



## 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.

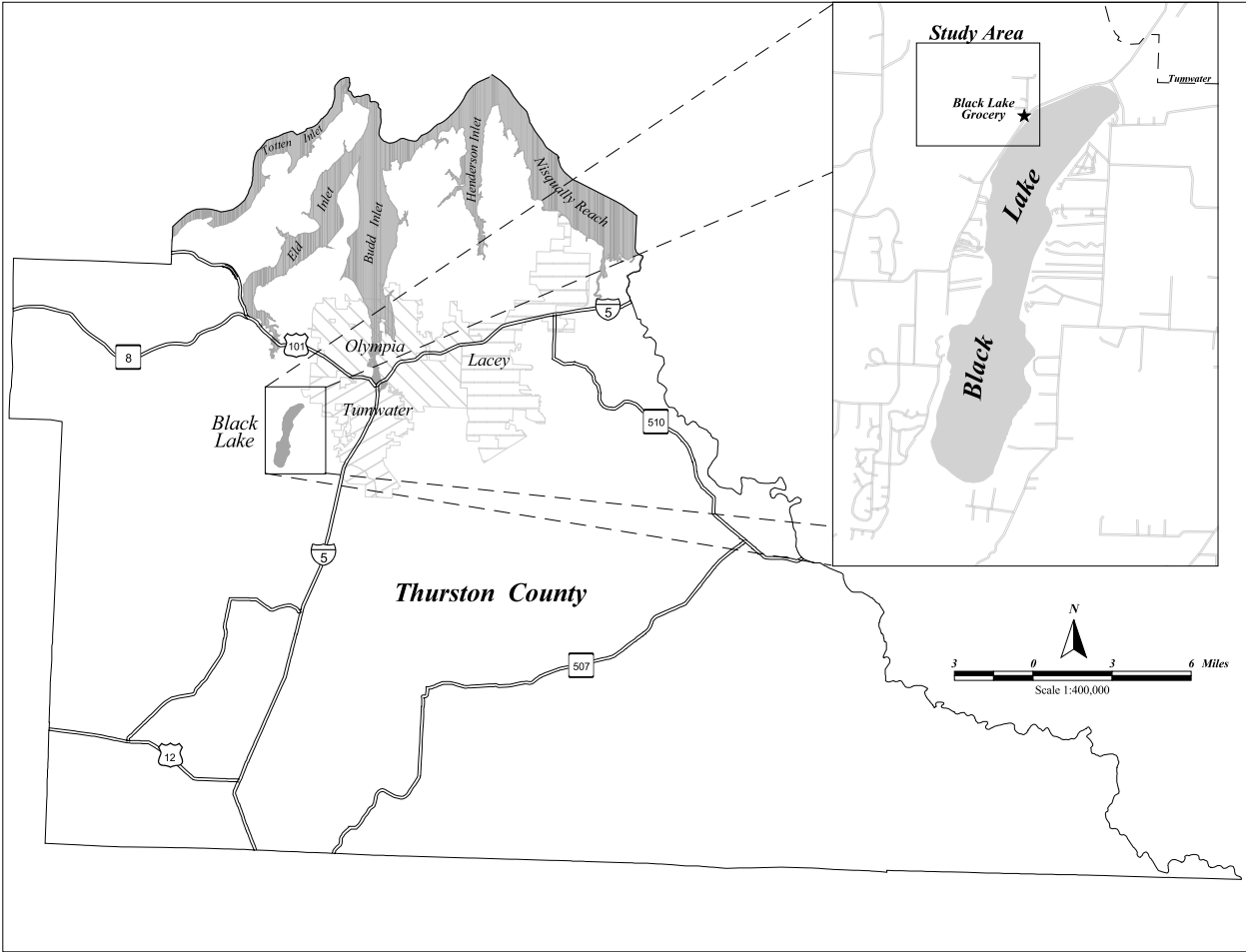


Figure 1. General Location of Black Lake and the Black Lake Grocery Site.

