considered to adversely affect aquatic infauna.

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Introduction

Black Lake, located west of Tumwater, Washington, is 2.6 miles long and has a surface area of 570 acres (Figure 1). The water source is thought to be a spring located in the wetlands adjacent to the southern extent of the lake. Black Lake's outflow is north into Black Lake Ditch and Percival Creek, and ultimately discharging to Capitol Lake and Budd Inlet. The lake has a mean depth of 19 feet and a maximum depth of 29 feet.

The Black Lake Grocery is currently an active convenience store located near the lake's northwest corner at 4409 Black Lake Boulevard SW. The store is situated on a 5.2-acre parcel of land approximately 100 feet from the lakeshore. In 1989, soil and groundwater beneath the site were found to be contaminated with gasoline-range petroleum hydrocarbons.

In 1992, the Washington State Department of Ecology (Ecology) conducted a site hazard assessment, and by 1995, six underground storage tanks and 1200 cubic yards of petroleum-contaminated soils were removed. The contaminated soil was bioremediated on site. Chemical analysis showed total petroleum hydrocarbons (TPH) and benzene, toluene, ethylbenzene, and xylenes (BTEX) exceeded Model Toxics Control Act Method-A cleanup levels at the excavation limits, but were not accessible below the adjacent county roads (Summit Envirosolutions, 2000). A remedial investigation was conducted, but lake sediments and water had never been evaluated for petroleum hydrocarbons or impacts to benthic communities.

In November 2004, a treatment wall was constructed near the lakeshore, downgradient of the site, for treating contaminated groundwater before entering the lake (Figure 2). The treatment wall is an interceptor trench installed perpendicular to groundwater flow at the downgradient location of the contaminant plume. The treatment wall is approximately 120 feet long, five feet wide, and 12 feet deep. The design of the trench required it to be filled with a reactive material to treat contaminated groundwater as it passes through.

The goal of the present study was to determine if petroleum hydrocarbon-related contamination had migrated into Black Lake from the Black Lake Grocery site. The objectives were to:

- ❖ *Phase I:* Determine through near-shore sediment and water sampling if petroleum products have migrated from the Black Lake Grocery site into the lake.
- ❖ *Phase II:* If results of Phase I sampling indicated the lake sediments were contaminated by petroleum hydrocarbons, evaluate the toxicity of the sediments and surface water through use of bioassays.

Table 1 lists the analytical parameter, collection containers, preservation method, and required holding time for each parameter.

Table 1. Sample Analysis, Containers, Preservation, and Holding Times.

| Parameter | Sample Container | Preservation | Holding Time ¹ |
|-----------------|---|---|-------------------------------|
| Sediment | | | |
| BTEX | 8 oz glass jar | Cool to 4° C | 14 days |
| TPH-Gasoline | 8 oz glass jar | Cool to 4° C | 14 days |
| PAHs | 8 oz glass jar | Cool to 4° C | 14 days |
| Lead | 4 oz glass jar | Cool to 4° C | 6 months |
| % Solids | 2 oz glass jar | Cool to 4° C | 7 days |
| Grain Size | 8 oz plastic jar | Cool to 4° C | 6 months |
| TOC | 2 oz glass jar | Cool to 4° C | 14 days |
| Water | | | |
| BTEX | 3-40 mL VOA vials w/ septum, per field station, plus 3 extra QC | 1:1 HCl, Cool to 4° C | 14 days if preserved with HCl |
| TPH-Gasoline | 3-40 mL VOA vials w/ septum, per field station | 1:1 HCl, Cool to 4° C | 14 days |
| Lead | 1 L HDPE bottle | HNO ₃ to pH <2 (by lab within 24 hours of arrival) | 6 months |

¹ = Holding time for BTEX, TPH-Gasoline, and PAH samples is until extraction.

VOA = volatile organics analysis

QC = quality control

Laboratory

All samples collected for the project were analyzed by MEL, except grain size which was contracted out by MEL. Table 2 shows the analytical parameter, any required preparation method, and the analytical reference required for study samples.

Table 2. Sample Analysis, Methods, and References.

| Parameter | Preparation Method | Method | Reference |
|-----------------|--------------------|--|--------------|
| Sediment | | | |
| BTEX | -- | EPA SW-846 Method 8021B | EPA 1996 |
| TPH-Gasoline | -- | NWTPH-Gx | Ecology 1997 |
| Lead | EPA 3050B | EPA 6020 | EPA 1996 |
| PAHs | EPA 3540C | EPA 8270C | EPA 1996 |
| % Solids | -- | EPA 160.3 | EPA 1996 |
| Grain Size | -- | Plumb 1981 | EPA/CE-80-1 |
| TOC | -- | Combustion/CO ₂ Measurement @ 70° C | PSEP 1997 |
| Water | | | |
| BTEX | -- | EPA SW-846 Method 8021B | EPA 1996 |
| TPH-Gasoline | -- | NWTPH-Gx | Ecology 1997 |
| Lead | EPA 200.8 | EPA 200.8 | EPA 1999 |

Data Quality

Manchester Environmental Laboratory (MEL) provides written quality assurance reviews for each data package analyzed in-house or from contract laboratories. The reviews include descriptions of analytical methods, holding times, instrument calibration checks, blank results, surrogate recoveries, matrix spike recoveries, and laboratory control samples. No problems were reported that compromised the usefulness or validity of the sample results. The complete set of quality assurance reviews for organic analyses are contained in Appendix B of this report.

