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Foreword

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This publication has been produced as part of the laboratory's strategic long-term research plan. It is published and made available by EPA's Office of Research and Development to assist the user community and to link researchers with their clients.

Sally Gutierrez, Director
National Risk Management Research Laboratory

CONTENTS

FIGURES

TABLES

APPENDICES

ABBREVIATIONS AND ACRONYMS

CH_4	methane
CO_2	carbon dioxide
COC	contaminant of concern
DO	dissolved oxygen
EPC	electronic pressure controlled
GC/MS	gas chromatography/mass spectrometry
HDPE	high density polyethylene
HP	Hewlett Packard
IS	internal standard
MSD	mass selective detector
NAPL	non-aqueous phase liquid
ORP	oxidation-reduction potential
PAH	polycyclic aromatic hydrocarbon
PCB	polychlorinated biphenyl
PFTBA	perfluorotributylamine
psi	pounds per square inch
PUF	polyurethane foam
QA	quality assurance
RIs	retention indices
rpm	rotations per minute
SIM	selected ion monitoring
SIS	surrogate internal standards
tPAH	total polycyclic aromatic hydrocarbon
U.S. EPA	United States Environmental Protection Agency
VOA	volatile organic analysis

EXECUTIVE SUMMARY

When sediments are rich in organic, anaerobic and aerobic processes, they generate biogenic gases, mainly methane (CH_4) and carbon dioxide (CO_2). A higher CH_4 content in the gas is indicative of methanogenic conditions and a reductive environment. This condition facilitates the transfer of contaminants of concern (COCs) from the sediment through the surrounding water to the atmosphere. Prior research at Eagle Harbor (Bainbridge Island, Washington) demonstrated that when polycyclic aromatic hydrocarbon (PAH) contaminated sediment was capped, biogenic gas began to percolate through the cap matrix. Prior research on polychlorinated biphenyl (PCB)-contaminated sediment at Lake Hartwell (Clemson, South Carolina) demonstrated that as the organic concentration in Lake Hartwell increased, the generation of gas increased. The volume of gas generated was dependent on many factors including the amount of sediment, seasonal conditions, depth of the lake, and water temperature.

The release of gas bubbles from sediments into overlying water (ebullition) is a major mechanism for the discharge of biogenic and geogenic gases into the water body. Microbial breakdown of sedimentary organic matter produces gas bubbles which are inherently hydrophobic and tend to accumulate both hydrophobic organic contaminants and colloids from porewater. Through this mechanism the ebullition of CH_4 and CO_2 in contaminated sediments may contribute to the release of CoCs from the sediment-water interface and into the water column. With the formation of gas bubbles in the sediment, a three phase benthic system exists: solid sediment particles, water and gas. Organic compounds present in sediment will partition between the solid sediment particles and liquid porewater based on the sorptive characteristics of the sediment and physicochemical properties of the COCs. Partitioning of the organic contaminant between the gas and water phase is determined by the gas-water partition coefficient of individual components of the COC. The transport of contaminants would therefore occur when gas bubbles, containing volatilized organic compounds, are ejected from the sediment and transported directly to the atmosphere. Transfer of organic contaminants from the gas bubbles to the overlying water may occur during transit through the water column as a result of gas to water partitioning. Microbial breakdown of sedimentary organic matter produces gases, which tend to migrate out of sediments into overlying water and are eventually vented to the atmosphere. Gas generation indicates that microorganisms are able to break down sedimentary organic matter for energy and nutrients. The duration of gas production is still unknown, since gas production is still occurring. No systematic column studies have explored the phenomenon of gas ebullition in sediments on the stability and effectiveness of the cap and consequently to the release of sediment/cap bound contaminants to overlying water.

This report describes the performance of microcosm and a bench-scale column studies to attempt to understand and quantify the release of COCs from uncapped and capped sediments. The gas ebullition through the sediment bed was simulated by sparging mixed anaerobic gas at two flow rates (6.5 and 18.5 mL/min).

The microcosm experiments indicated that the serum bottles tested maintained anaerobic conditions. Higher percentages of CH_4 and CO_2 were contained in the headspace of the Lake Hartwell serum bottles than the Eagle Harbor samples at 37 °C. No detectable level of gas was measured at the lower temperatures (10 °C and 25 °C) for either the Eagle Harbor or Lake Hartwell sediments. Higher concentrations of PAHs (ng/g) were observed in the Eagle Harbor sediment as the temperature increased from 10 °C to 37 °C. The concentrations of PCBs (ng/g) in the serum bottles containing Lake Hartwell sediment with an incubation temperature of 10 °C were higher than those incubated at 25 °C and 37 °C. However, the PCB concentrations (ng/L) in water increased as the incubation temperature increased from 10 °C to 37 °C. The PCBs in the Lake Hartwell sediment partitioned into the water phase more strongly at higher temperatures than lower temperatures.

The results of the simulated gas ebullition column experiments showed that the total polycyclic aromatic hydrocarbon (tPAH) captured by the polyurethane foam (PUF) during the 6^{th} and 19^{th} week sampling events from the uncapped Eagle Harbor columns at low gas flow rate (6.5 mL/min) conditions was more than the capped columns. The uncapped PUFs also recovered PAHs with higher molecular weights, which were not detected in the capped PUF. At high gas flow rates (18.7 mL/min), the PUFs captured more tPAH from the uncapped sediment columns than the capped columns. After 19-weeks of gas sparging, the PUFs for the capped column sorbed lower molecular weight PAH compounds, such as 1-methylnaphthalene and C1-naphthalenes, than the uncapped column. However, the PUFs from the uncapped columns consistently sorbed higher molecular weight PAH compounds than the capped column.

The PUFs at the outlet of columns containing Lake Hartwell spiked and unspiked sediment captured 1041 and 164 ng of tPCB, respectively, at low gas flow conditions. The PUFs also captured higher molecular weight PCBs (such as Cl5(110)) from the PCB spiked sediment.

During high gas sparging, the PUFs sorbed more PCBs from columns that were packed with unspiked Lake Hartwell sediment in comparison to the low flow columns. The transfer of PCBs from the sediment to the water column and thereafter to the air appeared to be more dependent on the sparging flow rate than the concentration of PCB in the sediment. Higher concentrations of PCBs (hydrophobic) could be sorbed in the sediment with a low risk of escape as long as the gas ebullition rate was low. Higher gas sparging also resulted in the release of higher molecular weight PCBs.

Section 1.0 PROJECT BACKGROUND AND OBJECTIVES

The release of gas bubbles from sediments into overlying water (ebullition) is a major mechanism for the discharge of biogenic and geogenic gases into the water body. Microbial breakdown of sedimentary organic matter produces gas bubbles which are inherently hydrophobic and tend to accumulate both hydrophobic organic contaminants and colloids from porewater. Through this mechanism the ebullition of methane (CH_4) and carbon dioxide (CO_2) in contaminated sediments, may contribute to the release of contaminants of concern (COCs) from the sediment-water interface and into the water column.

Previous research conducted by U.S. EPA for polycyclic aromatic hydrocarbon (PAH) contaminated sediments at Eagle Harbor (Bainbridge Island, Washington; Figure 1-2) also demonstrated the potential for dissolved gases to percolate through the in-place sediment cap material (sand) by convective or diffusive transport. It was hypothesized that biogenic gas transport may facilitate the migration of PAHs through the cap by providing avenues for release or solubilizing the COCs carrying them through the porous media dissolved in the gaseous molecules. The U.S. EPA has also quantified the volume of gas produced at various depths within the cap material and underlying sediments and found that gas production at this site was extremely low and that there was insufficient gas volume for PAHs analysis.

Previous research conducted by the United States Environmental Protection Agency (U.S. EPA) for polychlorinated biphenyl (PCB) contaminated sediments at Lake Hartwell, in Clemson, South Carolina (Figure 1-1), showed that high organic loading in sediments resulted in significant gas ebullition at the site. Studies were conducted over the course of one year and sediment gas production was quantified through the use of submerged gas collection chambers. Gas production rates were calculated and were shown to be highly dependant upon the lake depth, organic material and water temperature. Although the gas production in collection chambers was significant in certain test locations at Lake Hartwell, the volume of gas produced during these monitoring events was not sufficient to measure PCB content.

1.1 Problem Definition

The atmospheric concentration of CH_4 (a greenhouse gas) has risen ~1% per year (Ostrovsky, 2003); it is an important product of the anaerobic degradation of organic material in bottom sediment. Gas ebullition from the bottom sediments of natural water could substantially envelop the total methane flux. Ostrovsky (2003) reported the mean rising velocity of bubbles as 0.22 ± 0.1 cm/s by clean bubbles of ~0.6 mm radius or dirty bubbles with a radius of up to a few millimeters. Estimating gas emissions from lakes and reservoirs is difficult since there are at least four emission pathways which may be regulated differently:

- Ebullition flux,
- Diffusive flux,
- Storage flux, and
- Flux through the aquatic vegetation.

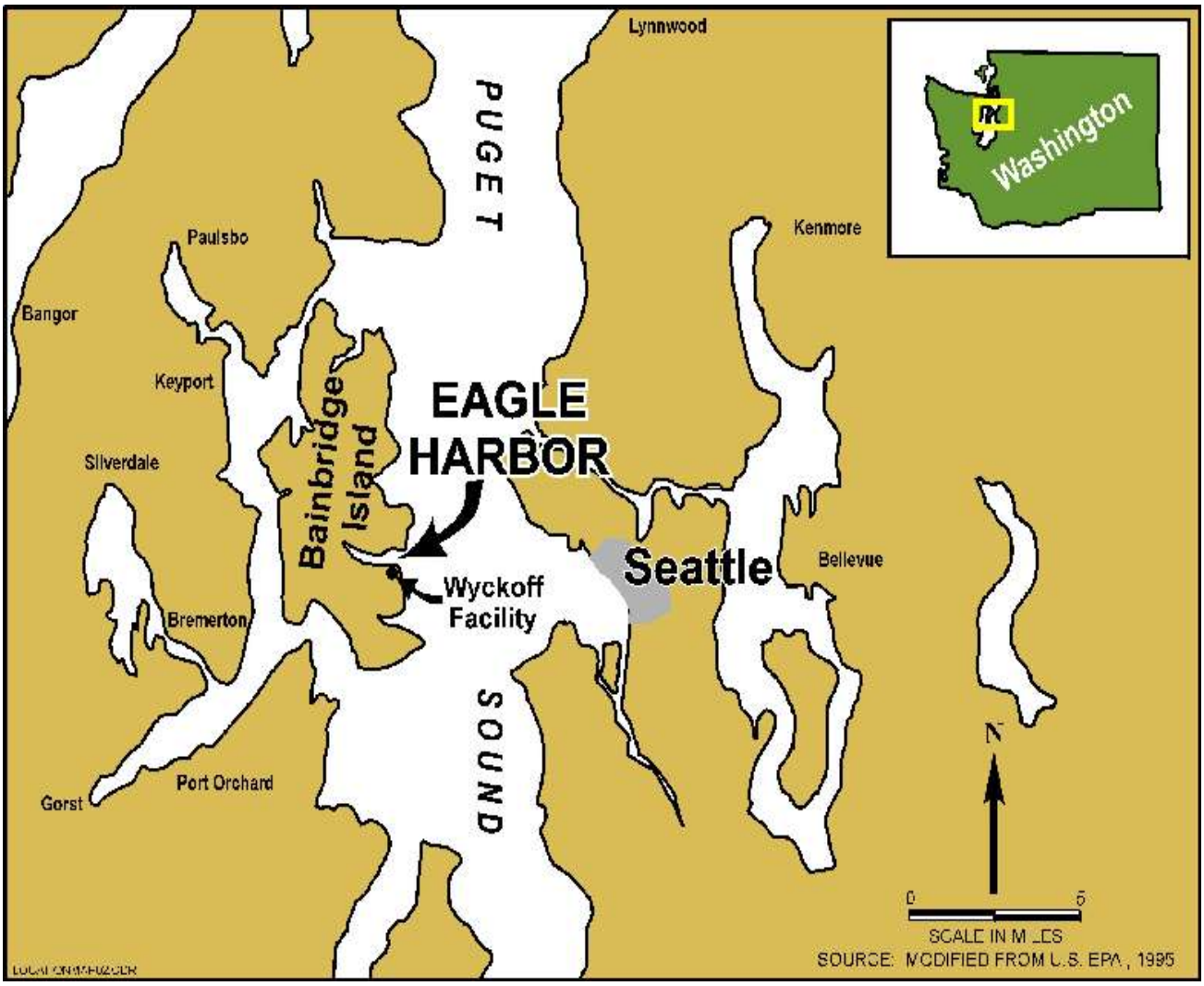


Figure 1-1. Eagle Harbor Site Map

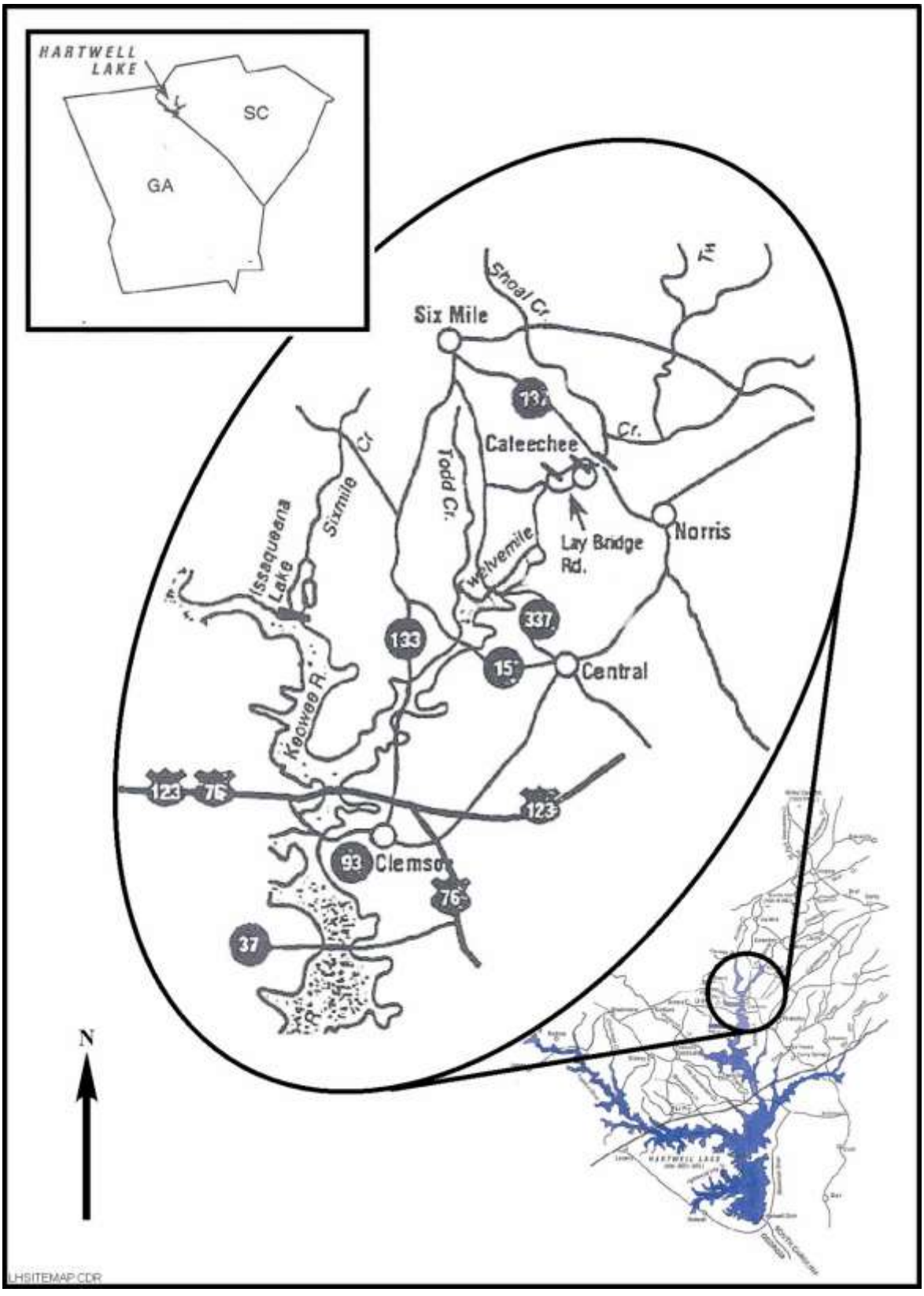


Figure 1-2. Lake Hartwell, South Carolina

Bastviken et al. (2004) reported that the majority of CH_4 production occurs in anoxic sediment. As a result of the diffusive export from anoxic sediment, CH_4 eventually enters the water column. As soon as CH_4 reaches an anoxic environment or water, a large proportion is likely oxidized by CH_4-oxidizing bacteria. Most of the CH_4 that reaches the upper mixed layer of the water column will be emitted by the diffusive flux. This flux component depends on the difference in CH_4 concentration between the water and the atmosphere, and on the physical rate of exchange between air and water, usually expressed as a piston velocity (turbulence, wind velocity) (Stumm and Morgan, 1996).

Though there is a substantial diurnal variation in CH_4 emissions (9 to 158% greater emission during the day), the average and median of gas emissions reported by Bastviken et al. (2004) were 69% and 53%, respectively. These authors reported that the average surface water CH_4 concentrations in 13 Swedish lakes were 0.08 - 1.89 µmole/L. Fendinger et al. (1992) reported that biogenic production of sediment gas bubbles typically contains 46 to 95% CH_4, 3 to 50% nitrogen, and trace quantities of CO_2 and hydrogen. The rate of bubble production from bottom sediment is a function of the composition, redox potential, microbial population, water depth and trophic status of the water body.

Organic compounds present in sediment will partition between the solid sediment particles and liquid porewater based on the sorptive characteristics of the sediment and physicochemical properties of the COCs. Microbial breakdown of sedimentary organic matter produces gases, which tend to migrate out of sediments into overlying water and are eventually vented to the atmosphere. With gas bubble formation in the sediment, a three phase benthic system exists: solid sediment particles, water and gas. The preferential pathway generated by gas migration may provide a means for the migration of separate phase material as well as contaminants to the sediment-water interface. Gas bubbles are inherently hydrophobic and tend to accumulate both hydrophobic organic contaminants and colloids from porewater, therefore their migration can have a significant effect on the transport of contaminants through the water column. The transport of contaminants would therefore occur when gas bubbles, containing volatilized organic compounds, are ejected from the sediment and transported directly to the atmosphere. The transfer of organic contaminants from the gas bubbles to the overlying water may occur during transit through the water column as a result of gas to water partitioning. Partitioning of the organic contaminant between the gas and water phase is determined by the gas-water partition coefficient of individual components of the COCs. Buoyancy driven migration of the gas opens channels through a cap, or if contained by an impermeable layer, may accumulate and potentially cause greater damage when ultimately released. The effective sediment-water exchange coefficients of PCBs (Thibodeaux et al., 2001) suggest that the heavier, more strongly partitioning congeners are moved more rapidly by particle-based processes (e.g., particle mixing by bioturbation) as they exhibit higher adsorption coefficients, whereas lighter congeners diffuse faster through porewater and benthic boundary layers.

Hughes et al. (2004) reported that gas generated by organic degradation processes in sediment has the ability to destabilize non-aqueous phase liquids (NAPLs). Microcosm experiments using Anacostia River sediment were conducted. Headspace analysis of the microcosms revealed the vast majority of the gas produced was CH_4, which is typical for anoxic sediments. The increase in gas generation with temperature is expected for methanogenic bacteria, since these organisms have an average optimal growth temperature of 37 °C. An initial gas consumption phase was observed in the microcosms, during which time residual O_2 in the water added to the system was consumed. This was followed by an acclimation period, which lasted at least five days at 35 °C, since gas production was not observed until after this time. Hughes et al. (2004) indicated that these two phases explain the relatively large standard deviation for gas production rates. Gas production continued for over 80 days, with the rates remaining constant. A sediment sample that was initially incubated at 4 °C for 60 days began generating gas when it was transferred to 35 °C, suggesting that the microbial population was dormant at 4 °C. Given the mass of sediment loaded into the bottles and its wet bulk density, the authors estimated

that the gas production at 22 °C from a sediment bed the size of a football field (300 ft × 150 ft × 1 ft) is estimated to be ~11,475 L of gas per day (11.5 m^3/day). Normalizing this value based on sediment-water interfacial area (41,827 m^2) yields a gas production rate of 2.74 L/m^2 day. This estimate is viewed as a slight overestimate of the actual ebullitive flux in the Anacostia River for two reasons:

- The natural bubble ebullition in tidal systems occurs in pulses, due to changes in hydrostatic water pressure accompanied with tidal flow. Ebullitive flux is "turned on" during low tide when overlying hydrostatic pressure is decreased, and then abruptly stops when high tide begins.
- The experimental design for obtaining the gas generation rate measures overpressure in the serum bottle, meaning that both trapped gas and bubbled gas is measured. This is not representative of field techniques, however, which typically measure only ebullitive flux from the sediment.