# Monitoring Program

Sediment and water samples were collected at seven locations within Black Lake on March 29 and 30, 2005 (Figure 2). Sediments were analyzed for TPH-gasoline, BTEX, PAHs, lead, percent solids, grain size, and total organic carbon (TOC). Water samples were analyzed for TPH-gasoline, BTEX, and lead. Ancillary water quality parameters included temperature and conductivity.

A Quality Assurance Project Plan was used as guidance for the study (Coots and Wittmann, 2005).

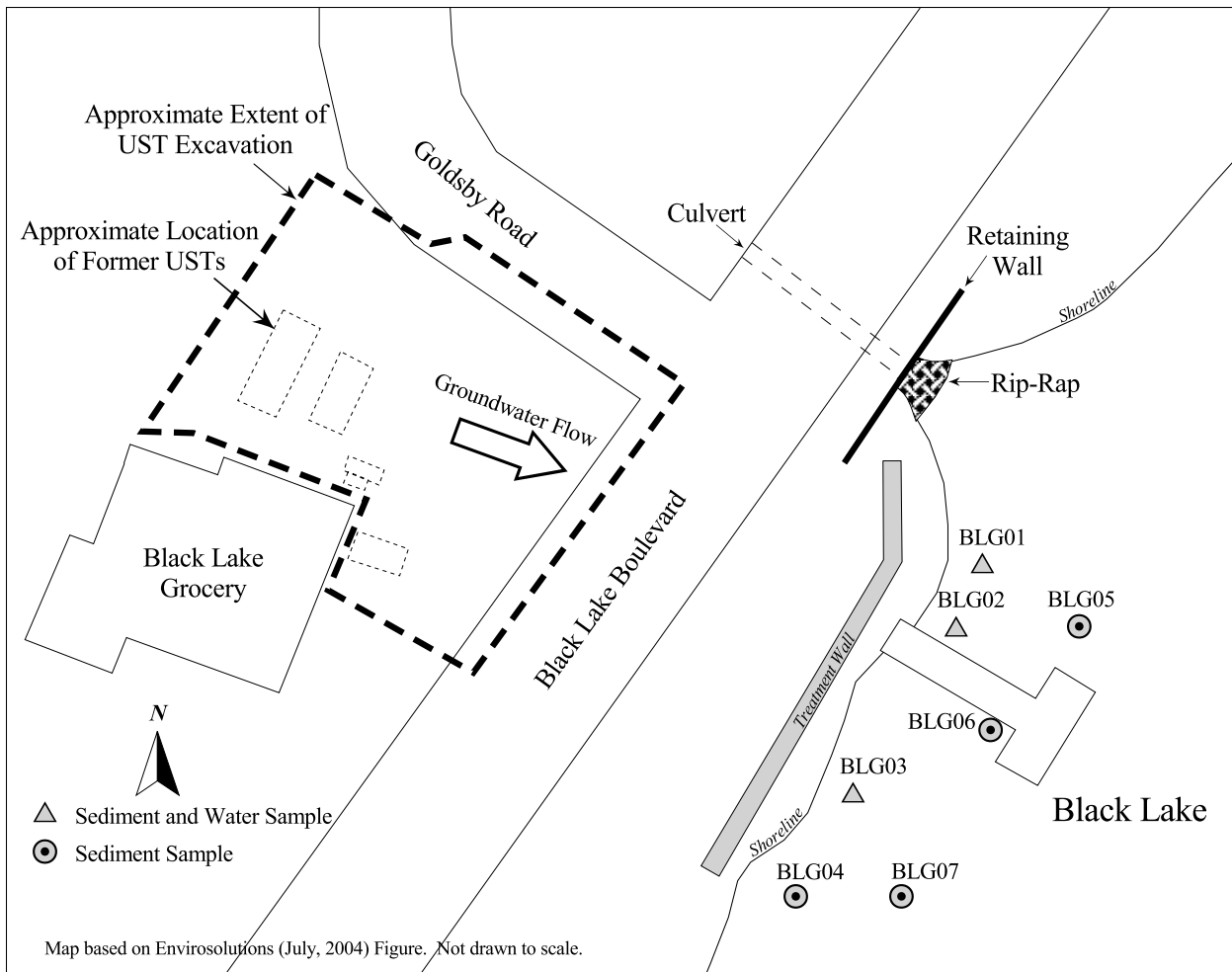


Figure 2. Black Lake Study Area Showing Sediment and Water Sampling Stations. (UST – underground storage tank)

## Methods

### Field

Sediments were collected from a 16-foot Wooldridge jet sled using a 0.05 m<sup>2</sup> stainless steel Ponar grab. Sampling stations were located by Global Positioning System (GPS) and recorded in field logs. Sample stations are shown on Figure 2. Coordinates and field log descriptions are provided in Table A1 and A2 in Appendix A.

Sediments were collected from a total of seven sites (Figure 2), with one additional set of replicate samples included for quality assurance purposes. To avoid volatilization of target analytes, the TPH-gasoline and BTEX samples were collected without homogenization and placed directly into appropriate jars based on their respective analytical methods. For other analyses, the sediments were homogenized prior to placement into sample containers.

Each sediment sample was a composite of equal portions of two separate grabs. Following an evaluation of acceptability, each sediment grab had overlying water siphoned off, and debris on the sediment surface was discarded prior to sub-sampling by stainless steel spoons and bowls. Materials in contact with the grab sampler were not retained for analysis.