Overall, a review of the data quality control and quality assurance from laboratory case narratives indicates analytical performance was good. In general, data met measurement quality objectives established in the Quality Assurance Project Plan (Coots and Wittmann, 2005). One exception was the field replicate sample analyzed as a matrix spike duplicate for lead in water (sample number 05134251) that had a 159% recovery reported. The laboratory analyst noted the high bias was due to an inhomogeneous sample. This sample was qualified as estimated (“J”) in the data report. No data were rejected, and all results were useable as qualified.

As an estimate of overall precision, field replicate and laboratory duplicate and triplicate analysis was conducted. Relative percent difference (RPD) was calculated for field replicate and laboratory duplicate results and relative standard deviation (RSD) for laboratory triplicates. These results are included in Tables A3 and A4 in Appendix A.

Field replicates are two independent samples collected one after the other at the same location. The mean RPD from field replicates analyzed for lead, total solids, and total organic carbon averaged 11.6%. Field replicates analyzed for PAHs had a mean RPD of 26.2%.

Laboratory duplicates and triplicates consist of one sample split into two or three samples and analyzed separately. The mean RSD for laboratory triplicates analyzed for total solids and total organic carbon was 1.37%. Laboratory duplicates analyzed for PAHs had a mean RPD of 29.4%.

All field quality assurance and result data are available in electronic format from Ecology’s EIM data management system: www.ecy.wa.gov/eim/index.htm (search User ID number RCOO0005).

Results

Sediment

Table 3 summarizes the results for grain size, TOC, and percent solids in sediment samples collected from Black Lake. Analysis for grain size showed silts and sands composed the largest fractions in the samples. The fines (silts + clay fraction) in samples ranged from 42.2 to 70.5 percent. TOC was moderate ranging from 3.03 to 5.20 %, while percent solids ranged from 23.6 to 34.9.

Table 3. Physical and Chemical Characteristics of Black Lake Sediments (%).

| Sample ID | Sample No. (05-) | Gravel | Sand | Silt | Clay | TOC | Solids |
|-----------|------------------|--------|------|------|------|------|--------|
| BLG01 | 134240 | 0.6 | 28.7 | 66.5 | 4.0 | 4.10 | 27.3 |
| BLG02 | 134242 | 8.1 | 39.5 | 48.1 | 4.3 | 5.20 | 24.8 |
| BLG03 | 134246 | 17.2 | 40.5 | 39.6 | 2.6 | 3.37 | 34.9 |
| BLG04 | 134248 | 0.0 | 42.8 | 54.9 | 2.5 | 3.03 | 33.8 |
| BLG05 | 134244 | 7.3 | 24.9 | 63.1 | 4.7 | 3.46 | 26.9 |
| BLG06 | 134249 | 0.3 | 34.3 | 60.6 | 4.7 | 4.64 | 24.3 |
| BLG07 | 134250 | 2.9 | 46.6 | 46.8 | 3.8 | 4.56 | 23.6 |

TOC – total organic carbon

An active newer dock, and remnants of a historical dock with only deteriorated piling tops remaining at the water surface, were within the sampling area (Figure 2). A significant amount of litter from dock users and debris from shoreline vegetation was encountered on the sediment surface while collecting samples. Within the sampling area, sediment depth was only an estimated 10 cm, overlaying what appeared to be blue clay.

Following collection, each grab was evaluated for acceptability and whether a sheen was present on the surface of the sediments. A significant amount of debris was on the sediment surface but no sheen was present.

Results for TPH-gasoline, BTEX, and lead in sediments are summarized in Table 4. No TPH-gasoline or BTEX was detected in sediment samples collected from the study area. Sediment chemistry, along with visual observations, indicate petroleum products are not currently migrating to Black Lake from the Black Lake Grocery site.

Low levels of lead and PAHs were detected in Black Lake sediments. Lead ranged from 11.8 to 28.2 mg/Kg, dw (parts per million). The mean lead concentration was less than 6% of the recommended freshwater sediment quality value (FSQV) of 335 mg/Kg, dw.