Gas generation indicates that microorganisms are able to break down sedimentary organic matter for energy and nutrients. The duration of gas production is still unknown. There have been no systematic column studies exploring the phenomenon of gas ebullition in sediments on the stability and effectiveness of the cap and consequently to the release of sediment/cap bound contaminants to overlying water.

1.2 Project Objective

The principal objective of this project is to better understand the effect of gas ebullition on the movement and release of PAHs for Eagle Harbor sediments and PCBs for Lake Hartwell sediments in controlled laboratory experiments. Sediment samples collected from two locations at each of these two sites were used to conduct batch and column experiments in the laboratory. The use of sediments from two locations provided the contaminant variability needed to conduct the experiments. Apart from geological differences, Eagle Harbor sediment was capped and Lake Hartwell was not capped. In regard to groundwater seeps, capping provides a means to control oxygen conditions within the groundwater plume and potentially provide the residence time to achieve degradation of compounds. The results obtained from these two site-specific sediments were evaluated.

The study was performed in two phases. Phase 1 involved bench-scale microcosm tests to measure and understand the volume of gas produced by each type of sediment at three test temperatures. Phase 2, which was conducted simultaneously, involved column tests to investigate the partitioning and mass transfer of COCs in sediment-water systems.

This laboratory study was conducted to address the following questions:

(1) Does the gas ebullition cause the release of PAHs and PCBs from the selected sediment-water systems?

(2) If the abovementioned COCs are releasing, can the COCs be quantified?

(3) Is the released concentration of contaminant dependent upon temperature of the sediment-water system?

(4) Is the released concentration of contaminant dependent upon the flow rate of gas bubbles passing through the water column?

1.3 Report Organization

The materials and experimental methods used for the microcosm and column tests are described in Section 2.0. Section 3.0 contains the results and discussion; and Section 4.0 presents a summary of the results from this study. The appendices present additional information regarding test results. Tables and Figures containing the individual test results are included in Appendices A and B. The analytical results including quality assurance (QA) narratives are included in Appendices C and D.

Section 2.0 MATERIALS AND METHODS

This section describes the details of the preparation of serum bottles and their incubation for the microcosm study. The setup and operation of columns to simulate the gas ebullition are also discussed. Various physical and analytical measurements conducted for the microcosm and column experiments are presented, including quantification of gas generated from the microcosm bottles, analysis of sediment and water for PCBs, PAHs, and atmospheric analysis (CO_2, O_2 and CH_4) of gas samples.

2.1 Collection of Sediment and Water Samples

Sediment for microcosm and column experiments were collected from Eagle Harbor, Washington, and Lake Hartwell, South Carolina using two discrete sampling methods discussed below.

2.1.1 Eagle Harbor Sediment Collection

Sediment samples were collected from Eagle Harbor at an approximate depth of six inches below the sediment surface (Figure 2-2). The sediments were collected using shovels in an uncapped area of the harbor on the east side of the peninsula during low tide. A total of two 5-gallon buckets were filled with these sediments and shipped to Battelle's laboratories for processing and analysis.

2.1.2 Lake Hartwell Sediment Collection

A box core sampler was used to collect sediments from Lake Hartwell. The core device was approximately 6 inches by 6 inches wide and 2 feet long. The box core barrel was hand driven from a work platform on the water and pushed to a depth of approximately 20 inches. Afterwards, the box core was retrieved and brought to the surface; the core location (georeference), time of collection and depth of recovery were recorded. In this manner, a total of two cores were collected from Transect O (Figure 2-1) and an additional two cores were collected from Transect P of the Twelve-Mile Creek arm of Lake Hartwell. Each of the cores was composited into 1.5 gallon bucket and prepared for shipment to the Battelle laboratory for processing and analysis.

2.1.3 Water Sample Collection

Water for microcosm and column experiments was also collected from Eagle Harbor and Lake Hartwell. At Eagle Harbor, water was collected directly into two 5 gallon buckets at the shoreline.

At Lake Hartwell, water was collected from a work platform on the water surface using a Van Dorn sampler. The sampler was lowered to approximately mid-depth in the water column (approximately 7 feet) and then brought up to the surface where it was composited from Transect O and P into two 5 gallon buckets.

All buckets were sealed and shipped to Battelle's laboratories, where they were stored at a controlled temperature (4±2°C). Before conducting the bench-scale experiments, both sediment and water samples were brought to room temperature.

2.2 Sediment Processing for Experiments

Prior to the bench-scale studies, a representative sample of sediment was collected from the center of each bucket and placed immediately into a glove-box containing an anaerobic atmosphere

consisting of nitrogen gas. Any twigs, shells, leaves or small stones were removed from the sediment samples. Compositing and homogenization were performed inside the glove box using a small mechanical mixer equipped with a stainless steel impeller. Mixing was performed as quickly and efficiently as possible to minimize drying and any impact to particle size. Visual observations, including sediment color, consistency, and odor, were recorded. After homogenization, sediment samples were transferred into serum bottles or glass columns as described in Section 2.3. During transfer, the sediments were periodically mixed to minimize stratification effects due to differential settling.

2.3. Preparation of Serum Bottles for Microcosm Study

Microcosm tests were conducted to determine the rate of gas generated from sediment and water from Eagle Harbor and Lake Hartwell sediments and the site-specific water. The study was conducted for 90-days with gas volume measurements taken after 1, 3, 7, 14, 21, 30, 45, 60 and 90 days. The tests were conducted using duplicate samples and killed control bottles for each time point.

Prior to the preparation of the microcosm bottles, portions of Eagle Harbor and Lake Hartwell sediments were transferred from sealed 5-gallon buckets to 1-L amber bottles. This transfer was performed inside a glove box under a nitrogen (anaerobic) environment. The sediment from these 1-L bottles were thereafter used to prepare the microcosm bottles.

The glass serum bottles, each having a capacity of 125-mL, were autoclaved three times for 20 minutes at 250 °F (121 °C) for sterilization. The serum bottles and other necessary supplies used to construct the microcosms (Table 2-1) were transferred into the anaerobic chamber. An oxygen meter was used to ensure that anaerobic chamber was oxygen free.

Table 2-1. Supplies and Accessories Used to Prepare the Microcosm Bottles

125-mL Microcosm Bottles	Bench top balance
20 mm Aluminum Crimp Caps	Spatula
20 mm Butyl Stoppers	200-mL Graduated Cylinder
Crimper	Micropipet
Funnel	Disposable glass pipet

Twenty-five grams of sediment was added into the narrow mouth of the serum bottles using a clean, thin-stemmed spatula. The weight of the sediment was recorded using the bench top balance. A funnel was inserted into the mouth of the bottle and a 200-mL graduated cylinder was filled to 125-mL with site-specific water. The balance was tared and the water was slowly poured into the funnel. The target volume was 120-mL for the Eagle Harbor bottles and 115-mL for the Lake Hartwell bottles, respectively. Different volumes were used because the grain-size composition of the sediment varied. The Eagle Harbor sediment was composed of fine to coarse granular elements and Lake Hartwell sediment was clayey material. A glass volumetric pipet was used to transfer site water into the appropriate microcosm bottles. Each volume of water added was measured gravimetrically using a top loading balance and the weight was recorded. The Eagle Harbor and Lake Hartwell sample parameters (including identification, weight of sediments and water in each of the serum bottles and duration of incubation) are shown in Tables 2-2 and 2-3, respectively. After transfer of sediment and water into the

serum bottles, each bottle was sealed with a butyl stopper and aluminum crimp. Figure 2-3 shows an example of the two prepared serum bottles.

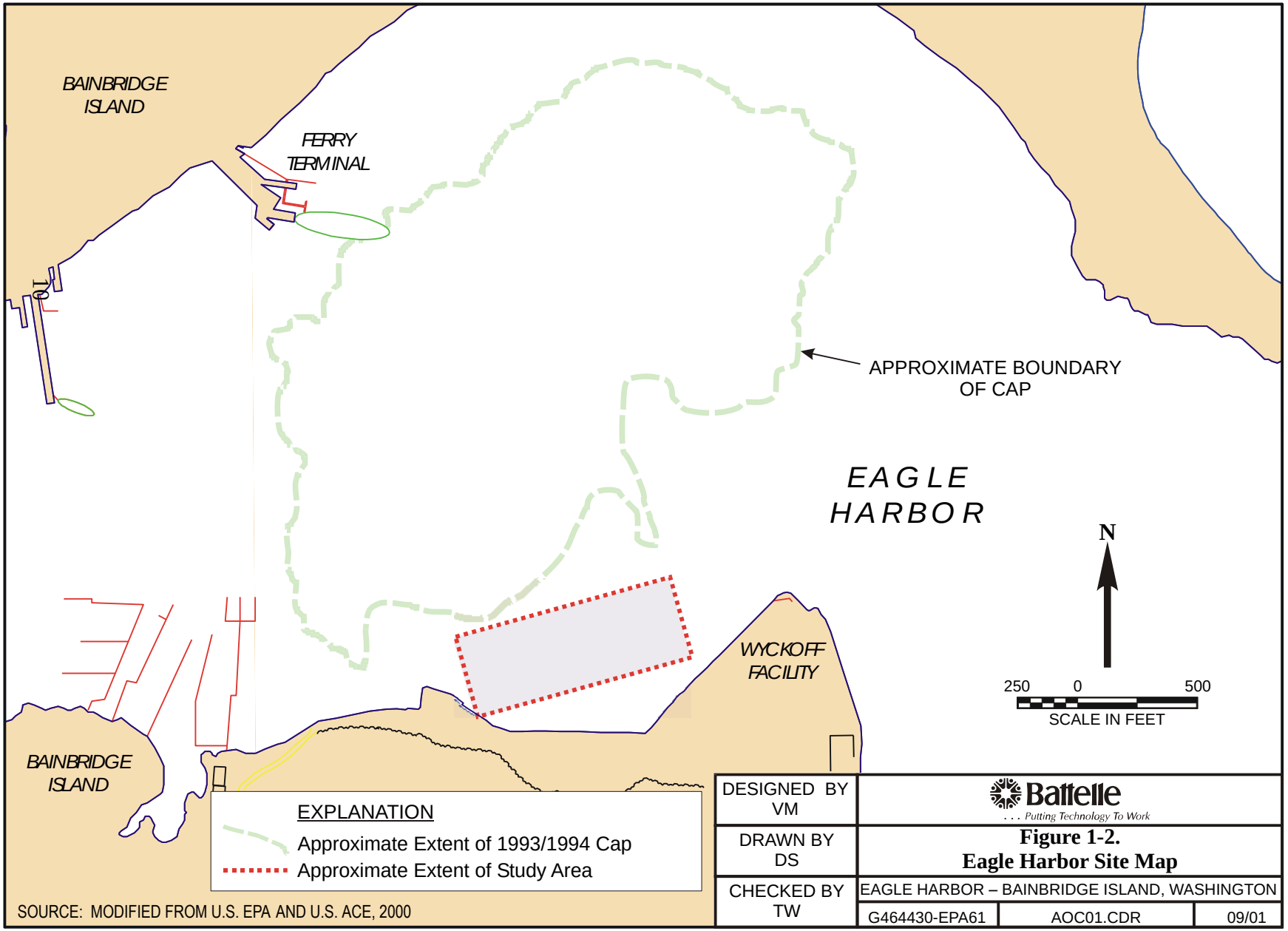


Figure 2-1. Eagle Harbor Site Map

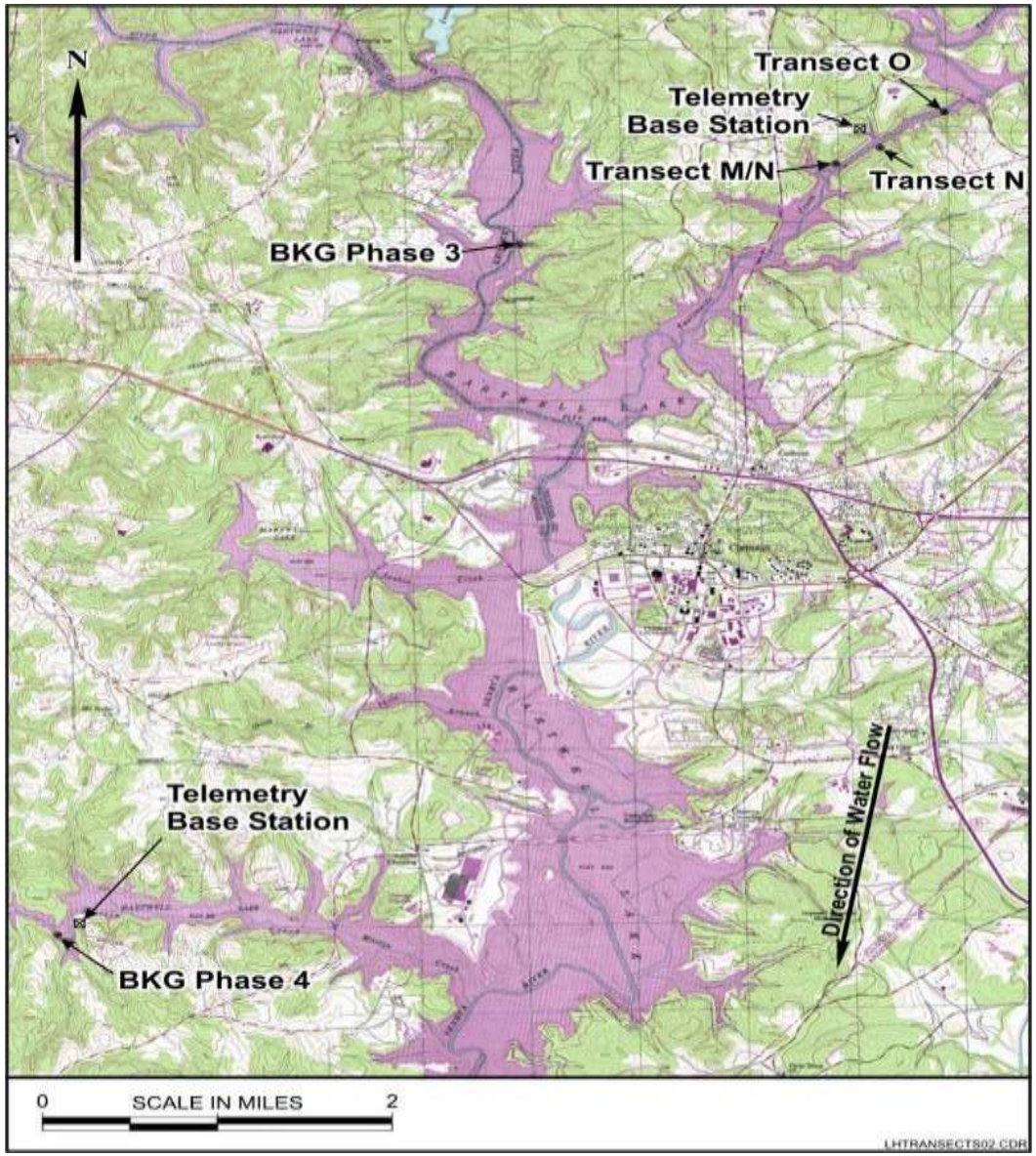


Figure 2-2. Lake Hartwell Site Transect

Killed controls were prepared for each time period. These killed control bottles were prepared in a similar manner to the regular sample bottles with the exception of the addition of 1-mL of 8% mercuric chloride ($HgCl_2$) solution.

Figure 2-3. Microcosm Bottles: Lake Hartwell (left) and Eagle Harbor (right)

A total of 162 serum bottles were prepared and placed in an inverted fashion on an orbital shaker table (New Brunswick Scientific; Series 25 Incubator-Shake) at approximately 50 rotations per minutes (rpm). The microcosms were incubated at three temperature conditions: 10 °C, 22 °C and 37 °C.

In addition, two larger bottles (~750 mL) were prepared with Eagle Harbor and Lake Hartwell sediment and site-specific water. A glass stem extending from the top of the bottle and a Teflon® union with a Teflon®-lined septa was used as a gas sampling port for atmospheric gas analysis. Figure 2-4 shows the two bottles containing sediment and water. The larger bottles were prepared with the same materials ratio as the 125-mL bottles (100 g of sediment and 450 mL of site water) in the glove box under nitrogen gas. The large bottles were kept in the orbital shaker at 50 rpm at 37 °C and were sampled for oxygen, CH_4 and CO_2 after 90-days of incubation.

2.4 Measurement of Gas Generation from Microcosm Bottles

The gas generated inside the 125-mL microcosm bottles was measured after 1, 3, 7, 14, 21, 30, 45, 60 and 90 days. The gas generated from each bottle could not be measured using a double syringe because of the relatively small volume of gas that was produced in each bottle. Therefore, a single syringe method was developed to quantify the small volume of gas generated inside the bottles. Five milliliters of deionized water was added to a 10-mL glass syringe with its piston removed. A 22-guage disposable needle was attached to the syringe. The number and duration of the bubbles released from the microcosm bottles were recorded by a counter as the needle pierced the butyl seal at the mouth of the

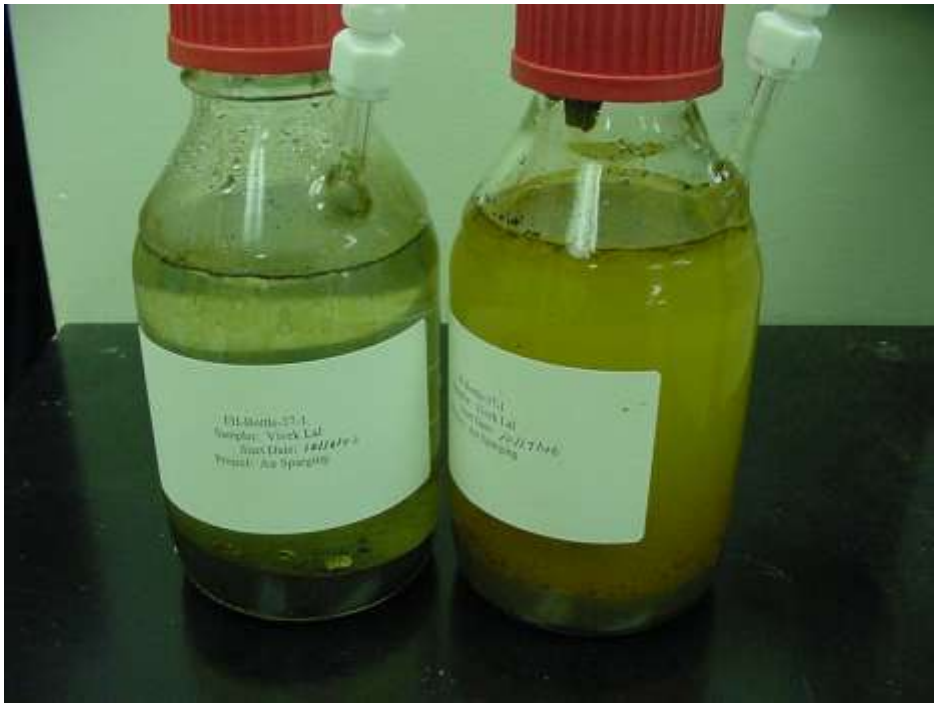


Figure 2-4. Larger Bottles with a Glass Stem

bottles (Figure 2-5). The number of bubbles was counted and the duration was measured with a stop watch. The images of the gas bubbles were captured by a digital camera (Sony Smart Zoom DSC-P52) and were digitized to calculate the average diameter. The volume of each bubble was determined to be 0.04163 mL.

The pH, oxidation-reduction potential (ORP) and dissolved oxygen (DO) were measured in the water of the microcosm bottles after two months of incubation. About 2 to 3 mL of water was extracted from the microcosm bottles with a syringe and added to a clean 40-mL volatile organic analysis (VOA) vial for these measurements. An Omega probe and Symphony DO probe were used for pH and DO measurements, respectively. Prior to the measurements, the pH probe was calibrated and an Orion ORP probe was calibrated with quinhydrone solutions. A three point calibration was conducted with the pH meter at a pH of 4, 7 and 10. The DO probe was air calibrated to reach the appropriate reading of 102.3% saturation. The extraction of microcosm water samples and the analyses of these samples were conducted in a glove box under nitrogen.

2.5 Column Study

A total of 11 columns were packed with sediment that was overlaid with site-specific water. Seven of the columns used Eagle Harbor sediment and water. Lake Hartwell sediment and water comprised the remaining columns. The columns were sparged with a mixture of CO_2 and CH_4 at two different flow rates for 19 weeks (133 days). Polyurethane foam (PUF) tubes were used at the outlet of the columns to entrap the organic compounds in the gas phase. The PUF samples were collected from the columns after six weeks and at the end of the study (19 weeks); they were then analyzed for 38 priority PAHs (Eagle Harbor) and 118 PCB congeners (Lake Hartwell). Sediment, cap material and water were also analyzed for PAH and PCB analyses after 19 weeks.