Water samples were collected at three stations (BLG01, BLG02, BLG03) by use of a peristaltic pump and dedicated Tygon tubing. Samples were collected 15 cm above the sediment water interface with care to avoid disturbance of the sediments. An additional sample was collected at each site for determination of temperature and conductivity, measured by a red-line alcohol thermometer and Beckman conductivity meter.

Immediately following collection, sample jars from each station were sealed in a zip-lock plastic bag, placed in a cooler with ice, and kept in a sample refrigerator at Ecology's headquarters building overnight. Samples were transported by courier to the Ecology Manchester Environmental Laboratory (MEL) the following morning. Chain of custody was maintained throughout the sample and analysis process.

All sample containers were provided by MEL, cleaned to EPA (1990) QA/QC specifications, and certified for trace organic analyses. All stainless steel sampling equipment was pre-cleaned with Liquinox detergent, then rinsed with deionized water, 10% nitric acid solution, and pesticide-grade hexane. Equipment was then air dried under a fume hood and completely wrapped in aluminum foil until used in the field. Each site had dedicated pre-cleaned equipment for sampling.

The sediment grab was also pre-cleaned and wrapped in aluminum foil prior to going into the field. Between sample stations, the grab was thoroughly scrubbed and rinsed with site water to avoid cross-contamination.



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 <sup>1</sup>
<b>Sediment</b>			
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
<b>Water</b>			
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 <sub>3</sub> to pH <2 (by lab within 24 hours of arrival)	6 months