Table 4. TPH-Gasoline, BTEX, and Lead in Black Lake Sediments ($\mu\text{g}/\text{Kg}$, dw; unless otherwise noted).

| Sample ID | Sample No. (05-) | Lead mg/Kg, dw | Benzene | Toluene | Ethyl-Benzene | m & p Xylene | o-xylene | Gasoline mg/Kg, dw |
|-----------|------------------|----------------|---------|---------|---------------|--------------|----------|--------------------|
| BLG01 | 134240 | 15.8 | 160U | 160U | 160U | 330U | 160U | 23U |
| BLG02 | 134242 | 16.7 | 190U | 190U | 190U | 390U | 190U | 27U |
| BLG03 | 134246 | 25.0 | 130U | 130U | 130U | 270U | 130U | 19U |
| BLG04 | 134248 | 11.8 | 140U | 140U | 140U | 280U | 140U | 19U |
| BLG05 | 134244 | 16.2 | 170U | 170U | 170U | 350U | 170U | 24U |
| BLG06 | 134249 | 28.2 | 190U | 190U | 190U | 370U | 190U | 26U |
| BLG07 | 134250 | 24.4 | 200U | 200U | 200U | 400U | 200U | 28U |

U = The analyte was not detected at or above the reported result.

Bold = The analyte is present in the sample.

In general, concentrations of individual PAHs were between 5 and 50 $\mu\text{g}/\text{Kg}$, dw (parts per billion), and total PAHs ranged from 12 to 218 $\mu\text{g}/\text{Kg}$, dw with a mean of 140 $\mu\text{g}/\text{Kg}$. The average of total PAHs in sediments collected from sites between 7 and 8 feet depth of water (BLG05, BLG06, BLG07) were roughly twice the average total PAHs (i.e., 95 $\mu\text{g}/\text{Kg}$ vs 200 $\mu\text{g}/\text{Kg}$) found in near-shore sediments collected between 3 and 5.5 feet (BLG01, BLG02, BLG03 and BLG04). The sample from site BLG06, collected from alongside the dock, had the highest total PAHs (Figure 3).

Petroleum sources have a higher percentage of alkyl-substituted low molecular weight PAHs (LPAHs) relative to their parent compounds (e.g., methyl-naphthalenes vs naphthalene) compared to combustion sources (Lake et al., 1979). The PAH patterns found in Black Lake sediments suggest combustion rather than petroleum sources (Table 5).

The sum of the individual high molecular weight PAHs (HPAH) was much greater than the sum of the individual LPAHs. This was expected given the weathering and higher volatility and solubility of the LPAHs. Levels of individual and total PAHs generally ran 2 to 3 orders of magnitude lower than the recommended FSQVs (Table 5). No previous Ecology studies of Black Lake had included PAHs, so comparisons were not possible.

PAHs are widely distributed in the environment. Petroleum and combustion of fossil fuels are sources of PAHs. The air is a common transport mechanism for PAHs associated with dust in addition to terrestrial run-off. Attached to airborne particles, PAHs can be transported long distances and deposited onto land and water surfaces.

Gasoline-powered outboard motors are also a source of PAHs to lakes. The docks located within the sampling area would increase the possibility of finding PAHs because of the concentration of outboard motor use. Two-stroke engines dominated the outboard engine field until more

recently and have been known to discharge a significant amount of gas and oil through normal operation. More modern outboards discharge exhaust directly into water through their propellers.

Results for the PAHs dibenzofuran and retene were also reported (Table 5). These semivolatile contaminants are commonly reported in urban sediments. Dibenzofuran and retene are often associated with wood waste. Retene, a resin acid, was detected in six of the seven sediment samples analyzed. Dibenzofuran was not detected.

Table 5. PAHs in Black Lake Sediments ($\mu\text{g}/\text{Kg}$, dw).