Figure 2-5. Measurement of Gas Bubbles from the Serum Bottles

Table 2-2. Eagle Harbor Serum Bottle Test Parameters

Sample ID	Description	Weight of Sediment (g)	Volume of Site water (ml)	Incubation Time (Days)
EH-10-1-1	Eagle Harbor Sediment and site water at 10 ˚C, Day 1	25.4	118.5	1
EH-10-1-2	Eagle Harbor Sediment and site water at 10 ˚C, Day 1, duplicate	25.3	120.0	
EHCT-10-1-1	Eagle Harbor Sediment and site water at 10 ˚C, Day 1, kill control	25.3	120.3	
EH-25-1-1	Eagle Harbor Sediment and site water at 25 ˚C, Day 1	25.3	119.1	
EH-25-1-2	Eagle Harbor Sediment and site water at 25 ˚C, Day 1, duplicate	25.4	119.7	
EHCT-25-1-1	Eagle Harbor Sediment and site water at 25 ˚C, Day 1, kill control	25.0	120.5	
EH-37-1-1	Eagle Harbor Sediment and site water at 37 ˚C, Day 1	25.4	118.7	
EH-37-1-2	Eagle Harbor Sediment and site water at 37 ˚C, Day 1, duplicate	25.0	119.3	
EHCT-37-1-1	Eagle Harbor Sediment and site water at 37 ˚C, Day 1, kill control	25.7	120.9	
EH-10-3-1	Eagle Harbor Sediment and site water at 10 ˚C, Day 3	25.0	120.2	3
EH-10-3-2	Eagle Harbor Sediment and site water at 10 ˚C, Day 3, duplicate	26.0	120.1	
EHCT-10-3-1	Eagle Harbor Sediment and site water at 10 ˚C, Day 3, kill control	25.6	120.0	
EH-25-3-1	Eagle Harbor Sediment and site water at 25 ˚C, Day 3	25.5	120.2	
EH-25-3-2	Eagle Harbor Sediment and site water at 25 ˚C, Day 3, duplicate	25.1	120.8	
EHCT-25-3-1	Eagle Harbor Sediment and site water at 25 ˚C, Day 3, kill control	25.2	120.4	
EH-37-3-1	Eagle Harbor Sediment and site water at 37 ˚C, Day 3	25.8	120.1	
EH-37-3-2	Eagle Harbor Sediment and site water at 37 ˚C, Day 3, duplicate	25.3	120.2	
EHCT-37-3-1	Eagle Harbor Sediment and site water at 37 ˚C, Day 3, kill control	25.0	120.3	
EH-10-7-1	Eagle Harbor Sediment and site water at 10 ˚C, Day 7	25.0	120.5	7
EH-10-7-2	Eagle Harbor Sediment and site water at 10 ˚C, Day 7, duplicate	25.6	119.9	
EHCT-10-7-1	Eagle Harbor Sediment and site water at 10 ˚C, Day 7, kill control	25.5	120.2	
EH-25-7-1	Eagle Harbor Sediment and site water at 25 ˚C, Day 7	25.8	120.1	
EH-25-7-2	Eagle Harbor Sediment and site water at 25 ˚C, Day 7, duplicate	25.4	120.1	
EHCT-25-7-1	Eagle Harbor Sediment and site water at 25 ˚C, Day 7, kill control	25.2	120.0	
EH-37-7-1	Eagle Harbor Sediment and site water at 37 ˚C, Day 7	25.2	120.0	
EH-37-7-2	Eagle Harbor Sediment and site water at 37 ˚C, Day 7, duplicate	25.4	120.1	
EHCT-37-7-1	Eagle Harbor Sediment and site water at 37 ˚C, Day 7, kill control	25.5	120.3	

Table 2-2. Eagle Harbor Serum Bottle Test Parameters (Continued)

Sample ID	Description	Weight of Sediment (g)	Volume of Site Water (ml)	Incubation Time (Days)
EH-10-14-1	Eagle Harbor Sediment and site water at 10 ˚C, Day 14	25.3	120.1	14
EH-10-14-2	Eagle Harbor Sediment and site water at 10 ˚C, Day 14, duplicate	25.7	120.3	
EHCT-10-14-1	Eagle Harbor Sediment and site water at 10 ˚C, Day 14, kill control	25.2	120.3	
EH-25-14-1	Eagle Harbor Sediment and site water at 25 ˚C, Day 14	25.4	120.1	
EH-25-14-2	Eagle Harbor Sediment and site water at 25 ˚C, Day 14, duplicate	25.5	120.0	
EHCT-25-14-1	Eagle Harbor Sediment and site water at 25 ˚C, Day 14, kill control	25.9	120.2	
EH-37-14-1	Eagle Harbor Sediment and site water at 37 ˚C, Day 14	26.0	120.1	
EH-37-14-2	Eagle Harbor Sediment and site water at 37 ˚C, Day 14, duplicate	25.5	119.9	
EHCT-37-14-1	Eagle Harbor Sediment and site water at 37 ˚C, Day 14, kill control	25.8	120.1	
EH-10-21-1	Eagle Harbor Sediment and site water at 10 ˚C, Day 21	25.5	120.1	21
EH-10-21-2	Eagle Harbor Sediment and site water at 10 ˚C, Day 21, duplicate	25.2	120.3	
EHCT-10-21-1	Eagle Harbor Sediment and site water at 10 ˚C, Day 21, kill control	25.8	120.1	
EH-25-21-1	Eagle Harbor Sediment and site water at 25 ˚C, Day 21	26.1	120.0	
EH-25-21-2	Eagle Harbor Sediment and site water at 25 ˚C, Day 21, duplicate	25.8	120.3	
EHCT-25-21-1	Eagle Harbor Sediment and site water at 25 ˚C, Day 21, kill control	25.3	120.0	
EH-37-21-1	Eagle Harbor Sediment and site water at 37 ˚C, Day 21	25.2	120.5	
EH-37-21-2	Eagle Harbor Sediment and site water at 37 ˚C, Day 21, duplicate	25.0	120.2	
EHCT-37-21-1	Eagle Harbor Sediment and site water at 37 ˚C, Day 21, kill control	25.5	120.2	
EH-10-30-1	Eagle Harbor Sediment and site water at 10 ˚C, Day 30	25.5	120.1	30
EH-10-30-2	Eagle Harbor Sediment and site water at 10 ˚C, Day 30, duplicate	25.8	120.4	
EHCT-10-30-1	Eagle Harbor Sediment and site water at 10 ˚C, Day 30, kill control	25.6	120.7	
EH-25-30-1	Eagle Harbor Sediment and site water at 25 ˚C, Day 30	25.8	120.0	
EH-25-30-2	Eagle Harbor Sediment and site water at 25 ˚C, Day 30, duplicate	24.8	120.7	
EHCT-25-30-1	Eagle Harbor Sediment and site water at 25 ˚C, Day 30, kill control	25.6	120.3	
EH-37-30-1	Eagle Harbor Sediment and site water at 37 ˚C, Day 30	25.0	120.2	
EH-37-30-2	Eagle Harbor Sediment and site water at 37 ˚C, Day 30, duplicate	25.4	120.0	
EHCT-37-30-1	Eagle Harbor Sediment and site water at 37 ˚C, Day 30, kill control	25.8	120.6	

Table 2-2. Eagle Harbor Serum Bottle Test Parameters (Continued)

Sample	Description	Weight of Sediment (g)	Volume of Site Water (ml)	Incubation Time (Days)
EH-10-45-1	Eagle Harbor Sediment and site water at 10 ˚C, Day 45	25.1	120.4	45
EH-10-45-2	Eagle Harbor Sediment and site water at 10 ˚C, Day 45, duplicate	25.1	120.0	
EHCT-10-45-1	Eagle Harbor Sediment and site water at 10 ˚C, Day 45, kill control	25.4	120.2	
EH-25-45-1	Eagle Harbor Sediment and site water at 25 ˚C, Day 45	25.3	120.2	
EH-25-45-2	Eagle Harbor Sediment and site water at 25 ˚C, Day 45, duplicate	25.8	120.1	
EHCT-25-45-1	Eagle Harbor Sediment and site water at 25 ˚C, Day 45, kill control	25.6	120.0	
EH-37-45-1	Eagle Harbor Sediment and site water at 37 ˚C, Day 45	25.4	120.0	
EH-37-45-2	Eagle Harbor Sediment and site water at 37 ˚C, Day 45, duplicate	25.0	120.1	
EHCT-37-45-1	Eagle Harbor Sediment and site water at 37 ˚C, Day 45, kill control	25.5	120.2	
EH-10-60-1	Eagle Harbor Sediment and site water at 10 ˚C, Day 60	25.6	120.2	60
EH-10-60-2	Eagle Harbor Sediment and site water at 10 ˚C, Day 60, duplicate	25.5	120.0	
EHCT-10-60-1	Eagle Harbor Sediment and site water at 10 ˚C, Day 60, kill control	25.4	120.1	
EH-25-60-1	Eagle Harbor Sediment and site water at 25 ˚C, Day 60	25.1	120.3	
EH-25-60-2	Eagle Harbor Sediment and site water at 25 ˚C, Day 60, duplicate	25.5	120.5	
EHCT-25-60-1	Eagle Harbor Sediment and site water at 25 ˚C, Day 60, kill control	25.5	120.0	
EH-37-60-1	Eagle Harbor Sediment and site water at 37 ˚C, Day 60	25.4	120.4	
EH-37-60-2	Eagle Harbor Sediment and site water at 37 ˚C, Day 60, duplicate	25.4	120.5	
EHCT-37-60-1	Eagle Harbor Sediment and site water at 37 ˚C, Day 60, kill control	25.1	120.1	
EH-10-90-1	Eagle Harbor Sediment and site water at 10 ˚C, Day 90	26.0	120.1	90
EH-10-90-2	Eagle Harbor Sediment and site water at 10 ˚C, Day 90, duplicate	25.8	120.2	
EHCT-10-90-1	Eagle Harbor Sediment and site water at 10 ˚C, Day 90, kill control	25.8	120.1	
EH-25-90-1	Eagle Harbor Sediment and site water at 25 ˚C, Day 90	25.2	121.1	
EH-25-90-2	Eagle Harbor Sediment and site water at 25 ˚C, Day 90, duplicate	25.2	120.3	
EHCT-25-90-1	Eagle Harbor Sediment and site water at 25 ˚C, Day 90, kill control	25.4	120.4	
EH-37-90-1	Eagle Harbor Sediment and site water at 37 ˚C, Day 90	25.2	120.1	
EH-37-90-2	Eagle Harbor Sediment and site water at 37 ˚C, Day 90, duplicate	25.6	120.2	
EHCT-37-90-1	Eagle Harbor Sediment and site water at 37 ˚C, Day 90, kill control	25.4	120.0	

Table 2-3. Lake Hartwell Serum Bottle Test Parameters

Sample Id	Description	Weight of Sediment (g)	Volume of Site water (ml)	Incubation Time (Days)
LH-10-1-1	Lake Hartwell Sediment and site water at 10 ˚C, Day 1	25.5	115.5	1
LH-10-1-2	Lake Hartwell Sediment and site water at 10 ˚C, Day 1, duplicate	25.2	115.0	
LHCT-10-1-1	Lake Hartwell Sediment and site water at 10 ˚C, Day 1, kill control	25.1	115.1	
LH-25-1-1	Lake Hartwell Sediment and site water at 25 ˚C, Day 1	25.1	115.0	
LH-25-1-2	Lake Hartwell Sediment and site water at 25 ˚C, Day 1, duplicate	25.4	115.2	
LHCT-25-1-1	Lake Hartwell Sediment and site water at 25 ˚C, Day 1, kill control	25.0	115.3	
LH-37-1-1	Lake Hartwell Sediment and site water at 37 ˚C, Day 1	25.0	115.1	
LH-37-1-2	Lake Hartwell Sediment and site water at 37 ˚C, Day 1, duplicate	25.0	115.2	
LHCT-37-1-1	Lake Hartwell Sediment and site water at 37 ˚C, Day 1, kill control	25.2	115.1	
LH-10-3-1	Lake Hartwell Sediment and site water at 10 ˚C, Day 3	25.2	115.1	3
LH-10-3-2	Lake Hartwell Sediment and site water at 10 ˚C, Day 3, duplicate	25.4	115.2	
LHCT-10-3-1	Lake Hartwell Sediment and site water at 10 ˚C, Day 3, kill control	25.2	115.3	
LH-25-3-1	Lake Hartwell Sediment and site water at 25 ˚C, Day 3	25.3	115.4	
LH-25-3-2	Lake Hartwell Sediment and site water at 25 ˚C, Day 3, duplicate	25.6	115.1	
LHCT-25-3-1	Lake Hartwell Sediment and site water at 25 ˚C, Day 3, kill control	25.2	115.3	
LH-37-3-1	Lake Hartwell Sediment and site water at 37 ˚C, Day 3	25.0	115.1	
LH-37-3-2	Lake Hartwell Sediment and site water at 37 ˚C, Day 3, duplicate	25.1	115.4	
LHCT-37-3-1	Lake Hartwell Sediment and site water at 37 ˚C, Day 3, kill control	25.2	115.0	
LH-10-7-1	Lake Hartwell Sediment and site water at 10 ˚C, Day 7	25.6	115.3	7
LH-10-7-2	Lake Hartwell Sediment and site water at 10 ˚C, Day 7, duplicate	25.5	115.0	
LHCT-10-7-1	Lake Hartwell Sediment and site water at 10 ˚C, Day 7, kill control	25.1	115.4	
LH-25-7-1	Lake Hartwell Sediment and site water at 25 ˚C, Day 7	25.4	115.1	
LH-25-7-2	Lake Hartwell Sediment and site water at 25 ˚C, Day 7, duplicate	26.0	115.7	
LHCT-25-7-1	Lake Hartwell Sediment and site water at 25 ˚C, Day 7, kill control	25.3	115.2	
LH-37-7-1	Lake Hartwell Sediment and site water at 37 ˚C, Day 7	25.5	115.2	
LH-37-7-2	Lake Hartwell Sediment and site water at 37 ˚C, Day 7, duplicate	24.9	115.4	
LHCT-37-7-1	Lake Hartwell Sediment and site water at 37 ˚C, Day 7, kill control	25.3	115.0	

Table 2-3. Lake Hartwell Serum Bottle Test Parameters (Continued)

Sample ID	Description	Weight of Sediment (g)	Volume of Site Water (ml)	Incubation Time (Days)
LH-10-14-1	Lake Hartwell Sediment and site water at 10 ˚C, Day 14	26.1	114.8	14
LH-10-14-2	Lake Hartwell Sediment and site water at 10 ˚C, Day 14, duplicate	25.8	115.3	
LHCT-10-14-1	Lake Hartwell Sediment and site water at 10 ˚C, Day 14, kill control	25.6	115.4	
LH-25-14-1	Lake Hartwell Sediment and site water at 25 ˚C, Day 14	25.4	115.3	
LH-25-14-2	Lake Hartwell Sediment and site water at 25 ˚C, Day 14, duplicate	25.4	115.3	
LHCT-25-14-1	Lake Hartwell Sediment and site water at 25 ˚C, Day 14, kill control	25.8	115.2	
LH-37-14-1	Lake Hartwell Sediment and site water at 37 ˚C, Day 14	25.3	115.3	
LH-37-14-2	Lake Hartwell Sediment and site water at 37 ˚C, Day 14, duplicate	25.3	115.2	
LHCT-37-14-1	Lake Hartwell Sediment and site water at 37 ˚C, Day 14, kill control	25.8	115.4	
LH-10-21-1	Lake Hartwell Sediment and site water at 10 ˚C, Day 21	26.0	114.8	21
LH-10-21-2	Lake Hartwell Sediment and site water at 10 ˚C, Day 21, duplicate	25.3	115.2	
LHCT-10-21-1	Lake Hartwell Sediment and site water at 10 ˚C, Day 21, kill control	25.1	115.4	
LH-25-21-1	Lake Hartwell Sediment and site water at 25 ˚C, Day 21	25.1	115.1	
LH-25-21-2	Lake Hartwell Sediment and site water at 25 ˚C, Day 21, duplicate	25.5	115.6	
LHCT-25-21-1	Lake Hartwell Sediment and site water at 25 ˚C, Day 21, kill control	25.2	115.0	
LH-37-21-1	Lake Hartwell Sediment and site water at 37 ˚C, Day 21	25.1	115.3	
LH-37-21-2	Lake Hartwell Sediment and site water at 37 ˚C, Day 21, duplicate	25.5	115.2	
LHCT-37-21-1	Lake Hartwell Sediment and site water at 37 ˚C, Day 21, kill control	25.2	115.1	
LH-10-30-1	Lake Hartwell Sediment and site water at 10 ˚C, Day 30	25.5	115.8	30
LH-10-30-2	Lake Hartwell Sediment and site water at 10 ˚C, Day 30, duplicate	25.5	115.3	
LHCT-10-30-1	Lake Hartwell Sediment and site water at 10 ˚C, Day 30, kill control	25.5	115.0	
LH-25-30-1	Lake Hartwell Sediment and site water at 25 ˚C, Day 30	26.0	115.1	
LH-25-30-2	Lake Hartwell Sediment and site water at 25 ˚C, Day 30, duplicate	25.6	115.5	
LHCT-25-30-1	Lake Hartwell Sediment and site water at 25 ˚C, Day 30, kill control	25.5	115.1	
LH-37-30-1	Lake Hartwell Sediment and site water at 37 ˚C, Day 30	25.5	115.2	
LH-37-30-2	Lake Hartwell Sediment and site water at 37 ˚C, Day 30, duplicate	25.8	115.2	
LHCT-37-30-1	Lake Hartwell Sediment and site water at 37 ˚C, Day 30, kill control	25.3	114.8	

Table 2-3. Lake Hartwell Serum Bottle Test Parameters (Continued)

Sample ID	Description	Weight of Sediment (g)	Volume of Site Water (ml)	Incubation Time (Days)
LH-10-45-1	Lake Hartwell Sediment and site water at 10 ˚C, Day 45	25.8	115.4	45
LH-10-45-2	Lake Hartwell Sediment and site water at 10 ˚C, Day 45, duplicate	25.2	115.8	
LHCT-10-45-1	Lake Hartwell Sediment and site water at 10 ˚C, Day 45, kill control	25.1	115.2	
LH-25-45-1	Lake Hartwell Sediment and site water at 25 ˚C, Day 45	25.9	115.0	
LH-25-45-2	Lake Hartwell Sediment and site water at 25 ˚C, Day 45, duplicate	26.0	115.1	
LHCT-25-45-1	Lake Hartwell Sediment and site water at 25 ˚C, Day 45, kill control	26.1	115.1	
LH-37-45-1	Lake Hartwell Sediment and site water at 37 ˚C, Day 45	25.9	115.7	
LH-37-45-2	Lake Hartwell Sediment and site water at 37 ˚C, Day 45, duplicate	25.2	115.6	
LHCT-37-45-1	Lake Hartwell Sediment and site water at 37 ˚C, Day 45, kill control	25.4	115.1	
LH-10-60-1	Lake Hartwell Sediment and site water at 10 ˚C, Day 60	25.0	115.0	60
LH-10-60-2	Lake Hartwell Sediment and site water at 10 ˚C, Day 60, duplicate	25.6	115.0	
LHCT-10-60-1	Lake Hartwell Sediment and site water at 10 ˚C, Day 60, kill control	25.8	115.2	
LH-25-60-1	Lake Hartwell Sediment and site water at 25 ˚C, Day 60	25.1	115.5	
LH-25-60-2	Lake Hartwell Sediment and site water at 25 ˚C, Day 60, duplicate	25.4	115.2	
LHCT-25-60-1	Lake Hartwell Sediment and site water at 25 ˚C, Day 60, kill control	25.7	115.2	
LH-37-60-1	Lake Hartwell Sediment and site water at 37 ˚C, Day 60	25.3	115.3	
LH-37-60-2	Lake Hartwell Sediment and site water at 37 ˚C, Day 60, duplicate	25.2	115.6	
LHCT-37-60-1	Lake Hartwell Sediment and site water at 37 ˚C, Day 60, kill control	25.3	115.0	
LH-10-90-1	Lake Hartwell Sediment and site water at 10 ˚C, Day 90	25.1	115.1	90
LH-10-90-2	Lake Hartwell Sediment and site water at 10 ˚C, Day 90, duplicate	25.3	115.3	
LHCT-10-90-1	Lake Hartwell Sediment and site water at 10 ˚C, Day 90, kill control	25.8	115.2	
LH-25-90-1	Lake Hartwell Sediment and site water at 25 ˚C, Day 90	25.1	115.6	
LH-25-90-2	Lake Hartwell Sediment and site water at 25 ˚C, Day 90, duplicate	25.6	115.3	
LHCT-25-90-1	Lake Hartwell Sediment and site water at 25 ˚C, Day 90, kill control	25.8	115.1	
LH-37-90-1	Lake Hartwell Sediment and site water at 37 ˚C, Day 90	25.4	115.6	
LH-37-90-2	Lake Hartwell Sediment and site water at 37 ˚C, Day 90, duplicate	25.6	115.1	
LHCT-37-90-1	Lake Hartwell Sediment and site water at 37 ˚C, Day 90, kill control	25.7	115.3	

2.5.1 Construction of Gas Ebullition Columns

The Eagle Harbor and Lake Hartwell columns were operated separately in laboratory hoods. Two-foot long glass columns, 2 inches in diameter with three side ports were used to construct the experiments. Two of the ports were positioned 4 inches from the column ends and another port was in the center of the column. The end of each column was threaded for affixing tube and pressure fittings.