<sup>1</sup> = 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
<b>Sediment</b>			
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 <sub>2</sub> Measurement @ 70° C	PSEP 1997
<b>Water</b>			
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](http://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	<b>15.8</b>	160U	160U	160U	330U	160U	23U
BLG02	134242	<b>16.7</b>	190U	190U	190U	390U	190U	27U
BLG03	134246	<b>25.0</b>	130U	130U	130U	270U	130U	19U
BLG04	134248	<b>11.8</b>	140U	140U	140U	280U	140U	19U
BLG05	134244	<b>16.2</b>	170U	170U	170U	350U	170U	24U
BLG06	134249	<b>28.2</b>	190U	190U	190U	370U	190U	26U
BLG07	134250	<b>24.4</b>	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 <sup>1</sup>
<b>Low Molecular Weight PAH (LPAH)</b>									
Naphthalene	57%	<b>11J</b>	<b>7.4J</b>	28U	28U	<b>8.4J</b>	<b>10J</b>	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	<b>3.3J</b>	28U	36U	41U	42U	1,070
Phenanthrene	71%	35U	<b>14J</b>	<b>22J</b>	28U	<b>24J</b>	<b>30J</b>	<b>39J</b>	<u>5,700</u>
Anthracene	14%	35U	31U	28U	28U	36U	41U	<b>8.5J</b>	1,230
2-Methylnaphthalene	29%	<b>8.9J</b>	31U	28U	28U	<b>4.2J</b>	41U	42U	469
1-Methylnaphthalene	0%	35U	31U	28U	28U	36U	41U	42U	-
2-Chloronaphthalene	0%	35U	31U	28U	28U	36U	41U	42U	-
<b>Total LPAH<sup>2</sup></b>	56%	<b>20</b>	<b>21</b>	<b>25</b>	ND	<b>37</b>	<b>40</b>	<b>48</b>	6,590 <sup>3</sup>
<b>High Molecular Weight PAH (HPAH)</b>									
Fluoranthene	86%	<b>28J</b>	<b>16J</b>	28U	<b>6.3J</b>	<b>29J</b>	<b>30J</b>	<b>55</b>	<u>11,000</u>
Pyrene	100%	<b>30J</b>	<b>16J</b>	<b>23J</b>	<b>5.9J</b>	<b>21J</b>	<b>36J</b>	<b>44</b>	8,790
Benzo(a)anthracene	86%	<b>16J</b>	<b>5.2J</b>	<b>11J</b>	28U	<b>9.1J</b>	<b>16J</b>	<b>20J</b>	4,260
Chrysene	86%	<b>24J</b>	<b>12J</b>	<b>20J</b>	28U	<b>18J</b>	<b>28J</b>	<b>36J</b>	5,940
Benzo(b)fluoranthene	0%	35U	31U	28U	28U	36U	41U	42U	<u>11,000<sup>4</sup></u>
Benzo(k)fluoranthene	57%	<b>57J</b>	<b>45J</b>	28U	28U	<b>56J</b>	<b>68J</b>	42U	<u>11,000<sup>4</sup></u>
Benzo(a)pyrene	14%	35U	31U	28U	28U	<b>10J</b>	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>
<b>Total HPAH<sup>2</sup></b>	60%	<b>155</b>	<b>94</b>	<b>54</b>	<b>12</b>	<b>143</b>	<b>178</b>	<b>155</b>	31,640
<b>Total PAH</b>		<b>175</b>	<b>115</b>	<b>79</b>	<b>12</b>	<b>180</b>	<b>218</b>	<b>203</b>	<u>60,000</u>
Dibenzofuran	0%	35U	31U	28U	28U	36U	41U	42U	399
Retene	86%	<b>97</b>	<b>31J</b>	<b>21J</b>	28U	<b>26J</b>	<b>75</b>	<b>42</b>	6020

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

<sup>2</sup> = Totals are for detected compounds only.

<sup>3</sup> = Total for LPAH does not include 1-methylnaphthalene, 2-methylnaphthalene, or 2-chloronaphthalene

<sup>4</sup> = 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.