| Site ID: Sample No. (05-): | Detection Frequency | BLG01 134240 | BLG02 134242 | BLG03 134246 | BLG04 134248 | BLG05 134244 | BLG06 134249 | BLG07 134250 | FSQV ¹ |
|---|------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|---------------------------|
| Low Molecular Weight PAH (LPAH) | | | | | | | | | |
| Naphthalene | 57% | 11J | 7.4J | 28U | 28U | 8.4J | 10J | 42U | 529 |
| Acenaphthylene | 0% | 35U | 31U | 28U | 28U | 36U | 41U | 42U | 470 |
| Acenaphthene | 0% | 35U | 31U | 28U | 28U | 36U | 41U | 42U | 1,060 |
| Fluorene | 14% | 35U | 31U | 3.3J | 28U | 36U | 41U | 42U | 1,070 |
| Phenanthrene | 71% | 35U | 14J | 22J | 28U | 24J | 30J | 39J | <u>5,700</u> |
| Anthracene | 14% | 35U | 31U | 28U | 28U | 36U | 41U | 8.5J | 1,230 |
| 2-Methylnaphthalene | 29% | 8.9J | 31U | 28U | 28U | 4.2J | 41U | 42U | 469 |
| 1-Methylnaphthalene | 0% | 35U | 31U | 28U | 28U | 36U | 41U | 42U | - |
| 2-Chloronaphthalene | 0% | 35U | 31U | 28U | 28U | 36U | 41U | 42U | - |
| Total LPAH² | 56% | 20 | 21 | 25 | ND | 37 | 40 | 48 | 6,590 ³ |
| High Molecular Weight PAH (HPAH) | | | | | | | | | |
| Fluoranthene | 86% | 28J | 16J | 28U | 6.3J | 29J | 30J | 55 | <u>11,000</u> |
| Pyrene | 100% | 30J | 16J | 23J | 5.9J | 21J | 36J | 44 | 8,790 |
| Benzo(a)anthracene | 86% | 16J | 5.2J | 11J | 28U | 9.1J | 16J | 20J | 4,260 |
| Chrysene | 86% | 24J | 12J | 20J | 28U | 18J | 28J | 36J | 5,940 |
| Benzo(b)fluoranthene | 0% | 35U | 31U | 28U | 28U | 36U | 41U | 42U | <u>11,000⁴</u> |
| Benzo(k)fluoranthene | 57% | 57J | 45J | 28U | 28U | 56J | 68J | 42U | <u>11,000⁴</u> |
| Benzo(a)pyrene | 14% | 35U | 31U | 28U | 28U | 10J | 41U | 42U | 3,300 |
| Indeno(1,2,3-cd)pyrene | 0% | 35U | 31U | 28U | 28U | 36U | 41U | 42U | <u>730</u> |
| Dibenzo(a,h)anthracene | 0% | 35U | 31U | 28U | 28U | 36U | 41U | 42U | <u>230</u> |
| Benzo(ghi)perylene | 0% | 35U | 31U | 28U | 28U | 36U | 41U | 42U | <u>1,200</u> |
| Total HPAH² | 60% | 155 | 94 | 54 | 12 | 143 | 178 | 155 | 31,640 |
| Total PAH | | 175 | 115 | 79 | 12 | 180 | 218 | 203 | <u>60,000</u> |
| Dibenzofuran | 0% | 35U | 31U | 28U | 28U | 36U | 41U | 42U | 399 |
| Retene | 86% | 97 | 31J | 21J | 28U | 26J | 75 | 42 | 6020 |

¹ = Recommended Freshwater Sediment Quality Values for PAHs. Underlined FSQVs are from Cubbage et al., 1997; other values are from Avocet Consulting, 2003.

² = Totals are for detected compounds only.

³ = Total for LPAH does not include 1-methylnaphthalene, 2-methylnaphthalene, or 2-chloronaphthalene

⁴ = Value is for total benzofluoranthenes.

Bold = The analyte is present in the sample.

J = Analyte was positively identified; the associated result is an estimate.

U = Analyte was not detected at or above the reported result.

ND = Analytes were not detected.

Results of PAHs in sediments are summarized in Table 5 and shown on Figure 3.