Teflon® end caps were screwed into each end of the column. A fritted glass disc was attached to the end of the cap, which was screwed onto the base of the columns. The fritted glass disc was used to diffuse the sparged gas from a Class A, 1200 lb/inch^2 (psi) cylinder (Scott Speciality Gas, Michigan) through the column. The gas mixture was 60% CH_4 and 40% CO_2. The gas composition was selected based on field research and results. Clamps were used to secure the columns to ring stands in the hood. A manifold was constructed out of 1/8 inch stainless steel tube for both the Eagle Harbor and Lake Hartwell columns. In the case of the Eagle Harbor columns the manifold consisted of partitioning the feed line from the cylinder into seven lines that led to the individual columns in the hood. The Lake Hartwell manifold consisted of four lines. A micro-flow meter was attached to each line from the manifold. A sensitive needle valve was attached to each line before the micro-flow meter. The needle valve was capable of making minute adjustments in the gas flow rate. A one-way flow check valve was attached to the pipe just before each column to prevent backflow of the feed lines from the water in the column. Two PUF tubes were attached together in series at the top of the column. The second PUF tube in series was used to capture contaminant break through the first PUF cartridge. The installation and connection steps involved bending ¼ inch tubing into a "U" shape. The tubing was secured into the Teflon® end caps with a ¼ inch male National Pipe Thread (NPT) fitting. These end caps were then screwed into place at the top of the column. Tygon™ tubing was used to connect the tapered end of the PUF tube to the ¼ inch tubing. The other end of the Tygon™ tube was pulled tightly over the ¼ inch stainless steel pipe. Silicon sealant and a tie strip were used to secure the pipe and the Tygon™ tube together. Two PUF tubes were connected in series by connecting the open ends together with ¾ inch Tygon™ tubing. A one inch section of ¾ inch Tygon™ tubing was placed into boiling water for 30-seconds in order to make the tubing malleable. The Tygon™ section was then placed over the open ends of the PUF tubes and allowed to cool. The Tygon™ cooled and shrunk around the PUF tubes creating a tight connection. In places where Tygon™ tube was used glass ends were fixed so that they were flush to each other to ensure that the Tygon™ tube was not exposed to the air flow, minimizing contaminant sorption onto the tubing.

The side ports of the columns were plugged using ¼ inch diameter, threaded Teflon® stoppers. The center port, 12 inches from the base of the column, had a Teflon® stopper with a Teflon®-lined septa opening. Column water was collected from the center port for measurements, such as pH, ORP, DO and turbidity. A schematic diagram of the Eagle Harbor columns is shown in Figure 2-6. A similar setup was used for the four Lake Hartwell columns. Figures 2-7 and 2-8 show the actual Eagle Harbor and Lake Hartwell columns during operation.

2.5.2 Packing of Columns

Measured amounts of pea gravel were added 3-inches from the base of the column with a 500-mL wide mouth beaker. An aluminum mesh disc 2-inches in diameter was added after the pea gravel in order to separate the pea gravel and sediment layers. Wet packing of sediment was used for all of the columns. Measured amounts of sediment were added to achieve a height of 3-inches. The sediment was added into the column by using a large spatula. The PAH concentration of Eagle Harbor sediment was approximately 386,000 ng/g-dry total PAH. The Lake Hartwell sediment concentration was deemed

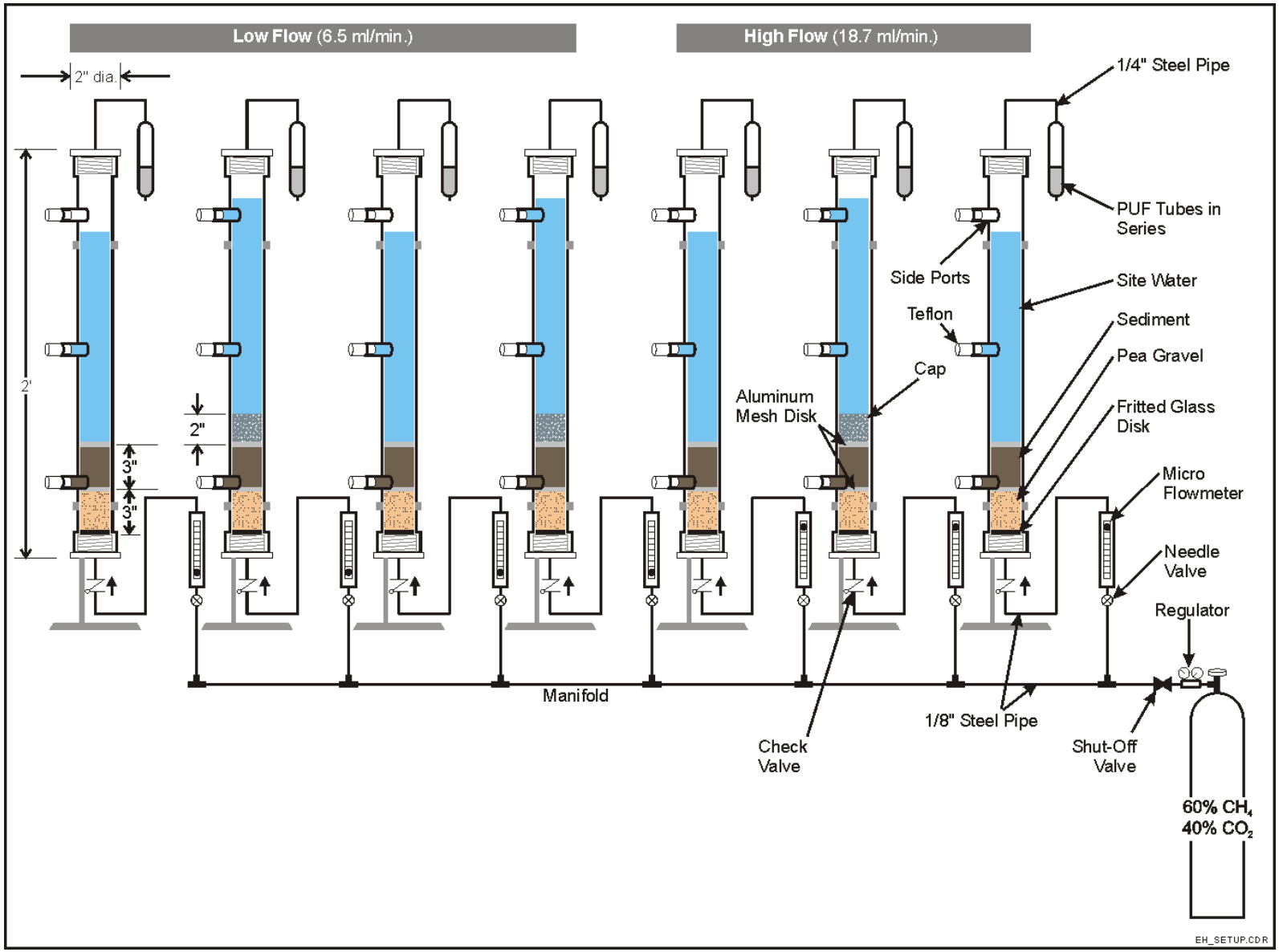


Figure 2-6. Schematic Diagram of Eagle Harbor Column

insufficient to ensure detectable gas phase concentrations during column operations; approximately 2800 ng/g dry total PCB. Therefore, it was spiked with 2 µg/g of Aroclor mix 2. This Aroclor mix was chosen because it best represented the congener makeup of the Lake Hartwell sediment. Two ampoules of Aroclor mix 2 were added to 300 g of Lake Hartwell sediment in a 1-L high density polyethylene (HDPE) bottle. The bottle was tumbled overnight at 29 rpm in a rotary apparatus (Associated Design & Mfg. Co., Virginia, Model 3740-12-BRE).

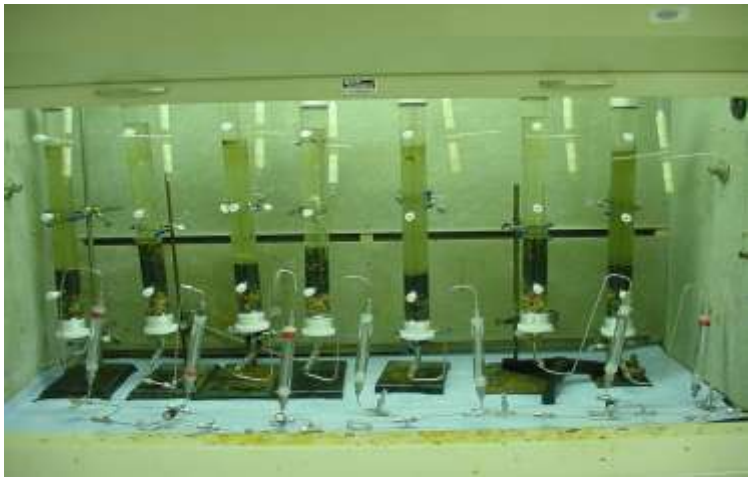


Figure 2-7. Photograph of Eagle Harbor Columns

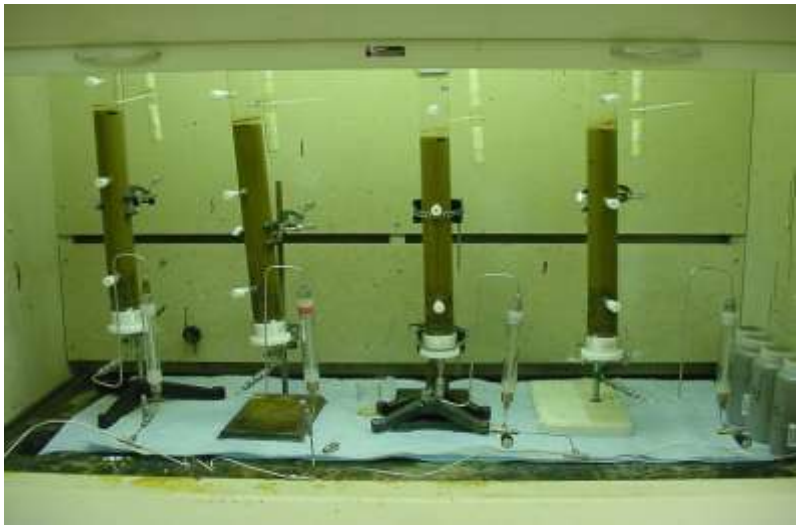


Figure 2-8. Photograph of Lake Hartwell Columns

Additional aluminum mesh discs were placed over the sediment for the columns designated for the cap. Three of the seven Eagle Harbor Columns had the cap. Two-inches of cap material were added in measured amounts with a spatula. The weights of the pea gravel, sediment and cap material for the Eagle Harbor and Lake Hartwell columns are listed in Table 2-4. Eagle Harbor and Lake Hartwell water was added to the columns using a 1000-mL graduated cylinder. Each column had 750-mL of site-specific water.

Table 2-4. Column Parameters of Eagle Harbor and Lake Hartwell Setup

Eagle Harbor						
Column No.	Column Description	Pea Gravel (g)	Sediment (g)	Cap (g)	Corrected Flow (ml/min)	Methane Flux (L/m^2-d)
1	Low flow, uncapped	208.5	290.5	NA	6.5	4618
2	Low Flow, capped	196.0	342.0	200.5		
3	Low flow, uncapped	197.5	272.0	NA		
4	Low flow, capped	182.5	242.0	211.5		
5	High flow, uncapped	212.0	253.0	NA	18.7	13280
6	High Flow, capped	207.0	248.0	215.0		
7	High Flow, uncapped	232.5	270.5	NA		
Lake Hartwell						
8	Low flow	181.5	149.0	NA	6.5	4618
9	High flow	179.0	150.0	NA	18.7	13280
10	Low flow, PCB spiked	212.5	144.0	NA	6.5	4618
11	Low flow, PCB spiked	177.0	142.5	NA		

2.5.3 Variation of Gas Flow through the Columns

Two flow conditions, high and low, were maintained for the Eagle Harbor and Lake Hartwell columns. The flow conditions were controlled by throttling the control valves. The low flow condition was selected by throttling the valve measured by the microflow meters. The high level flow conditions were controlled via the maximum opening of the control valve that can measure flow by the microflow meter. Microflow meters (Gilmont Instruments, Illinois) have a scale from 0 to 100 which corresponds to a percentage of the maximum flow rate the flow meter can measure. The Eagle Harbor and one of the Lake Hartwell microflow meters had a range from 0 to 15 mL/min for air. Three of the Lake Hartwell flow meters used for the low flow condition had a range from 0 to 10 mL/min for air. The low flow columns were set at 30% of the maximum measurable flow rate and the high flow columns were set at 85% for the 0 to 15 mL/min flow meters. The three low flow Lake Hartwell columns using the 0 to 10 mL/min microflow meters were set at 56% in order to correspond to the same low condition flow rate as the Eagle Harbor columns. The actual corrected flow rate was calculated with correction factors which take into account the type of gas used and the pressure of the supplied gas. The correction factors were determined from a chart supplied by the vendor. The correction factor for CH_4 was 1.35 and the correction factor for CO_2 was 0.81. The pressure correction was 1.29 as the gas was supplied at 10 psig from the gas regulator (Table 2-5).

Table 2-5. Correction Factors for the Gas Mixture and Pressure

Percentage	Gas	Flow Correction Factors	10 psig Regulated Pressure	Total Correction Factor
60	CH_4	1.35	1.29	1.46
40	CO_2	0.81		

The calculated correction factor for a 60% CH_4 and 40% CO_2 mixture supplied at 10 psig was 1.46 (shown in Equation 1). Thus, at 30% of the maximum measurable flow rate of 15 mL/min, the actual flow rate of the gas mixture was 6.5 mL/min.

$$(CH_4\text{Factor}) \cdot 0.6 + (CO_2\text{Factor}) \cdot 0.4 \pm (\text{PressureFactor}) = 1.46 \qquad \text{(Equation 1)}$$

2.5.4 Analyses of Column Materials

After six weeks of continuous gas sparging through the columns, the PUF filters were removed from the top of the columns and sent to Battelle's laboratory at Duxbury, Massachusetts for PCBs and PAH analyses. A new set of PUFs were immediately replaced at the outlet of the columns. After 19 weeks of continuous gas sparging operation of the columns, the gas supply was turned off and the manifold was disconnected from the column feed lines. The standing column water at the top of the sediment was carefully decanted into 1-L amber bottle. The sediment and cap (wherever applicable) were removed with a long armed spatula and added into 250-mL glass bottles with a Teflon®-lined cap. The glass bottles were wrapped in aluminum foil. The amounts of water, sediment and cap material recovered were measured gravimetrically. The water, sediment, cap material and PUFs were sent for analyses at Battelle's Duxbury laboratory. In Figure 2-9, typical Eagle Harbor sample containers are shown.

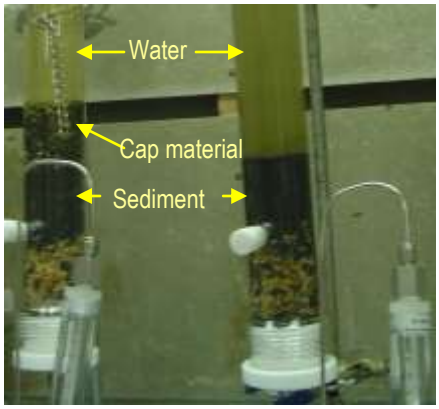


Figure 2-9. Eagle Harbor Water, Cap and Sediment (after 19-weeks)

2.5.5 Measurements of pH, ORP, DO and Turbidity

The pH, ORP, DO and turbidity were measured for overlying water in the columns and the porewater from the sediment. A 50-mL syringe was used to collect approximately 25-mL from the side port of the column as shown in Figure 2-10. The turbidity was measured first using a HACH 2300DR followed by the ORP and DO measurements. The pH, ORP and DO measurements were conducted inside the glove box under a nitrogen environment. All of the pH and DO probes were calibrated under ambient conditions and the ORP probe was checked using a quinhydrone solution. These measurements were also conducted for the sediment porewater. Porewater was collected by centrifuging 10-grams of column sediment in a centrifuge tube for 45 minutes at 3250 rpm (Bekman Centrifuge). The probes were placed in centrifuge tubes and dipped into the porewater that had been separated from the precipitated sediment.

2.6 Analytical Techniques: PCBs and PAH

2.6.1 Sediment Sample Processing

Sediment samples were extracted for PCB congeners or PAHs following Battelle SOP 5-192. Approximately 30 g of wet sediment were mixed with sodium sulfate (a drying agent), fortified with surrogate internal standards (SIS), and extracted three times with methylene chloride using shaker table techniques. The combined extracts were dried over anhydrous sodium sulfate and cleaned using alumina column (Battelle SOP 5-329), activated copper (Battelle SOP 5-328) and size exclusion high performance liquid chromatography (HPLC) (Battelle SOP 5-191). The post-HPLC extract was solvent-exchanged to n-hexane, concentrated to approximately 1 mL, and fortified with a set of internal standards (IS).

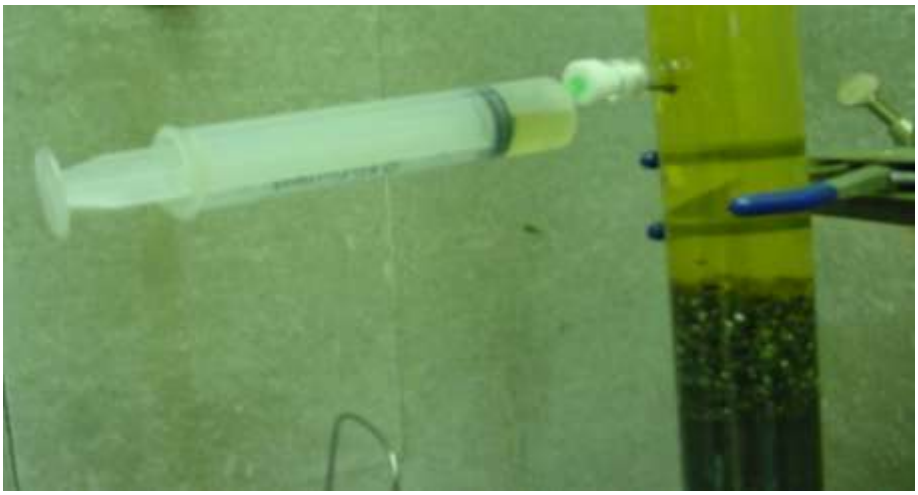


Figure 2-10. Removal of Column Water for pH, ORP, DO and Turbidity Measurements

2.6.2 PUF Sample Processing

PUF samples were extruded from their cartridges into pre-cleaned Teflon® extraction vessels and extracted like solids, following procedures defined in Battelle SOP 5-192. The initial extraction was performed in n-hexane (as opposed to methylene chloride). Prior to alumina column cleanup, the extract was solvent exchanged into methylene chloride; the extract cleanup proceeded in the same manner as in the sediment processing section.

2.6.3 Large Volume (≥1 L) Water Sample Processing

Water samples were extracted for PCB congeners or PAHs following Battelle SOP 5-200. Approximately 1 L of the water sample was fortified with SIS and extracted three times with methylene chloride using separatory funnel techniques. The combined extract was dried over anhydrous sodium sulfate and cleaned using alumina column chromatography (Battelle SOP 5-329), activated copper (Battelle SOP 5-328), and HPLC (Battelle SOP 5-191). The post-HPLC extract was solvent-exchanged to n-hexane, concentrated to approximately 0.5-mL, and fortified with IS.

2.6.4 Small Volume (≤0.5 L) Water Sample Processing

Water samples were centrifuged to remove particulates and extracted for PCB congeners or PAHs following Battelle SOP 5-200. Approximately 125 mL of the water sample was fortified with SIS and extracted three times with methylene chloride using separatory funnel techniques. The amount of solvent was adjusted to reflect the volume of water extracted. The combined extract was dried over anhydrous sodium sulfate and cleaned using alumina column chromatography (Battelle SOP 5-329), activated copper (Battelle SOP 5-328), and HPLC (Battelle SOP 5-191). The post-HPLC extract was solvent-exchanged to n-hexane, concentrated to approximately 0.25-mL, and fortified with IS.