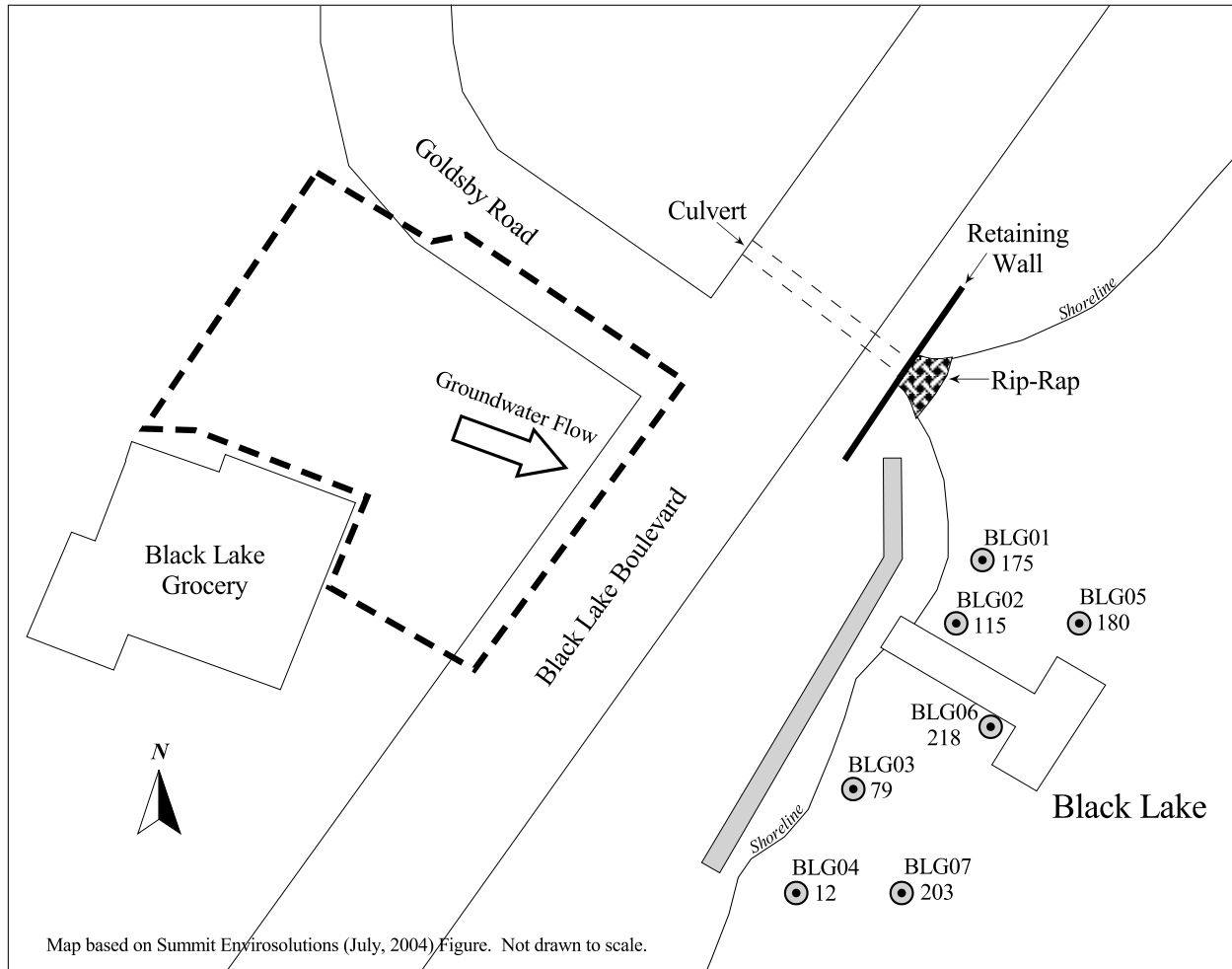


Figure 3. Total PAHs in Black Lake Sediments ( $\mu\text{g}/\text{Kg}$ , dry weight).

## 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	<b>0.13</b>	1.0U	1.0U	1.0U	2.0U	1.0U	0.14U
BLG03	134247	<b>0.18</b>	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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Project No. 0551-002.

## 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 <sup>1</sup>	RSD <sup>2</sup>
Lead in Water ( <i>ug/L</i> )							
Field Dup.	134247/134252	BLG03/BLGREP	0.18	0.22		20%	
Lead in Sediment ( <i>ug/Kg</i> )							
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.