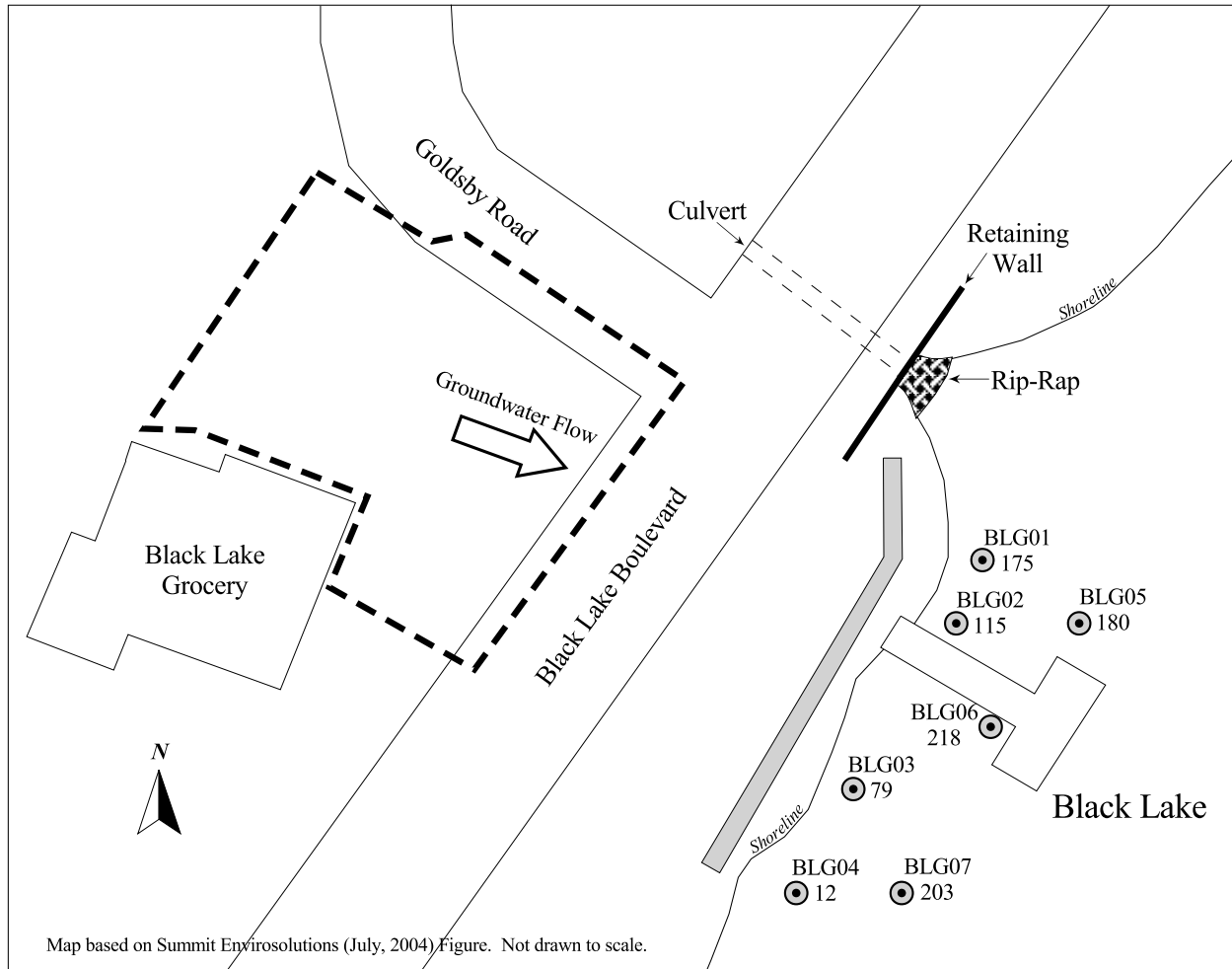


Figure 3. Total PAHs in Black Lake Sediments ($\mu\text{g}/\text{Kg}$, dry weight).

Water

Results for TPH-gasoline, BTEX, and lead in water are summarized in Table 6. No TPH-gasoline or BTEX was detected in water samples collected from the study area. Lead was detected in two of the three samples collected, slightly above the reporting limit.

Table 6. TPH-Gasoline, BTEX, and Lead in Black Lake Water ($\mu\text{g/L}$; unless otherwise noted).

| Site ID | Sample No. (05-) | Lead | Benzene | Toluene | Ethyl-Benzene | m- & p-xylene | o-xylene | Gasoline (mg/L) |
|---------|------------------|-------------|---------|---------|---------------|---------------|----------|-----------------|
| BLG01 | 134241 | 0.10U | 1.0U | 1.0U | 1.0U | 2.0U | 1.0U | 0.14U |
| BLG02 | 134243 | 0.13 | 1.0U | 1.0U | 1.0U | 2.0U | 1.0U | 0.14U |
| BLG03 | 134247 | 0.18 | 1.0U | 1.0U | 1.0U | 2.0U | 1.0U | 0.14U |

U = The analyte was not detected at or above the reported result.

Bold = The analyte is present in the sample.

Conclusions

No significant chemical contamination of target analytes was found in sediments or water samples collected from the Black Lake study area. The proposed Phase II bioassay sampling, contingent upon finding TPH-gasoline or BTEX during Phase I sampling, was not conducted.

Although low concentrations of PAHs were detected in sediments, they generally were between two to three orders of magnitude below recommended freshwater sediment quality values (FSQVs), and appear to be from combustion sources. Lead in sediments was also low, with the highest value reported more than an order of magnitude below the recommended FSQV.

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Appendix A. Sampling Information and Results

Table A1. Locations of Surface Sediments and Water Sample Sites in Black Lake

Table A2. Field Log Descriptions of Surface Sediments

Table A3. Field Replicate and Laboratory Triplicate Results for Lead, Total Solids,
and Total Organic Carbon

Table A4. Field Replicate and Laboratory Duplicate Results for PAHs.

Table A1. Locations of Surface Sediments and Water Sample Sites in Black Lake (decimal degrees).

| Station | Latitude | Longitude |
|---------|----------|-----------|
| BLG01 | 47.0077 | -122.9745 |
| BLG02 | 47.0076 | -122.9746 |
| BLG03 | 47.0075 | -122.9746 |
| BLG04 | 47.0074 | -122.9747 |
| BLG05 | 47.0076 | -122.9744 |
| BLG06 | 47.0075 | -122.9745 |
| BLG07 | 47.0074 | -122.9746 |

Datum = NAD27

Table A2. Field Log Descriptions of Surface Sediments.