2.6.5 Instrumental Analysis

Gas chromatography/mass spectrometry (GC/MS) analysis for semi-volatile organics (e.g., PAH) was performed according to Battelle SOP 5-157, *Identification and Quantitation of Polynuclear Aromatic*

Hydrocarbons (PAH) by Gas Chromatography/Mass Spectrometry. This method is based on SW846 Method 8270C (U.S. EPA, 1996). The 8270M target compounds were determined using high-resolution capillary GC/MS. The GC/MS analysis for PCB congeners was performed following protocols defined in Battelle SOP 5-315, *Identification and Quantification of Polychlorinated Biphenyl Congeners (PCB), PCB Homologues, and Chlorinated Pesticides by Gas Chromatography/Mass Spectroscopy in the Selected Ion Monitoring (SIM) Mode*. The method protocols in this Battelle SOP are based on key components of the PCB congener analysis approach described in U.S. EPA Method 1668A (U.S. EPA 1999), using SW846 8270M as the base method. The analytical systems are comprised of a Hewlett-Packard (HP) 6890 GC equipped with an electronic pressure controlled (EPC) inlet and an HP 5973 mass selective detector (MSD) operating in the SIM mode to achieve the necessary sensitivity and specificity.

The analytical systems are tuned with perfluorotributylamine (PFTBA), calibrated with a minimum of a six-point calibration consisting of each individual target compound with an approximate analyte concentration range of 0.005 to 10 ng/µL for semi-volatiles and 0.002 to 1 ng/µL for PCB congeners. The validity of the initial calibration is monitored with a continuing calibration check analysis at least every 12 hours. Quantification of individual target compounds is performed by the method of internal standards, using the relative response factors versus the retention indices (RIs) (the data are not surrogate corrected).

2.7 Analytical Techniques: Gas Analysis

The samples were received at Microseeps Inc.'s (Pittsburgh, Pennsylvania) laboratory in the sealed serum vial in which they were prepared. It was unknown in the planning stage whether there would be an excess pressure generated in the headspace, or if the headspace pressure would simply be atmospheric. To be conservative, it was decided to assume that no excess pressure would be generated and to employ a headspace from which a 10 mL aliquot could be removed.

The samples were sub-sampled by insertion of a locking, gas-tight syringe through the septum. Prior to insertion the plunger of the syringe was completely depressed and the syringe was fit with a 21-gauge stainless-steal disposable needle. The needle was inserted through the septum and the plunger was allowed to expand to release any excess pressure. This is how the excess pressure was measured.

Since there was no excess pressure, the plunger was drawn back to 10 mL. The syringe was then locked, effectively closing the path between the syringe barrel and the headspace. The plunger was then released and under atmospheric pressure the volume of the gas was somewhat less than 10 mL. The lock was opened, and the plunger drawn to a number above 10, until an appropriate mass of sub-sample was collected.

For CO_2, CH_4 and oxygen concentration measurements the aliquot was then directly injected onto a GC column. The GC was operated and the results quantified according to SOP-AM20Gax. Reporting limits, quality control parameters, and so on are discussed in that SOP.

Section 3.0 RESULTS AND DISCUSSION

3.1 Microcosm Study

The main objective of the microcosm study was to determine the amount of gas generated at various times (1, 3, 7, 14, 21, 30, 45, 60, 90-days) and under different temperature conditions. The site-specific properties of sediments and water from the two sites (Eagle Harbor and Lake Hartwell) are expected to have an impact on the amount of gas generated.

Tables 3-1 and 3-2 show the number of bubbles generated, corresponding gas volume, and composition of gas obtained from the headspace gas analysis. Separate sets of sacrificial bottles were used for gas volume measurement and composition analyses.

The Eagle Harbor serum bottles showed minimal or no measurable gas measured at 10°C and 25 °C. The maximum volume of gas generation was observed after 3-days at 25 °C, where 0.54 and 0.79 mL gas volume were measured in duplicate samples. There were measurable amounts of gas generated from the kill controlled samples at 10°C and 25°C during the early sampling time intervals. However, as the study progressed to 90-days, no gas was measured in the killed controls. At 37 °C, gas was measured at all time intervals.

There were no significant levels of the measured gases in the headspace of any of the Eagle Harbor sediment samples that were incubated for 14 days and 90 days. The killed controls generated increased levels of CO_2 in the headspace, which was similar to the Lake Hartwell bottles. There was a decrease in oxygen concentration in the headspace from 10 °C to 25 °C for the Eagle Harbor sediment bottles that were incubated for 90 days.

At 10 °C, no gas was measured from the Lake Hartwell bottles during all sampling time events. At room temperature (25 °C), about 0.4 mL of gas was measured at both 30 and 60-days of incubation. However, over the duration of the study, no significant change in gas generation with time was observed for the samples incubated at 10 °C to 25 °C. Though gas was generated from the day-3 killed control bottle, subsequent measurements of sacrificial killed control bottles showed no gas generation. At 37 °C, gas was measured in each bottle including the kill controls during each time withdrawal events. The gas measured from the bottles at 37 °C might be due to the water vapor generated at higher temperatures and/or due to the higher biological activities at a higher incubation temperature. However, no change in gas generation was observed with an increase in incubation time from day 1 to day 90. In Figure 3-1, the average gas measurement and the kill control for Lake Hartwell bottles are plotted.

After incubation of 14-days and 90-days, the 125-mL serum bottles were packed in wet ice and sent for headspace analysis. The percentage of CH_4 measured in the headspace was 3.1% and 2.4 % for the duplicate bottles and 1.9% for the kill control for the day 14 bottles incubated at 37 °C. The percentage of CH_4 was below detection limits (<0.200%) at 10 °C and 25 °C. Thus, it appears that the higher temperatures facilitated the production of CH_4 in the Lake Hartwell bottles after 14-days. Furthermore, there was a decrease in oxygen and an increase in CO_2 and CH_4 in the 14-day bottles as the temperature increased from 10 °C to 37 °C. CO_2 was the prevalent gas measured in the kill controls at all temperature conditions. However, it is not clear how the addition of mercuric chloride in the killed control bottles at all three temperature conditions caused an increased production of CO_2 compared with the bottles with no mercuric chloride added.

There was an increase in CH_4 production from 14-days to 90-days for the bottles at 25 °C. Also, the headspace of larger bottles that were incubated for 90 days at 37 °C contained mostly CO_2 and oxygen.

3.1.1 Sediment and Water Analysis of Microcosm Bottles

After an incubation of 90 days, the serum bottles containing sediments and water from Eagle Harbor Lake and Hartwell were sent to Battelle's Duxbury laboratory. The sediment and water in the bottles were analyzed for PAHs in the Eagle Harbor samples and PCBs in the Lake Hartwell samples.

In Figure 3-1, the concentrations of PAHs (ng/g-dry) in the Eagle Harbor sediment were plotted at various incubation conditions. The PAHs are listed on the x-axis from left to right from lower to higher molecular weight. The sediment at 10 °C, 25 °C, 37 °C and non-incubated are adjacent to each other in the bar diagram. There is a higher concentration of PAH in the sediment as the temperature increases from 10 °C to 37 °C. This pattern holds true from low to high molecular weight of PAH compounds. The concentration profile of the PAHs from low to high molecular weight concentrations remains unchanged due to temperature effects. For example, the average concentration of phenanthrene is the highest for all temperatures and also for the non-incubated sediment.

The water in the 90-day serum bottles containing Eagle Harbor sediment was also analyzed for PAHs. In Figure 3-2, the PAH concentrations (ng/L) were at various incubation conditions. As with the sediment plot, the PAHs are arranged on the x-axis from low to high molecular weight. An inverse relationship is observed in comparison with the water. The concentration of PAH in the water decreases from low temperature (10 °C) to higher temperature 37°C. This trend is consistent as the PAH molecular weight increases.

The Lake Hartwell sediment was analyzed for 118 congeners of PCBs. The bar diagram of PCB concentrations (ng/g) versus various congeners for incubation conditions were plotted in Figure 3-3. After incubation for 90-days, the concentration of PCBs was higher at the lower temperature (10°C) sediment than the sediment incubated at higher temperatures (25 °C and 37 °C).

Figure 3-3 also shows the change in PCB concentrations (ng/L) in water at the various incubation temperatures. The PCB concentration in water was lower for the 10 °C incubated sediment than that of the higher temperatures. This trend is opposite of the Lake Hartwell sediment.

3.1.2 pH and Redox Potential of Microcosm Bottles

The pH and redox potential of water in the incubated serum bottles containing Eagle Harbor and Lake Hartwell sediments were conducted inside a glove box under a nitrogen environment. A 2-mL aliquot of water was extracted from the bottles using a 22-guage needle. A more detailed description of the pH and ORP procedure is described in the Materials and Methods section. In Table 3-3, the pH and ORP values were tabulated for the serum bottles containing the Eagle Harbor and Lake Hartwell sediments and site-specific water. Incubation temperatures of the serum bottles were also shown in the table. At the end of incubation, the pH of the water in Eagle Harbor varied between 7.3 and 8.3. The ORP of the same bottles varied between -210 to -240 mV (i.e., Eh varied from -10 to -40 mV) (Figure 3-4). These ORP values indicated that these bottles were at methanogenic conditions at the end of the incubation period. The change in incubation temperature did not impact the changes in pH and ORP of the equilibrated water at the end of the incubation period. The killed control bottles containing Eagle Harbor sediment that were spiked with 1-mL of 8% mercuric chloride showed relatively lower pH and higher ORP values than the sample bottled. The ORP of the killed control bottles incubated at 10 °C and 25 °C ranged between 132 to 140 mV indicating the presence of aerobic environment in the microcosm bottles in the absence of biological activities. The measured ORP value of the killed control bottle at

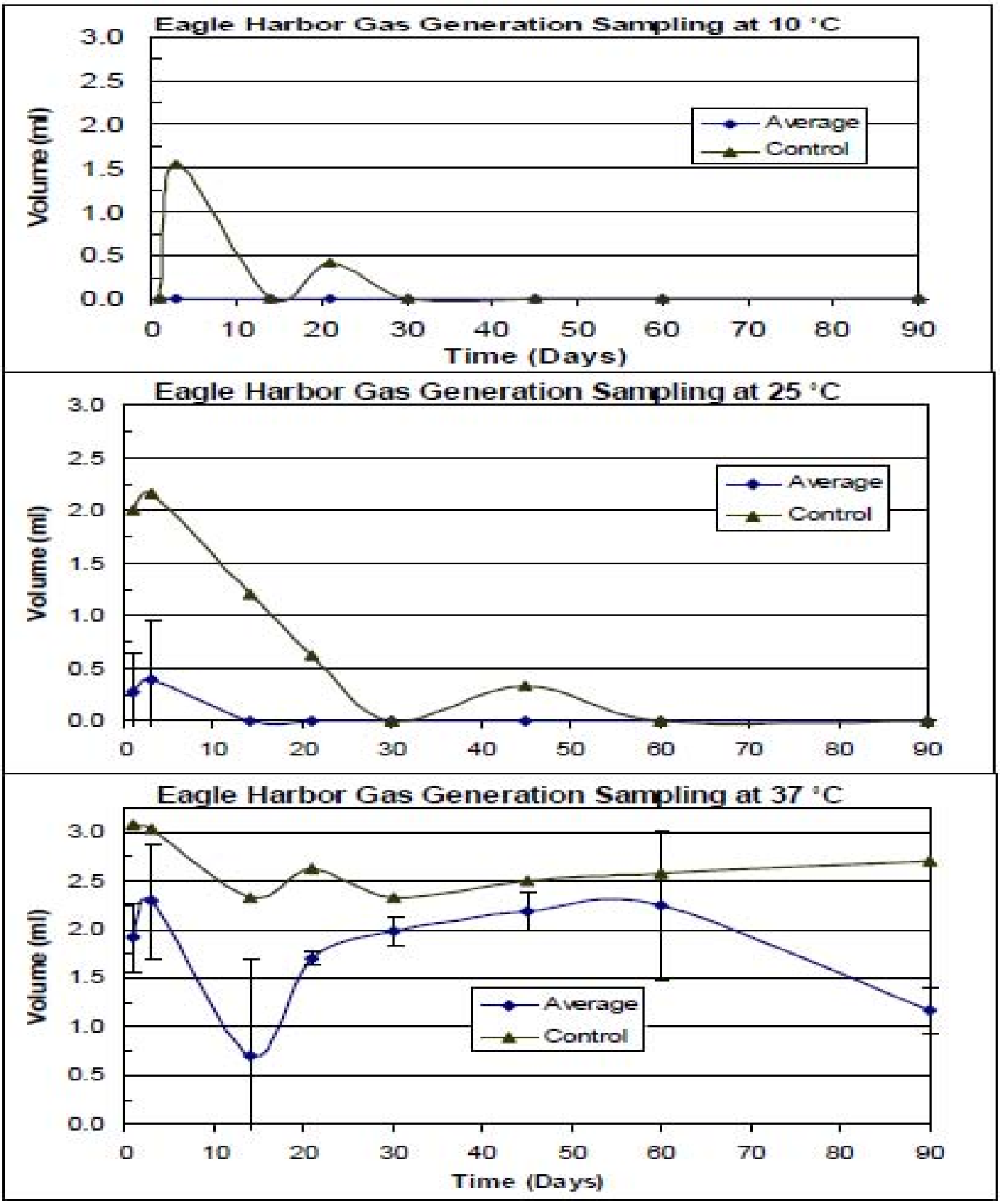


Fig 3-1. Eagle Harbor Gas Generation at 10°C, 25°C, and 37°C

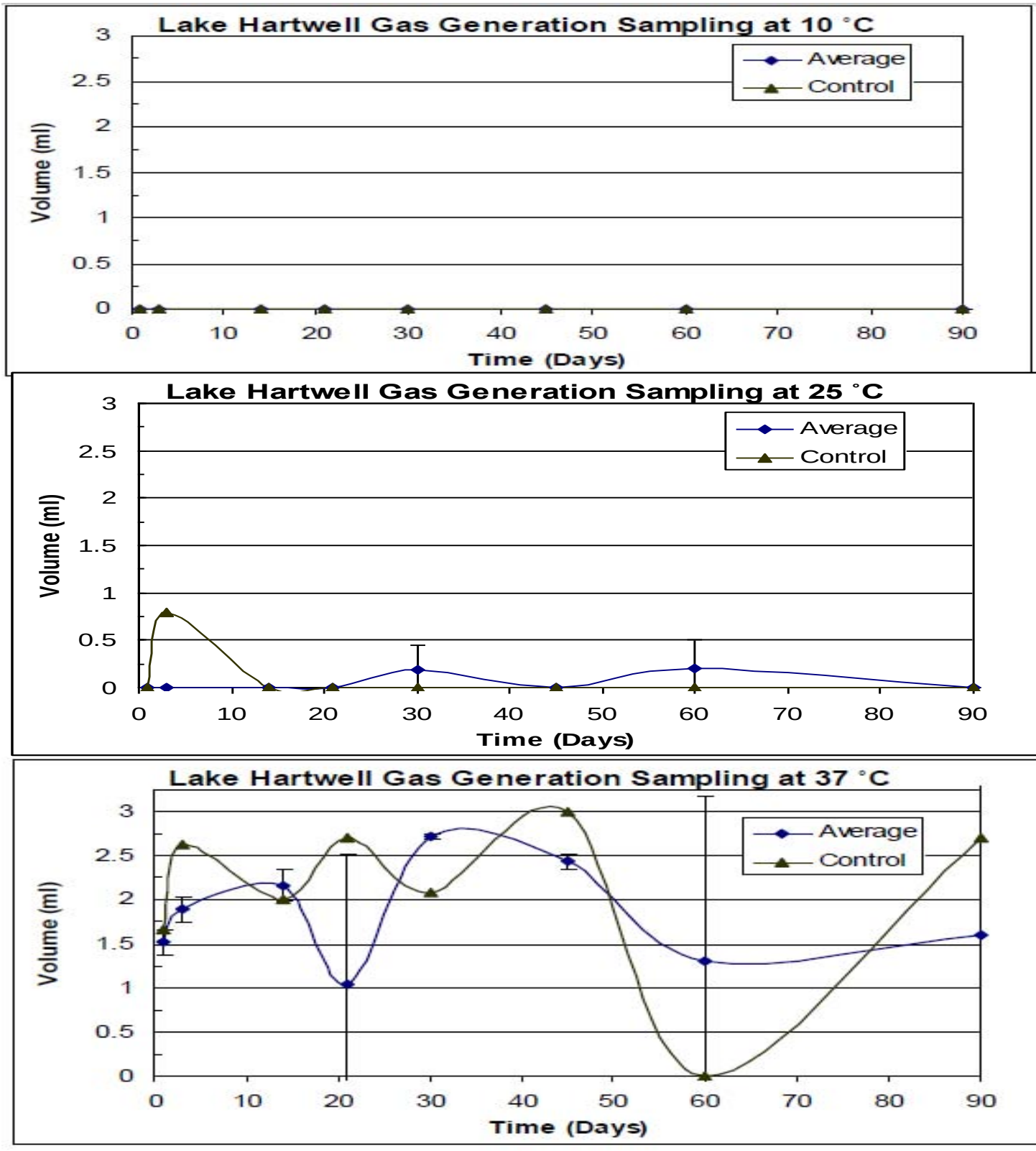


Figure 3-2. Lake Hartwell Gas Generation at 10°C, 25°C, and 37°C

Table 3-1. Gas Generation and Headspace Analysis of Microcosm Bottles Containing Eagle Harbor Sediment

Sample Id	Number of Bubbles	Total Gas Volume (mL)	Time (s)	Incubation Time (days)	Carbon Dioxide %	Methane %	Oxygen %
EH-10-1-1	NA	NA	NA	1	NA	NA	NA
EH-10-1-2	NA	NA	NA		NA	NA	NA
EHCT-10-1-1	NA	NA	NA		NA	NA	NA
EH-25-1-1	NA	NA	NA		NA	NA	NA
EH-25-1-2	NA	NA	NA		NA	NA	NA
EHCT-25-1-1	48	2.00	33.08		NA	NA	NA
EH-37-1-1	52	2.16	29.07		NA	NA	NA
EH-37-1-2	40	1.67	34.47		NA	NA	NA
EHCT-37-1-1	74	3.08	29.84		NA	NA	NA
EH-10-3-1	NA	NA	NA	3	NA	NA	NA
EH-10-3-2	NA	NA	NA		NA	NA	NA
EHCT-10-3-1	37	1.54	33.60		NA	NA	NA
EH-25-3-1	13	0.54	19.24		NA	NA	NA
EH-25-3-2	19	0.79	24.63		NA	NA	NA
EHCT-25-3-1	52	2.16	28.41		NA	NA	NA
EH-37-3-1	45	1.87	27.84		NA	NA	NA
EH-37-3-2	65	2.71	53.29		NA	NA	NA
EHCT-37-3-1	73	3.04	34.00		NA	NA	NA
EH-10-14-1	NA	NA	NA	14	0.330	<0.200	0.210
EH-10-14-2	NA	NA	NA		0.340	<0.200	0.250
EHCT-10-14-1	NA	NA	NA		4.600	<0.200	0.410
EH-25-14-1	NA	NA	NA		0.440	<0.200	0.320
EH-25-14-2	NA	NA	NA		0.310	<0.200	0.220
EHCT-25-14-1	29	1.21	49.29		4.000	<0.200	0.810
EH-37-14-1	34	1.42	35.47		0.390	<0.200	0.220
EH-37-14-2	NA	NA	NA		0.360	<0.200	0.230
EHCT-37-14-1	56	2.33	49.27		4.100	<0.200	0.760
EH-10-21-1	NA	NA	NA	21	NA	NA	NA
EH-10-21-2	NA	NA	NA		NA	NA	NA
EHCT-10-21-1	10	0.42	26.68		NA	NA	NA
EH-25-21-1	NA	NA	NA		NA	NA	NA
EH-25-21-2	NA	NA	NA		NA	NA	NA
EHCT-25-21-1	15	0.62	18.62		NA	NA	NA
EH-37-21-1	42	1.75	20.45		NA	NA	NA
EH-37-21-2	40	1.67	28.80		NA	NA	NA
EHCT-37-21-1	63	2.62	33.80		NA	NA	NA

Table 3-1. Gas Generation and Headspace Analysis of Microcosm Bottles Containing Eagle Harbor Sediment (Continued)

Sample Id	Number of Bubbles	Bubble Volume (ml)	Time (s)	Incubation Time (days)	Carbon Dioxide %	Methane %	Oxygen %
EH-10-30-1	NA	NA	NA	30	NA	NA	NA
EH-10-30-2	NA	NA	NA		NA	NA	NA
EHCT-10-30-1	NA	NA	NA		NA	NA	NA
EH-25-30-1	NA	NA	NA		NA	NA	NA
EH-25-30-2	NA	NA	NA		NA	NA	NA
EHCT-25-30-1	NA	NA	NA		NA	NA	NA
EH-37-30-1	50	2.08	25.22		NA	NA	NA
EH-37-30-2	45	1.87	30.42		NA	NA	NA
EHCT-37-30-1	56	2.33	29.06		NA	NA	NA
EH-10-45-1	NA	NA	NA	45	NA	NA	NA
EH-10-45-2	NA	NA	NA		NA	NA	NA
EHCT-10-45-1	NA	NA	NA		NA	NA	NA
EH-25-45-1	NA	NA	NA		NA	NA	NA
EH-25-45-2	NA	NA	NA		NA	NA	NA
EHCT-25-45-1	8	0.33	20.69		NA	NA	NA
EH-37-45-1	56	2.33	29.47		NA	NA	NA
EH-37-45-2	49	2.04	26.86		NA	NA	NA
EHCT-37-45-1	60	2.50	31.25		NA	NA	NA
EH-10-60-1	NA	NA	NA	60	NA	NA	NA
EH-10-60-2	NA	NA	NA		NA	NA	NA
EHCT-10-60-1	NA	NA	NA		NA	NA	NA
EH-25-60-1	NA	NA	NA		NA	NA	NA
EH-25-60-2	NA	NA	NA		NA	NA	NA
EHCT-25-60-1	NA	NA	NA		NA	NA	NA
EH-37-60-1	67	2.79	36.45		NA	NA	NA
EH-37-60-2	41	1.71	26.40		NA	NA	NA
EHCT-37-60-1	62	2.58	34.02		NA	NA	NA
EH-10-90-1	NA	NA	NA	90	0.660	<0.200	0.720
EH-10-90-2	NA	NA	NA		0.860	<0.200	0.840
EHCT-10-90-1	NA	NA	NA		3.200	<0.200	0.260
EH-25-90-1	NA	NA	NA		0.410	<0.200	0.180
EH-25-90-2	NA	NA	NA		0.440	<0.200	0.210
EHCT-25-90-1	NA	NA	NA		3.900	<0.200	0.210
EH-37-90-1	24	1.00	23.20		1.800	<0.200	1.100
EH-37-90-2	32	1.33	28.29		1.600	<0.200	1.300
EHCT-37-90-1	65	2.71	38.09		NA	NA	NA

Table 3-2. Gas Generation and Headspace Analysis of Microcosm Bottles Containing Lake Hartwell Sediment

Sample Id	Number of Bubbles	Bubble Volume (ml)	Time (s)	Incubation Time (days)	Carbon Dioxide %	Methane %	Oxygen %
LH-10-1-1	NA	NA	NA	1	NA	NA	NA
LH-10-1-2	NA	NA	NA		NA	NA	NA
LHCT-10-1-1	NA	NA	NA		NA	NA	NA
LH-25-1-1	NA	NA	NA		NA	NA	NA
LH-25-1-2	NA	NA	NA		NA	NA	NA
LHCT-25-1-1	NA	NA	NA		NA	NA	NA
LH-37-1-1	34	1.42	18.44		NA	NA	NA
LH-37-1-2	39	1.62	33.21		NA	NA	NA
LHCT-37-1-1	40	1.67	24.80		NA	NA	NA
LH-10-3-1	NA	NA	NA	3	NA	NA	NA
LH-10-3-2	NA	NA	NA		NA	NA	NA
LHCT-10-3-1	NA	NA	NA		NA	NA	NA
LH-25-3-1	NA	NA	NA		NA	NA	NA
LH-25-3-2	NA	NA	NA		NA	NA	NA
LHCT-25-3-1	19	0.79	22.87		NA	NA	NA
LH-37-3-1	48	2.00	18.21		NA	NA	NA
LH-37-3-2	43	1.79	30.82		NA	NA	NA
LHCT-37-3-1	63	2.62	31.62		NA	NA	NA
LH-10-14-1	NA	NA	NA	14	<0.200	<0.200	0.240
LH-10-14-2	NA	NA	NA		<0.200	<0.200	0.260
LHCT-10-14-1	NA	NA	NA		1.800	0.380	0.170
LH-25-14-1	NA	NA	NA		<0.200	<0.200	0.250
LH-25-14-2	NA	NA	NA		<0.200	<0.200	0.230
LHCT-25-14-1	NA	NA	NA		2.900	0.790	0.180
LH-37-14-1	55	2.29	21.81		0.350	3.100	0.170
LH-37-14-2	49	2.04	40.81		0.350	2.400	0.210
LHCT-37-14-1	48	2.00	28.49		3.700	1.900	0.320
LH-10-21-1	NA	NA	NA	21	NA	NA	NA
LH-10-21-2	NA	NA	NA		NA	NA	NA
LHCT-10-21-1	NA	NA	NA		NA	NA	NA
LH-25-21-1	NA	NA	NA		NA	NA	NA
LH-25-21-2	NA	NA	NA		NA	NA	NA
LHCT-25-21-1	NA	NA	NA		NA	NA	NA
LH-37-21-1	50	2.08	28.69		NA	NA	NA
LH-37-21-2	NA	NA	NA		NA	NA	NA
LHCT-37-21-1	65	2.71	26.44		NA	NA	NA

Table 3-2. Gas Generation and Headspace Analysis of Microcosm Bottles Containing Lake Hartwell Sediment (Continued)

Sample Id	Number of Bubbles	Bubble Volume (ml)	Time (s)	Incubation Time (days)	Carbon Dioxide %	Methane %	Oxygen %
LH-10-30-1	NA	NA	NA	30	NA	NA	NA
LH-10-30-2	NA	NA	NA		NA	NA	NA
LHCT-10-30-1	NA	NA	NA		NA	NA	NA
LH-25-30-1	9	0.37	13.49		NA	NA	NA
LH-25-30-2	NA	NA	NA		NA	NA	NA
LHCT-25-30-1	NA	NA	NA		NA	NA	NA
LH-37-30-1	65	2.71	23.64		NA	NA	NA
LH-37-30-2	66	2.75	27.42		NA	NA	NA
LHCT-37-30-1	50	2.08	23.80		NA	NA	NA
LH-10-45-1	NA	NA	NA	45	NA	NA	NA
LH-10-45-2	NA	NA	NA		NA	NA	NA
LHCT-10-45-1	NA	NA	NA		NA	NA	NA
LH-25-45-1	NA	NA	NA		NA	NA	NA
LH-25-45-2	NA	NA	NA		NA	NA	NA
LHCT-25-45-1	NA	NA	NA		NA	NA	NA
LH-37-45-1	60	2.50	22.45		NA	NA	NA
LH-37-45-2	57	2.37	18.63		NA	NA	NA
LHCT-37-45-1	72	3.00	31.61		NA	NA	NA
LH-10-60-1	NA	NA	NA	60	NA	NA	NA
LH-10-60-2	NA	NA	NA		NA	NA	NA
LHCT-10-60-1	NA	NA	NA		NA	NA	NA
LH-25-60-1	10	0.42	23.29		NA	NA	NA
LH-25-60-2	NA	NA	NA		NA	NA	NA
LHCT-25-60-1	NA	NA	NA		NA	NA	NA
LH-37-60-1	63	2.62	33.09		NA	NA	NA
LH-37-60-2	NA	NA	NA		NA	NA	NA
LHCT-37-60-1	NA	NA	NA		NA	NA	NA
LH-10-90-1	NA	NA	NA	90	0.230	<0.200	0.300
LH-10-90-2	NA	NA	NA		0.490	<0.200	0.530
LHCT-10-90-1	NA	NA	NA		2.700	<0.200	0.250
LH-25-90-1	NA	NA	NA		0.380	1.800	0.310
LH-25-90-2	NA	NA	NA		0.390	1.800	0.340
LHCT-25-90-1	NA	NA	NA		2.800	0.890	0.240
LH-37-90-1	77	3.21	38.22		3.200	<0.200	6.700
LH-37-90-2	NA	NA	NA		4.900	<0.200	3.900
LHCT-37-90-1	65	2.71	39.49		NA	NA	NA

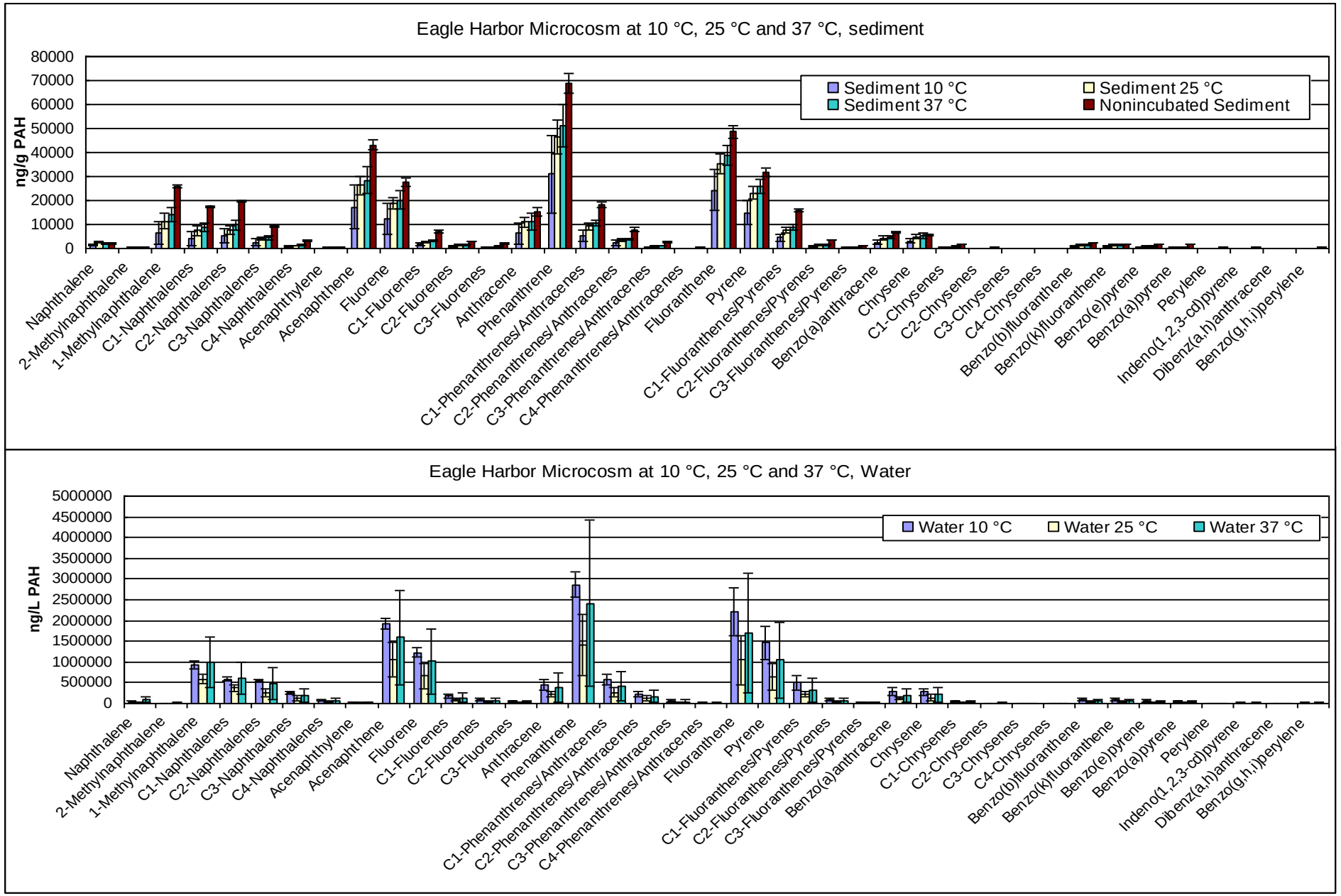
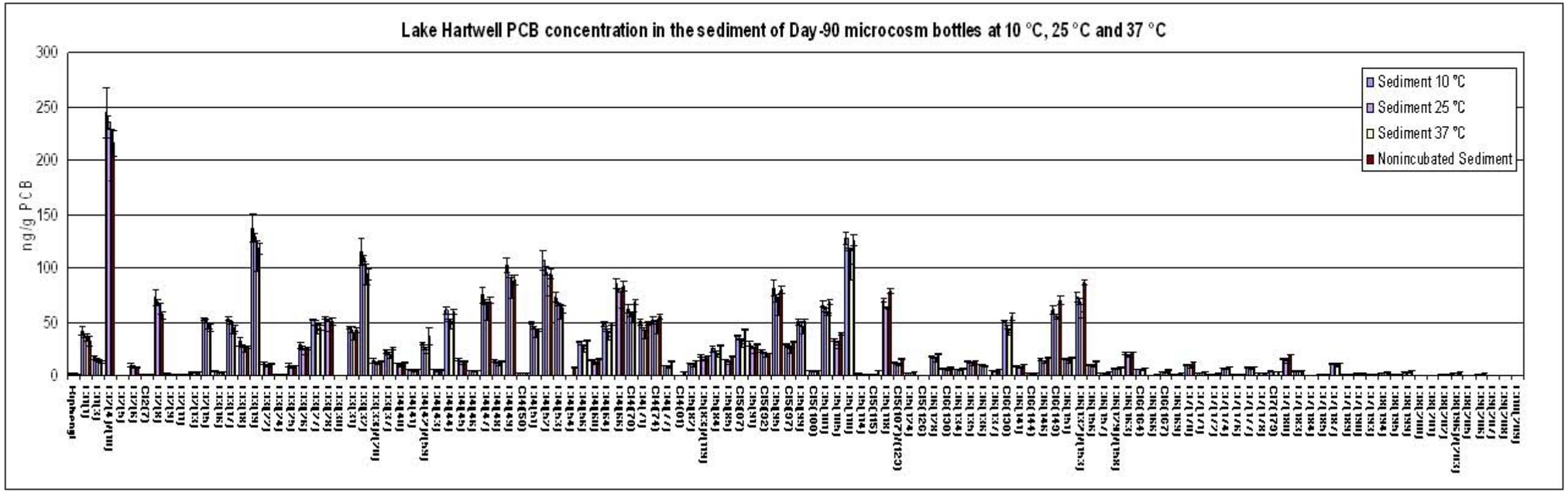


Figure 3-3. Eagle Harbor Microcosm Bottles (Sediment [upper] and Water [lower] Concentrations at 10 °C, 25°C and 37 °C)



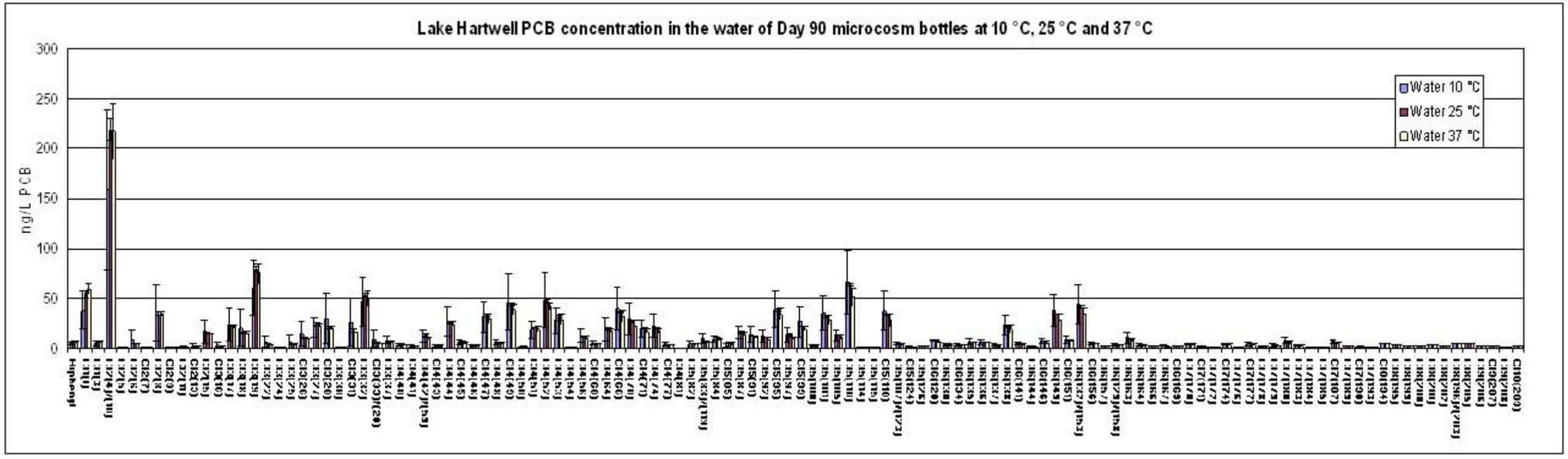


Figure 3-4. Lake Hartwell Microcosm Sediment (upper) and Water (lower) after 90-days of Incubation at 10 °C, Room Temperature and 37 °C

37 °C was -20 mV. It was anaerobic, but it was not as anaerobic as the other sample bottles containing viable bacteria.

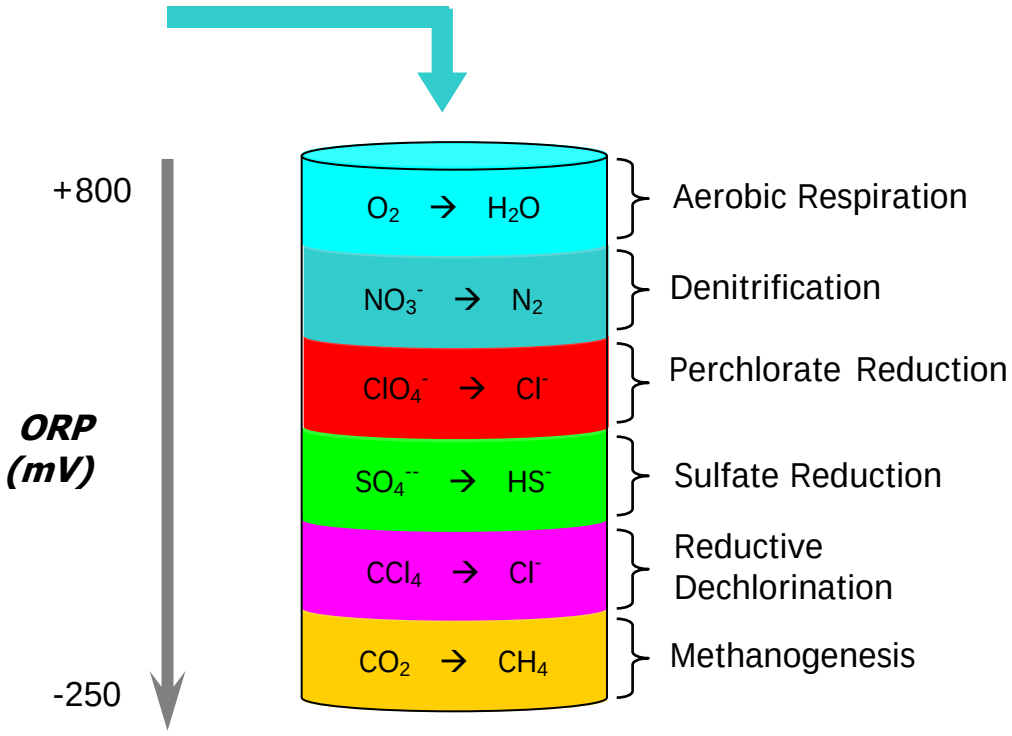


Figure 3-5. Relationship between the Redox Potential and Idealized Terminal Electron Acceptor Process

The pH values of the microcosm bottles containing Lake Hartwell sediments after incubation varied between 6.4 and 6.9. The ORP in the water after the incubation period was around -25 mV for the bottles incubated at 10 °C and 25 °C. The ORP value was lower in the bottle that was incubated at 37 °C than those at the other two temperatures. The measured pH value was also lower for the killed controls in comparison with the other unkilled bottles, as observed for the bottles containing Eagle Harbor sediment. Unlike the bottles containing Eagle Harbor sediment, the ORP of the killed control bottles containing Lake Hartwell sediment maintained anaerobic conditions at all incubation temperatures.