| Station | Water Depth (ft) | Date | Time | Sediment Penetration (cm) | Sample Description |
|---------|------------------|---------|------|---------------------------|---|
| BLG01 | 3.5 | 3/29/05 | 1200 | 8.0 | Gray to black, sulfur smell; wood debris. *T = 11.5 Cond = 85 |
| BLG02 | 3.75 | 3/29/05 | 1300 | 7.0 | Woody debris, blue clay below sediment. T = 11.5 Cond = 85 |
| BLG03 | 5.5 | 3/30/05 | 1200 | 9.0 | Gray-green to black with coontail, tree debris; blue clay below sediment. T = 11.0 Cond = 85 |
| BLG04 | 4.0 | 3/30/05 | 1515 | 7.0 | Dark green with tree debris and root mass; slight sulfur smell. |
| BLG05 | 7.5 | 3/29/05 | 1530 | 5.0 | Gray to black, blue clay below sediment. |
| BLG06 | 7.5 | 3/30/05 | 1050 | 9.0 | Dark gray to black, blue clay below sediment. |
| BLG07 | 8.0 | 3/30/05 | 1450 | 8.0 | Dark green to brown, fairly free of wood debris. |

* T = temperature (°C) and Cond = conductivity (umhos) of water samples.

Table A3. Field Replicate and Laboratory Triplicate Results for Lead, Total Solids, and Total Organic Carbon.

| QA Sample | Sample Nos. (05-) | Field ID | Result 1 | Result 2 | Result 3 | RPD ¹ | RSD ² |
|--------------------------|----------------------|---------------|-------------|-------------|-------------|------------------|------------------|
| Lead in Water (ug/L) | | | | | | | |
| Field Dup. | 134247/134252 | BLG03/BLGREP | 0.18 | 0.22 | | 20% | |
| Lead in Sediment (ug/Kg) | | | | | | | |
| Field Dup. | 134246/134251 | BLG03/BLGREP | 25.0 | 23.8 | | 4.9% | |
| Total Solids (%) | | | | | | | |
| Field Dup. | 134246/134251 | BLG03/BLGREP | 34.9 | 28.2 | | 21.2% | |
| Lab Trip. | 134240 | BLG01/REP 1&2 | 27.3 | 26.9 | 26.9 | | 0.85% |
| TOC (%) | | | | | | | |
| Field Dup. | 134246/134251 | BLG03/BLGREP | 3.37 | 3.38 | | 0.30% | |
| Lab Trip. | 134240 | BLG01/REP 1&2 | 4.10 | 4.25 | 4.22 | | 1.89% |
| Mean RPD/RSD | | | | | | 11.6% | 1.37% |

1 = RPD is defined as the difference between two results divided by their mean, times 100.

2 = RSD is defined as the standard deviation of multiple results divided by the mean, times 100.

Table A4. Field Replicate and Laboratory Duplicate Results for PAHs.

| Field Replicates | Sample Nos. 05134246 and 05134251 | | |
|--------------------|-----------------------------------|-----------|---------|
| PAH | Results 1 | Results 2 | RPD (%) |
| Fluorene | 3.3J | 35U | - |
| Phenanthrene | 22J | 35U | - |
| Fluoranthene | 28U | 31J | - |
| Pyrene | 23J | 29J | 23.1 |
| Retene | 21J | 26J | 21.3 |
| Benzo(a)anthracene | 11J | 15J | 30.8 |
| Chrysene | 20J | 27J | 29.8 |
| | | Mean RPD | 26.2% |

| Laboratory Duplicates | Sample No. 05134240 | | |
|-----------------------|---------------------|-----------|---------|
| PAH | Results 1 | Results 2 | RPD (%) |
| Naphthalene | 11J | 27J | 84.2 |
| 2-Methylnaphthalene | 8.9J | 20J | 76.8 |
| Fluoranthene | 28J | 30J | 6.9 |
| Pyrene | 30J | 32J | 6.5 |
| Retene | 97 | 67 | 36.6 |
| Benzo(a)anthracene | 16J | 17J | 6.1 |
| Chrysene | 24J | 26J | 8.0 |
| Benzo(k)fluoranthene | 57J | 63J | 10.0 |
| | | Mean RPD | 29.4% |

RPD – Relative percent difference

Appendix B. Case Narratives for Individual Analyses

Data Qualifier Codes

- U - The analyte was not detected at or above the reported result.
- J - The analyte was positively identified. The associated numerical result is an estimate.
- UJ - The analyte was not detected at or above the reported estimated result.
- REJ - The data are unusable for all purposes.
- NAF- Not analyzed for.
- N - For organic analytes there is evidence the analyte is present in this sample.
- NJ - There is evidence that the analyte is present. The associated numerical result is an estimate.
- NC - Not calculated
- E - The concentration exceeds the known calibration range.
- bold-** The analyte was present in the sample. (Visual Aid to locate detected compounds on report sheet.)

Manchester Environmental Laboratory
7411 Beach Dr E, Port Orchard, Washington 98366

Case Narrative

March 24, 2005

Subject: Black Lake Sediment/Water Study – 13 Project

Sample(s): 05134240-52

Officer(s): Randy Coots

By: Bob Carrell

NWTPH-Gx Analysis

Analytical Method

The water samples, sediment samples, a sample duplicate and method blanks were analyzed by the NWTPH-Gx method which, in the case of water, involves purging a portion of the water of its volatile compounds, trapping the analytes then desorbing them to the inlet of a gas chromatograph (GC) where they are separated by the chromatographic column and determined by flame ionization detection (FID) for total gasoline. For soil samples it involves extracting an aliquot of sediment with methanol then adding a portion of the methanol extract to water and purging it.

Holding Times

The samples were analyzed within the recommended sample holding times.

Calibration

The initial eleven point gasoline calibration used a linear fit which had a correlation coefficient of greater than 0.99 and no standard point varied from its true value by more than +/- 15%. The mid-range calibration check sample for target analytes was within +/- 15% of its true value at the beginning, middle and end of the analyses.

Blanks

No analytically significant levels of analyte were detected in the method blank associated with this sample.

Surrogates

The surrogate recoveries were acceptable and within QC acceptance limits of 70% to 130%.

Sample Duplicate

The results of the sample duplicate were acceptable.

Laboratory Control Spike

None prepared.

Manchester Environmental Laboratory
7411 Beach Dr E, Port Orchard, Washington 98366

Case Narrative

April 14, 2005

Subject: Black Lake Sediment/Water Study - 13 Project

Sample(s): 05134240-52

Officer(s): Randy Coots

By: Bob Carrell

BTEX Analyses

Analytical Method

The soil samples, a BTEX laboratory control spike and a method blank were extracted and analyzed by the BTEX method which involves extracting a portion of the sample with methanol, then purging an aliquot of that methanol in water, trapping the analytes then desorbing them to the inlet of a gas chromatograph (GC) where they are separated by the chromatographic column and determined by flame ionization detection (FID) for total gasoline and photoionization detection (PID) for BTEX. For the water samples, a portion of the water was purged, the analytes trapped then desorbed and analyzed as above.

Holding Times

The samples were analyzed within the accepted holding times.

Calibration

The initial eight point BTEX calibrations used linear fit which had correlation coefficients of greater than 0.99 and no standard point varied from its true value by more than +/- 15%. The mid-range calibration check sample for target analytes showed high bias for the BTEX compounds. Since no BTEX compounds were found at the limit of quantitation no qualifiers were necessary due to a high biased calibration check standard (CCV).

Blanks

No analytically significant levels of analyte were detected in the method blank associated with this sample.

Surrogates

The surrogate recoveries were acceptable and within QC acceptance limits of 70% to 130% except for the 1,4-dibromo-2-methyl benzene surrogate for the method blank OBW05094TX (136%). Since there is high bias and no target analytes were found at the quantitation limit, no qualifiers were added.

Sample Duplicates

None analyzed.

Laboratory Control Spikes

The results of the LCS were acceptable.

Manchester Environmental Laboratory
7411 Beach Dr E, Port Orchard, Washington 98366

Case Narrative

April 13, 2005

Subject: Black Lake Sediment/Water Study - 13

Sample(s): 05-134240, -134242, -134244, -134246 and -134248 to -134251

Officer(s): Randy Coots

By: Dickey Huntamer

Semivolatiles

PAH

Analytical Method(s)

These samples were Soxhlet extracted using acetone and analyzed by SW846 Method 8270 using capillary GC and a mass spectrometer detector. Silica gel cleanup was used to clean up the sample extracts.

Holding Times

All samples were prepared and analyzed within the method holding times.

Instrument Tuning

Calibration against DFTPP is acceptable for the initial calibration, continuing calibration and all associated sample analyses.

Calibration

The average relative response factors for target analytes were above the minimums and % Relative Standard Deviations were within the maximum of 15% for the initial calibration. The average relative response factors for target analytes were above the minimums and % Relative Standard Deviations were within the maximum of 20% for the continuing calibration except for carbazole which had a high response. No qualifiers were added to the sample results since carbazole was not detected in the samples.

Blanks

No target compounds were detected in the laboratory blanks.

Surrogates

The surrogate recoveries were reasonable, acceptable, and within QC limits of 18% to 137% for d14-terphenyl, 50% to 150% for d10-pyrene and 30% to 115% for 2-fluorobiphenyl.

Matrix Spikes

Sample -134242 was used for the sediment matrix spike in the first extraction set. All recoveries except for carbazole were within the acceptable range of 50% to 150% in LMX1 but the matrix spike duplicate LMX2 apparently did not extract and nothing was detected. Sample -134250 was used for the matrix spikes in the re-extractions of samples -134246 and -134250. Carbazole recovery was also high but carbazole was not detected in any of the samples so no additional qualifiers were added to the results.

Replicates

Sample-134240 was analyzed in duplicate.

Laboratory Control Samples

Recovery data were within QC limits of 50% to 150% for the laboratory fortified blank, OL05101S1 in the second extraction. No compounds were recovered in OL05090S1 due to failures of the extraction apparatus.