Table 3-3. pH and ORP of Lake Hartwell and Eagle Harbor Microcosm Bottles after 120-Days

Sample ID	Incubation Temperature (°C)	pH	ORP (mV)
EH-10-1	10	7.54	-242.0
EH-10-2	10	7.37	-221.0
EHCT-10-1	10	6.91	139.5
EH-25-1	25	7.55	-254.0
EH-25-2	25	8.34	-256.4
EHCT-25-1	25	7.28	132.1
EH-37-1	37	7.53	-226.6
EH-37-2	37	7.40	-209.9
EHCT-37-1	37	7.12	-19.9
LH-10-1	10	6.88	-26.3
LH-10-2	10	6.40	-20.5
LHCT-10-1	10	6.13	-10.0
LH-25-1	25	6.88	-19.0
LH-25-2	25	6.92	-24.1
LHCT-25-1	25	6.27	-34.1
LH-37-1	37	6.82	-111.2
LH-37-2	37	6.81	-52.1
LHCT-37-1	37	6.29	-60.9

3.2 Column Study

The results of the simulated gas ebullition columns for Eagle Harbor sediment and Lake Harbor sediment are discussed in Sections 3.2.1 and 3.2.2, respectively. Columns packed with Eagle Harbor sediments and Lake Hartwell sediments were evaluated for two gas flow conditions: a) at a flow rate of 6.5 mL/min, referred as "low" flow condition in this report, and b) at a flow rate of 18.7 mL/min, referred as "high" flow condition in this report. The simulated gas sparging rate through the columns were selected based on the literature data, the results of the microcosm tests conducted, and the laboratory practicality. The simulated gas ebullition rates are discussed in Section 2.3.3.

For the column studies, there are four compartments – contaminated sediment and/or cap layer, water column, gas layer, and PUF. Gas bubbles take contaminants from the sediment and water layers by partitioning process, and release them as they transit the PUFs. The other major transport pathway is the water entrainment in PUFs with the bubble. The CH_4 gas bubbles brought sediment particles into the water column upon leaving the sediment. The larger, heavier particles fell back to the sediment bed, while the smaller, lighter particles remained suspended in the water column. The larger methane flux generated stronger forces on the particles resulting in higher suspensions of solids in the water column. These gas bubbles not only take up the contaminant from the pore water in the contaminated sediment but also suspend fine particulates in the water column. Both contaminated sediment suspended particulates and gas bubbles release contaminants (PCBs and PAHs) into the water column. The driving force for mass transfer and organic desorption from gas and sediment particles is expected to be large at the

beginning of the test as organic concentration in the water was relatively small. This results in an increase in organic concentration in the water during the initial stages of the tests. With time, the driving force decreases as the aqueous phase concentration increases. As the gas bubbles escapes the water column they entrain a fraction of organic to the PUFs. At the beginning of the experiments, the concentrations of organics in the PUFs increase slowly. Once the organic concentration in the water column reaches equilibrium with the sediment particles, the bubbles transport organic from both sediment porewater and water column.

Gas flux influences the mass distribution of PCBs and PAHs. It is obvious that the higher the flux of gas passing through the column, the more organics carried into the PUFs. The total organic mass collected in the PUFs are proportional to the gas flux.

3.2.1 Eagle Harbor Columns

Simulated gas ebullition at the low and high flow rates through the various columns packed with Eagle Harbor sediments influenced the results of the various parameters.

- The impact on pH, redox potential, dissolved oxygen and turbidity of the overlayed water by the gas ebullition of the columns are discussed in Section 3.2.1.1.
- The PAHs captured by the PUFs located at the outlet of the columns containing capped sediment and uncapped sediment under low and high flow conditions were analyzed after 6-weeks and 19-weeks of continuous gas ebullition operation. In the case of PUFs collected after 6-weeks of operation, the primary and secondary PUFs from each column were analyzed for PAHs (or PCBs in the Lake Hartwell samples) individually. However, at the end of the study (19-weeks), a composite sample containing both the primary and secondary PUFs from the columns was analyzed. The results of PUF analysis are discussed in Section 3.2.1.2.
- PAHs contain four-, five-, six- or seven-member rings, but those with five or six are most common. PAHs with two rings are more soluble in water and more volatile than the PAHs of three rings or more. As molecular weight increases, aqueous solubility and vapor pressure decrease. The aqueous solubility decreases approximately one order of magnitude for each additional ring. Because of these properties, PAHs in the environment are found primarily in soil and sediment, as opposed to water or air. PAHs are also often found in particles suspended in water and air. After 19-weeks of operation of the columns, the concentrations of the PAHs were measured in sediment, water and cap materials of each column. The profiles of PAHs in the sediment, water and cap are compared at low and high flow conditions in Section 3.2.1.3.
- The mass of the total polycyclic aromatic hydrocarbon (tPAH) in initial sediment and various other phases after 19-weeks of operation (sediment, cap, water, and PUF materials) were compared by estimating the loss or recovery of tPAH in sediment, water, PUF, or cap material (Section 3.2.1.4).

3.2.1.1 pH, Redox Potential, Dissolved Oxygen and Turbidity

At the end of gas sparging operation, the pH, ORP, DO and turbidity of the standing water from each column were analyzed. Water was extracted by piercing the needle of a syringe at the side port of the column. The measurements were taken immediately after extraction to minimize the interaction with air.

The Eagle Harbor water pH was ~6.5, ORP ranged between -50 to -80 mV and the DO ranged between 0.70 and 0.80 mg/L at the end of the gas ebullition (see Table 3-4). The negative value of ORP suggests an anaerobic environment achieved by the column due to the sparging of a mixture of 60% CH_4 and 40% CO_2 gas through the columns. The difference in turbidity values indicated that the water in the capped columns was clearer than the uncapped columns, even at high flow

3.2.1.2 PUF Analysis

Two PUFs were attached in series at the outlet of the Eagle Harbor columns. The second PUF was included to ensure the capture of PAHs in case the first PUF had reached its saturation capacity with respect to the COCs.

Eagle Harbor column #1 and #3 were sparged at low flow (6.5 mL/min) and were constructed without cap materials to simulate uncapped sediment conditions. Eagle Harbor column #2 and #4 were gas sparged at low flow and cap materials were applied at the top of the sediment layer to simulate capped sediment. In Figure 3-6, the amounts of PAHs (38-priority PAHs in nanograms) for capped and uncapped columns were plotted after 6-weeks and 19-weeks of gas sparging at low flow conditions. The PUF data represented in Figure 3-6 was the sum from both PUFs in series at six weeks. The average value of the duplicate samples is presented in this figure. The individual PUF data (ng/PUF) for individual samples are listed in Appendix B. It was observed that the PUFs attached to the uncapped columns captured more PAHs than the capped columns for both time intervals (i.e., 6-weeks and 19-weeks of gas sparging). The cap materials attenuated PAH migration from the sediment phase to the water and ultimately to the gas phase by sorbing these compounds. The lower molecular weight of the PAHs captured by the PUFs at the outlet of the capped and uncapped columns was because of the relatively higher water solubilities and vapor pressure of these compounds. However, the PUFs on the

Table 3-4. Eagle Harbor pH, ORP, DO and Turbidity of Column Water at the End of Gas Ebullition

Column No.	Column Description	pH	ORP (mV)	Dissolved Oxygen (mg/L)	Turbidity (FTU)
1	Low flow, uncapped	6.553	-87.5	0.64	73
2	Low Flow, capped	6.539	-71.0	0.71	18
3	Low flow, uncapped	6.517	-67.0	0.73	57
4	Low flow, capped	6.601	-81.0	0.75	25
5	High flow, uncapped	6.598	-58.1	0.83	187
6	High Flow, capped	6.570	-52.1	0.80	16
7	High Flow, uncapped	6.571	-55.8	0.80	72

uncapped columns were capturing higher molecular weight PAHs than the capped columns. Phenanthrene (11,691 ng) was the highest molecular weight compound identified from the PUFs of the

uncapped column. The most recovered compound from the PUFs was 1-methylnaphthalene, a lower molecular weight PAH, for both the capped and uncapped low flow columns. These results showed that cap materials can be effective in attenuating relatively higher molecular weight compounds (hydrophobic) by providing additional sorptive surface than the native sediment.

Columns #5 and #7 containing Eagle Harbor sediment (uncapped) and Column #6 containing Eagle Harbor sediment and cap material were sparged at a high gas flow (18.7 mL/min). The other column containing Eagle Harbor sediment and cap material was not successful and data was not available. The average amount of PAH (in nanograms) captured in the PUFs from the high flow, capped and uncapped Eagle Harbor columns after 6 and 19 weeks are shown in Figure 3-7. At 6-weeks, the PUFs connected to the capped columns collected less PAH than the uncapped columns. Furthermore, the PUFs from the uncapped columns also collected higher molecular weight PAH compounds, such as fluorine, than the capped column after 6-weeks.

After 19-weeks, the PUFs for the capped column sorbed more of the lower molecular weight, such as 1-methylnaphthalene and C1-naphthalenes compounds than the uncapped columns. However, the uncapped PUFs consistently adhered to the higher molecular weight PAH compounds than the capped column. For example, the average amount of pyrene extracted from the capped column was 4856 ng in comparison to 1401 ng extracted from the uncapped columns.

3.2.1.3 PAH Concentration Profile in Eagle Harbor Sediment and Water

The average amount of 38-priority PAH compounds present in the initial Eagle Harbor sediment was compared with the uncapped and capped columns after gas sparging for 19 weeks. Figure 3- 8 shows a comparison in the amount of PAHs at low flow conditions. Though the magnitude of the amount of PAHs recovered from the sediments varied, the relative distribution of PAHs (profile) was consistent for initial Eagle Harbor sediment and uncapped and capped sediments that were gas sparged for 19 weeks. Similar trends were also observed for sediments that were gas sparged at high flow conditions.

Similar plots of PAH profiles were prepared for the water at the low flow condition. Before the initiation of gas sparging, the Eagle Harbor water had very low levels of PAHs. After sparging for 19-weeks, portions of the PAH from the sediment were partitioned into the water phase. The relative distributions of PAHs in the water from the uncapped and capped sediment columns were similar under high gas flow conditions (Figure 3-9). The water from the capped sediment column had a tPAH of 128044 ng and the same from the uncapped sediment column was 145568 ng. The concentration of tPAH in water from the uncapped sediment column was more than that of the capped sediment column.

3.2.1.4 Mass Balance of tPAH

The tPAH in the various phases was calculated by adding the various PAH compounds recovered from sediment, cap (if present), water, and PUF at the end of the gas sparging. The amount not recovered was considered to be lost. This un-recovered amount from various phases was also estimated as percentage lost.

In Figure 3-10, the bars represent the amount of tPAH in various Eagle Harbor media at low flow (6.5 mL/min) conditions at the beginning of gas sparging (i.e., t = 0) and after 19-weeks of gas sparging through various columns. The tPAH captured from both 6- and 19-weeks PUFs were also included. The uncapped sediment had more PAH losses, 55% from the initial sediment in comparison with the capped sediment of 42%. The capped column recovered 3.9% of the lost PAH, which were seen in the water, cap material and PUFs. The uncapped column recovered 2.8% of the PAH losses, which were accounted for

from the water and PUF. The remaining PAH losses could not be accounted for because of the following reasons:

- PAH losses from the sediment occurred as the columns were packed at the beginning of the gas ebullition tests and as they were unpacked at the end of the tests.
- The binding of PAHs on the PUF Tenex material may not be strong enough to prevent any volatilization losses. During the continuous operation of the columns under the ventilated hood, a portion of PAH sorbed on the PUFs could have volatilized.
- The residence time of the PAH vapor through the PUF may not have been sufficient to achieve high sorption capacity.
- A portion of the PAHs could have adhered to the stainless steel piping and the tygon tubing at the top of the column before entering the PUF.
- The CO_2 and CH_4 gas could have stripped sorbed PAHs off the Tenex material as it traversed through the PUFs.

The tPAH bar diagram was also prepared for the columns that were gas sparged at high flow condition. As shown in Figure 3-11, the uncapped sediment had more PAH loses, 47.8% than the capped sediment of 28.2%. The capped column recovered 11.5% of the PAH losses, which were captured in the water, cap material and PUF. The uncapped column recovered 7.1% of the PAH loses, which were seen in the water and PUF.

3.2.1.5 PAH in Cap Material

Two inches of clean, coarse site-specific cap material (gravel) was at the top of the Eagle Harbor sediment as described in the materials and methods and previous sections. After 19 weeks of gas sparging the cap material was separated selectively from the column and was sent to Battelle's analytical laboratory for PAH analysis. Figure 3-12 shows the cap performance to adhere/attenuate the PAH during high and low gas flow conditions. It appeared from the graphs that the cap material was able to sorb more (~2.9 times) PAH at the lower flow rate. The high flow cap material sorbed 360659 ng tPAH and the low flow cap material sorbed 1030019.1 ng.

The relative distributions of PAHs sorbed by the cap material were the same under low and high gas flow conditions. It is interesting to note that both the high and low cap material adsorbed fluoranthene more than any other PAH.

3.2.2 Lake Hartwell Columns

Columns packed with Lake Hartwell sediment were evaluated for two gas flow conditions: a) at a flow rate of 6.5 mL/min, referred as "low" flow condition in this report, and b) at a flow rate of 18.7 mL/min, referred as "high" flow condition in this report. Unlike Eagle Harbor columns, no cap material was used for Lake Hartwell columns.

3.2.2.1 pH, Redox Potential, Dissolved Oxygen and Turbidity

The pH of the water in the Lake Hartwell columns ranged between 5.7 and 6.5 as seen in Table 3-5. The DO and ORP values indicated that the columns were anaerobic. Lake Hartwell sediment consisted of clay rich material, most of which were in suspended conditions during the gas sparging operation. The turbidity of the overlying water at the end of the gas sparging experiments measured a value in excess of 460 FTU, which was the upper range of the HACH meter.

Table 3-5. Lake Hartwell Equilibrium Water pH, ORP, DO and Turbidity Measurements After 19-weeks Gas Sparging Operations

Column No.	Column Description	pH	ORP (mV)	Dissolved Oxygen (mg/L)	Turbidity (FTU)
8	Low flow	5.754	41.8	0.35	>460
9	High flow	6.396	-74.1	0.06	>460
10	Low flow, PCB spiked	6.580	-138.1	0.06	>460
11	Low flow, PCB spiked	6.383	-109.3	0.05	>460

3.2.2.2 PUF Analysis

Two PUFs were attached in series at the outlet of the Lake Hartwell columns. The second PUF was included to ensure the capture of PCBs in the Lake Hartwell samples in case the first PUF had reached its saturation capacity with respect to the COCs. After 6 and 19 weeks of gas sparging through the Lake Hartwell columns, the PUFs at the outlet of the columns were sent to Battelle's analytical

laboratory for PCB congener (118) analysis. The amounts of PCB congeners sorbed by the PUFs at low gas sparging through the unspiked and spiked Lake Hartwell sediment are plotted in Figure 3-13. The unspiked and spiked Lake Hartwell sediment had 161449 ng and 248953 ng of tPCB, respectively. The PUFs adsorbed more PCBs from the spiked columns at both 6 and 19 weeks than the unspiked columns at the same low flow rate. The PUFs that sorbed gas from week 6 through week 19 (i.e., a total duration of 13 weeks) not only sorbed more PCBs but also sorbed higher molecular weight PCBs in comparison with the PUFs that were used for the first 6 weeks of gas sparging operation. At low gas flow rates, the PUFs captured 1041 ng of tPCB for the columns with PCB spiked sediment and 164 ng for the columns with unspiked Lake Hartwell sediment. After 19-weeks, the PUFs sorbed higher molecular weight PCBs, such as Cl5(110) with the PCB spiked sediment. After 19-weeks, Cl3(19) was the highest molecular weight congener sorbed by the PUFs attached to the column containing unspiked sediment.

At high gas sparging (Figure 3-14), the PUF adsorbed 1507 ng from columns with unspiked Lake Hartwell sediment, in comparison to the low flow columns which adsorbed 164 ng of tPCBs. Higher gas sparging also caused the release of PCBs with higher molecular weights. For example, the PUF detected Cl6 (149) at 18.5 ml/min for unspiked Lake Hartwell sediment, whereas C13 (19) was the heaviest compound detected at lower flow.

3.2.2.3 Mass Balance of tPAH

The amount of total PCB concentrations initially in the Lake Hartwell sediment (unspiked and spiked), water and PUFs at the beginning of the gas sparging experiments and at the end of 19-weeks gas sparging are plotted in Figures 3-15 and 3-16. Figure 3-15 shows the mass balance of PCBs in unspiked Lake Hartwell sediment at high and low gas flow conditions. Figure 3-16 shows the same for the unspiked and spiked sediment at low gas flow conditions. The sediment in the columns under low flow lost 18.3% tPCB in comparison with the original unspiked Lake Hartwell sediment over the course of 19-weeks of gas sparging. The column water and PUF recovered 0.9% of the lost tPCB. At high flow the unspiked sediment lost 35.0% tPCB. The water and PUF recovered 2.9% of the lost PCB. The higher gas sparging flow rate resulted in more escape of PCBs. The chemical analysis of the spiked sediment at the end of the study showed that on average it had a higher amount of tPCB (283582 ± 54819 ng) than the initial tPCB concentration in the sediment (248953 ng). This discrepancy might be due to the non-homogeneity of the sediments in the columns. However, the water and the PUFs of the columns containing Lake Hartwell sediment recovered 356 and 1041 ng of tPCB, respectively, for the spiked columns at low gas flow conditions.

A conceptual diagram depicting the sediment and contaminant movement in uncapped contaminated sediment and capped contaminated sediment during gas ebullition is shown in Figure 3-17. Based on the tests performed, the pathway of gas ebullition facilitated sediment contaminant transport through sediment systems can be postulated. In case of an uncapped system, the simulated gas injected through the bottom of the column take up contaminants from pore water in the contaminated sediment via gas/water partitioning and would rise up into the water column. It was visually observed that the gas bubbles bring the sediment particles as they move through the sediment-water interface. The heavier particles sink back to the sediment after release and the lighter particles remain in the water column. In case of Lake Hartwell, the clay particles from the sediment samples formed slurry (see Figure 2-8). The contaminated particles in the slurry will desorb contaminants into the water phase. The gas bubbles also facilitate the transport of contaminants transport from the porewater to the water column. These activities increase the contaminant concentration in the water phase. As the gas traverse through the water column and break the gas-water interface, contaminants are released into the gas/emply space of the column. In the capped system, the gas injected through the contaminated sediment move through the cap material and the gas bubbles release the contaminants into the porewater in the cap and water column. Though gas movement has resulted mixing of the sediment and sand at the sediment-sand interface, the reduction in

sediment suspension in the water column was observed. The cap layer could have acted as a filter inhibiting sediment suspension, which reduced the source of contaminant into the water column.