Comments

Two compounds, benzo(b)fluoranthene and benzo(k)fluoranthene experienced chromatographic problems and their peaks could not be resolved. As a result half the peak was assigned to benzo(b)fluoranthene and the other half to benzo(k)fluoranthene.

All results for benzo(b)fluoranthene and benzo(k)fluoranthene were qualified as estimates "J" if detected.

Quantitation limits are elevated from normal levels due to the low percent solids <30%.

The data are useable as qualified.

Manchester Environmental Laboratory
7411 Beach Dr E, Port Orchard, Washington 98366

Case Narrative

April 14, 2005

Subject: Metals Black Lake Sediment/Water Study - 13

Project No: 119805

Officer: Randy Coots

By: Dean Momohara

Summary

The samples were analyzed and/or digested using the following methods: EPA method 3050B and 200.8 for the digestion of solid and liquid samples, respectively, and EPA method 200.8 (ICPMS) for the analysis of lead.

All analyses requested were evaluated by established regulatory quality assurance guidelines.

Sample Information

Samples were received by Manchester Environmental Laboratory on 3/30/05 and 3/31/05. All coolers were received within the proper temperature range of 0°C - 6°C. The samples were received in good condition. The liquid samples were received unpreserved and were preserved upon receipt. Twelve (12) samples were received and assigned laboratory identification numbers 134240 - 134244 and 134246 – 134252.

Holding Times

All analyses were performed within established EPA holding times.

Calibration

Instrument calibrations and calibration checks were performed in accordance with the appropriate method. All initial and continuing calibration checks were within control limits. The calibration correlation coefficients were within the acceptance range of 1.000 - 0.995. The instrument was calibrated with a NIST traceable standard and verified to be in calibration with a second source NIST traceable standard. Balances are professionally calibrated yearly and calibrated in-house daily. Soil drying oven temperatures were recorded before and after each analysis batch and were within acceptable limits.

Method Blanks

No analytically significant levels of analyte were detected in the method blanks associated with these samples.

Matrix Spikes

One of the matrix spike (MS) recoveries for sample 134251 was greater than the acceptance limit. The sample appears inhomogeneous. The source sample was qualified as an estimate. All other MS recoveries were within the acceptance limits of 75% - 125%.

Replicates

All duplicate relative percent differences were within the acceptance range of 0% - 20%.

Laboratory Control Samples

All laboratory control sample recoveries were within the acceptance limits of 85% - 115%.

Other Quality Assurance Measures and Issues

All internal standard recoveries were within acceptance limits.

Please call Dean Momohara at (360) 871-8808 to further discuss this project.

cc: Project File

Manchester Environmental Laboratory
7411 Beach Dr E, Port Orchard, Washington 98366

Case Narrative

April 10, 2005

Subject: General Chemistry Black Lake Sediments/Water Study - 13

Project No: 119805

Officer: Randy Coots

By: Dean Momohara

Summary

The samples were analyzed by the following methods: Standard Methods 2540G for percent solids and PSEP – TOC for total organic carbon (TOC).

All analyses requested were evaluated by established regulatory quality assurance guidelines.

Sample Information

Samples were received by Manchester Environmental Laboratory on 3/30/05 and 3/31/05. All coolers were received within the proper temperature range of 0°C - 6°C. All samples were received in good condition. Eight (8) samples were received and assigned laboratory identification numbers 134240, 134242, 134244, 134246 and 134248 – 134251.

Holding Times

All analyses were performed within established EPA holding times.

Calibration

TOC instrument calibrations and calibration checks were performed in accordance with the appropriate method. All initial and continuing calibration checks were within control limits. The calibration correlation coefficient was within the acceptance range of 1.000 - 0.995. Balances are professionally calibrated yearly and calibrated in-house daily. Oven temperatures were recorded before and after each analysis batch and were within acceptable limits.

Method Blanks

For TOC analysis, no analytically significant level of analyte was detected in the method blanks associated with these samples.

Matrix Spikes

NA

Replicates

All duplicate relative percent differences were within the acceptance range of 0% - 20%.

Laboratory Control Samples

The TOC laboratory control sample recovery was within the acceptance limits of 57% - 143%.

Please call Dean Momohara at (360) 871-8808 to further discuss this project.

cc: Project File

Manchester Environmental Laboratory
7411 Beach Dr E, Port Orchard, Washington 98366

Case Summary

May 10, 2005

Project: Black Lake Sediment

Samples: 13-4240, 4242, 4244, 4246, 4248-4251

Laboratory: Analytical Resources, Inc.

By: Pam Covey

The sediment samples required Grain Size analyses using the Puget Sound Estuary Protocol (PSEP) method. The samples were received at the Manchester Environmental Laboratory and shipped to the contract lab on April 12, 2005 for Grain Size analyses. One sample was analyzed in triplicate and was within the QA limits.

The analyses were reviewed for qualitative and quantitative accuracy, validity and usefulness.

If you have any questions, please call me at 360-871-8827.