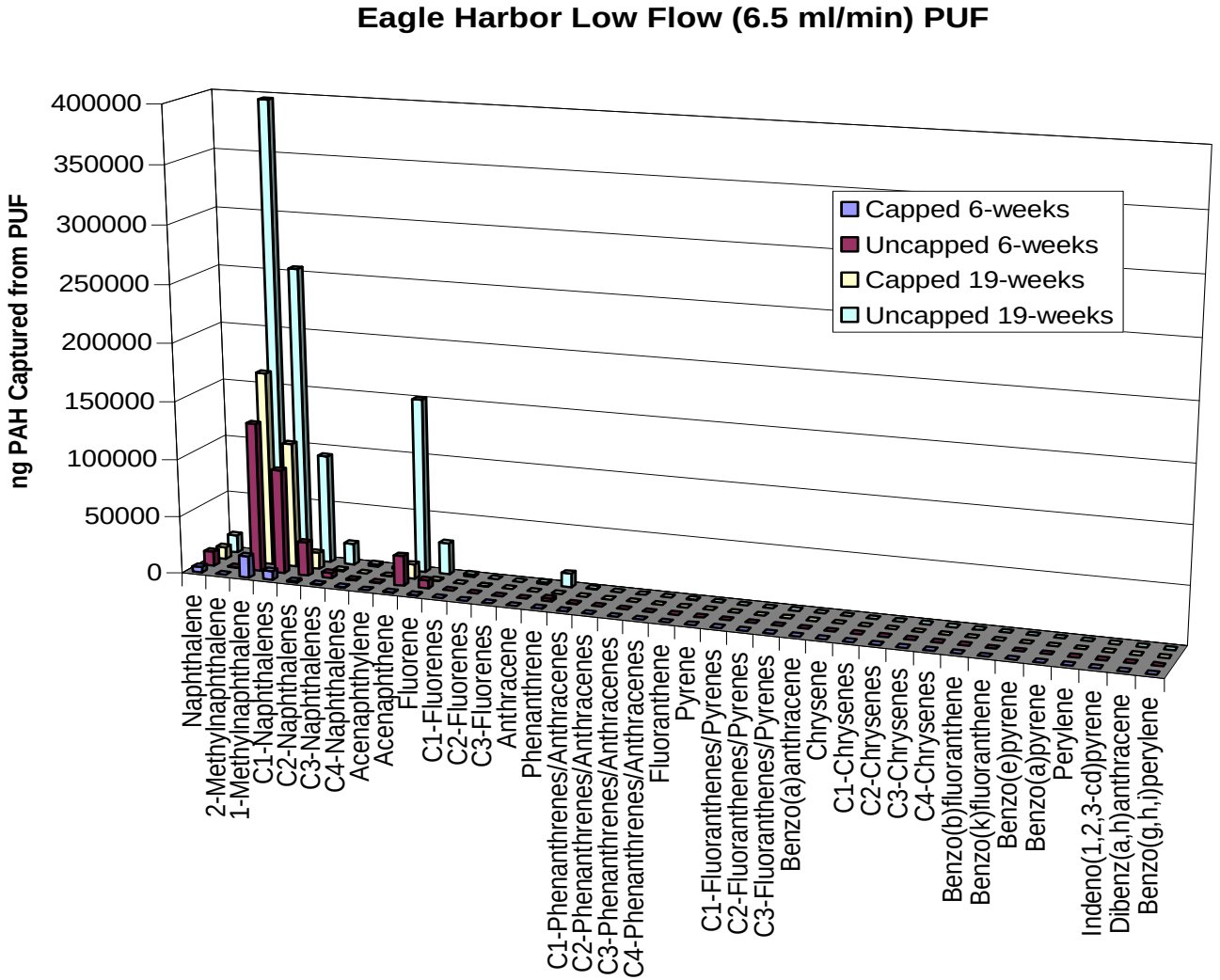


Figure 3-6. PAHs Recovered from the Eagle Harbor Sediment (with and without cap) after Low Flow Gas Sparging for 6-Weeks and 19-Weeks

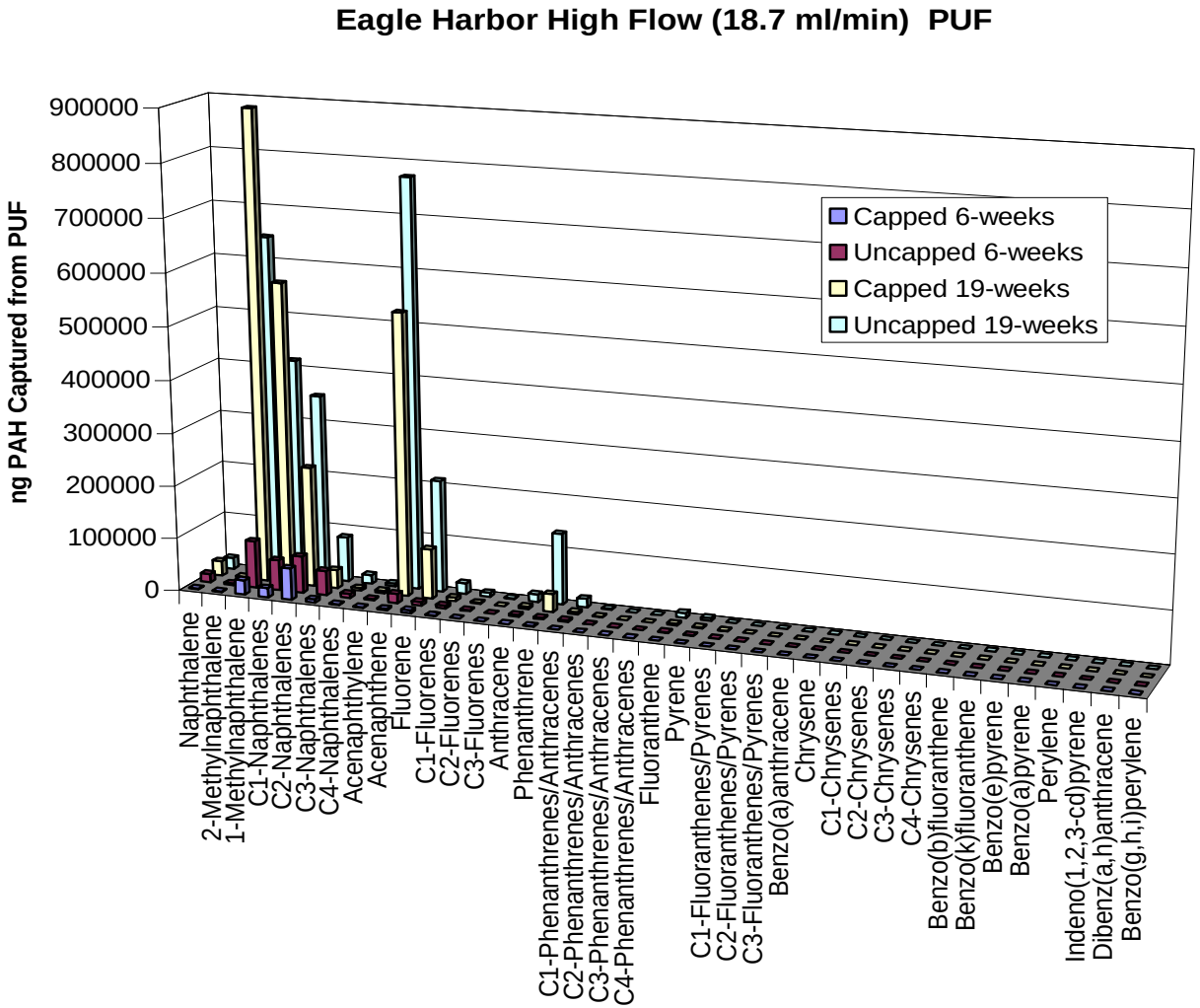


Figure 3-7. PAHs Recovered from the Eagle Harbor Sediment (with and without cap) after High Flow Gas Sparging for 6-weeks and 19-weeks

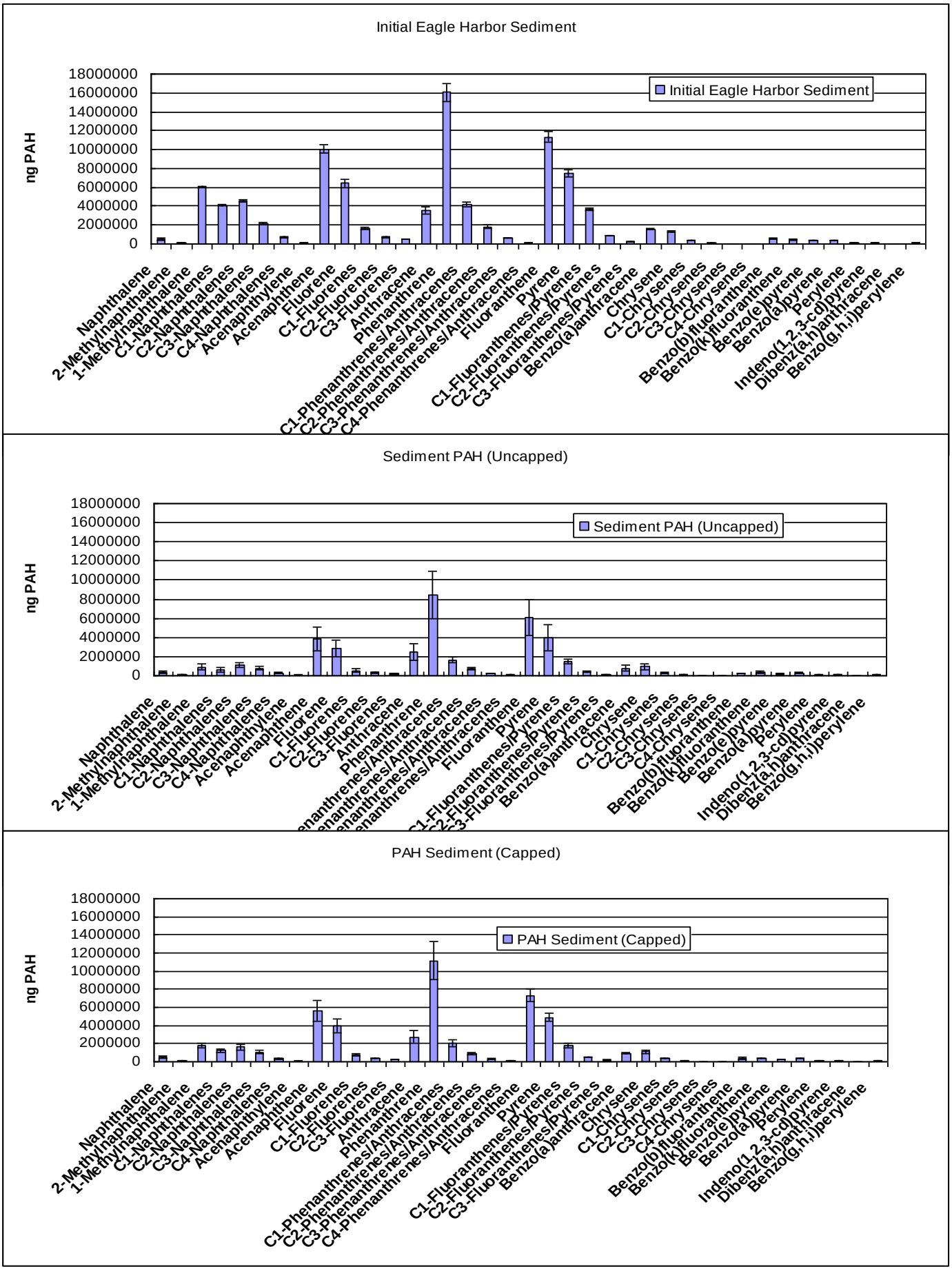


Figure 3-8. PAH Profiles of Eagle Harbor Initial, Uncapped and Capped Sediment (low flow)

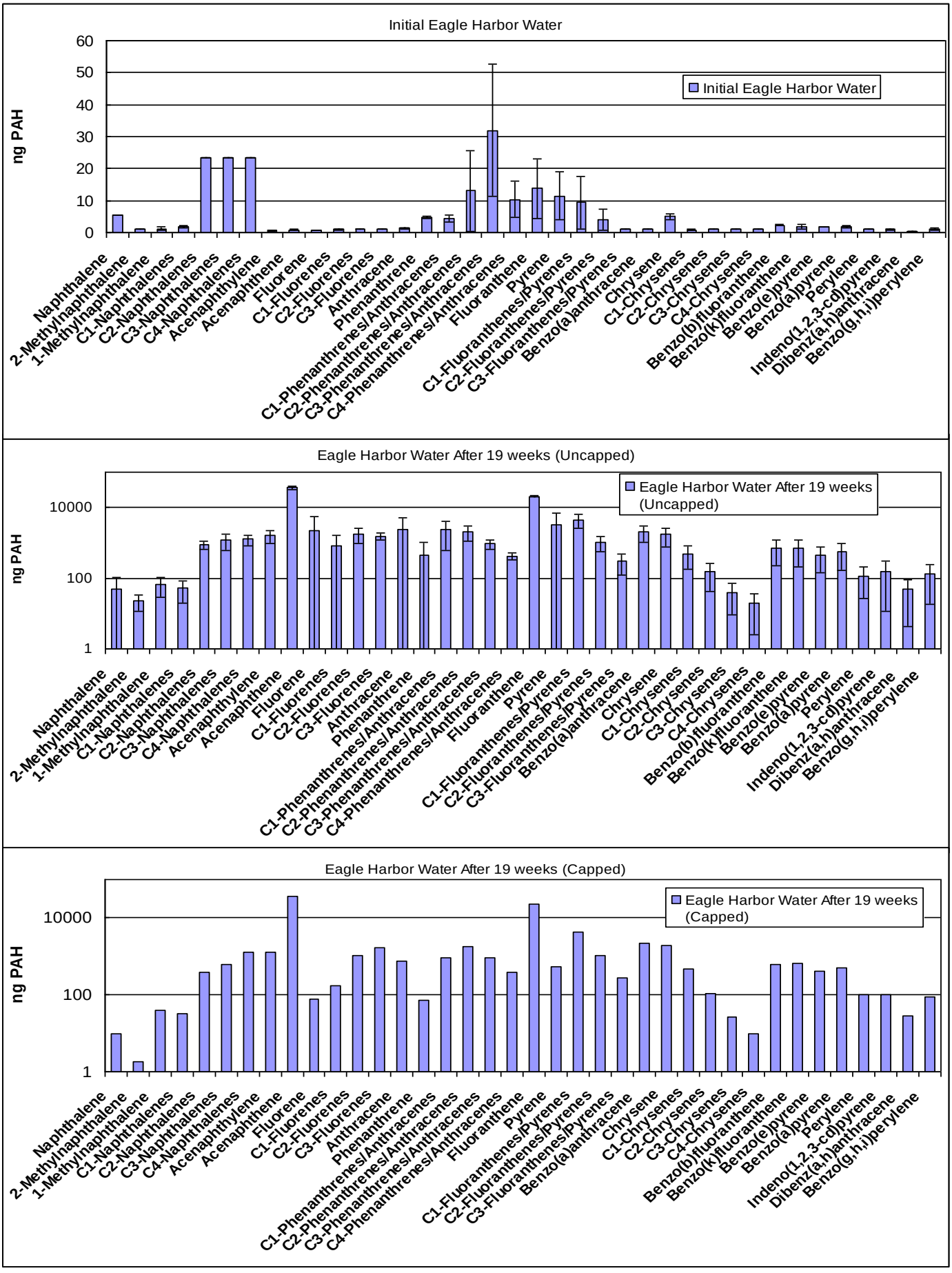


Figure 3-9. PAH Profiles of Eagle Harbor Initial, Uncapped and Capped Water (high flow) tPAH

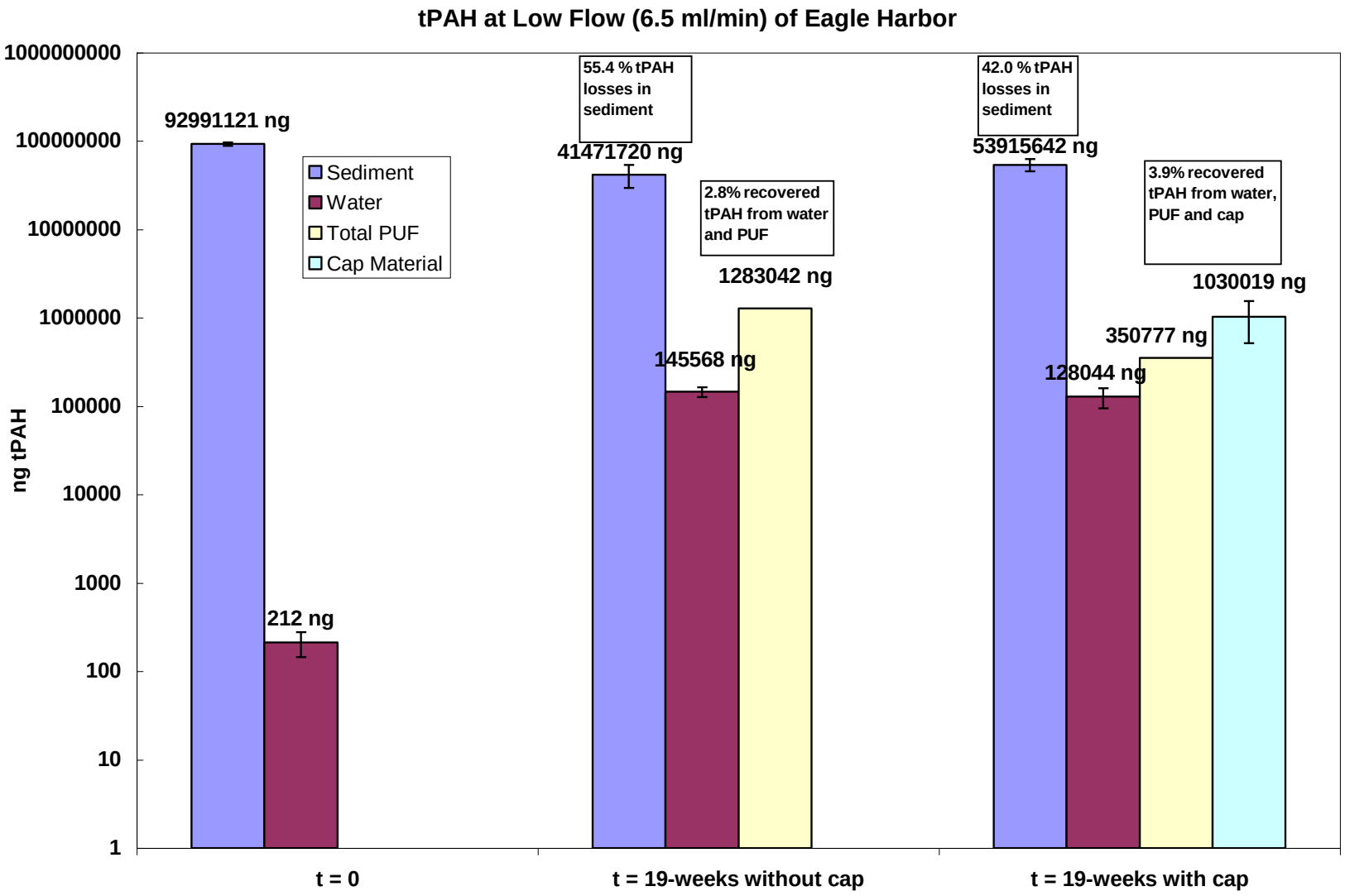


Figure 3-10. The Amount of tPAH in the Initial Sediment and Water and the Sediment, Water, Cap and PUF after 19-weeks for Low Flow Columns (6.5 ml/min)

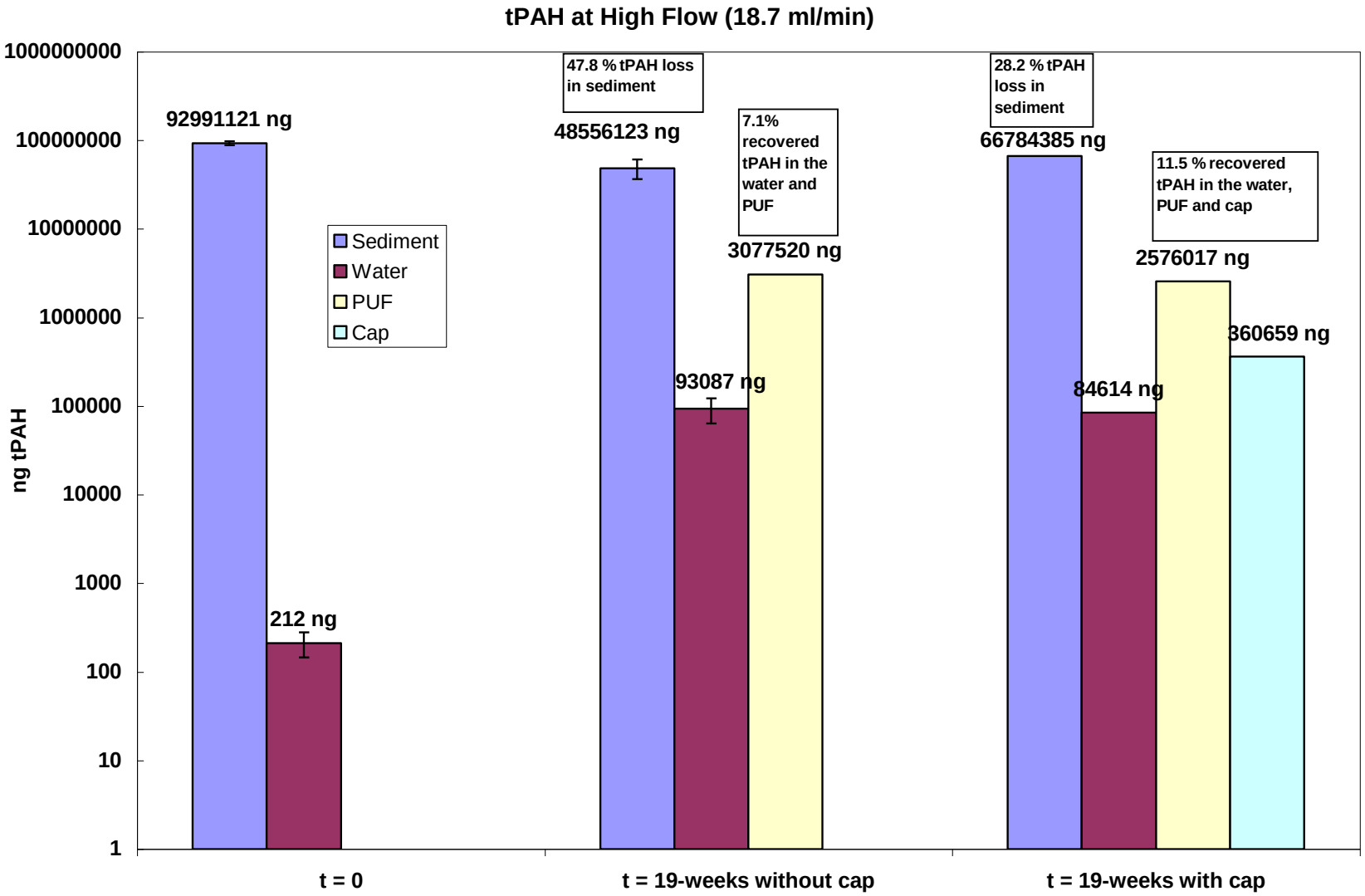


Figure 3-11. The Amount of PAH in the Initial Sediment and Water and the Sediment, Water, Cap and PUF After 19-weeks for High Flow Columns (18.7 ml/min)

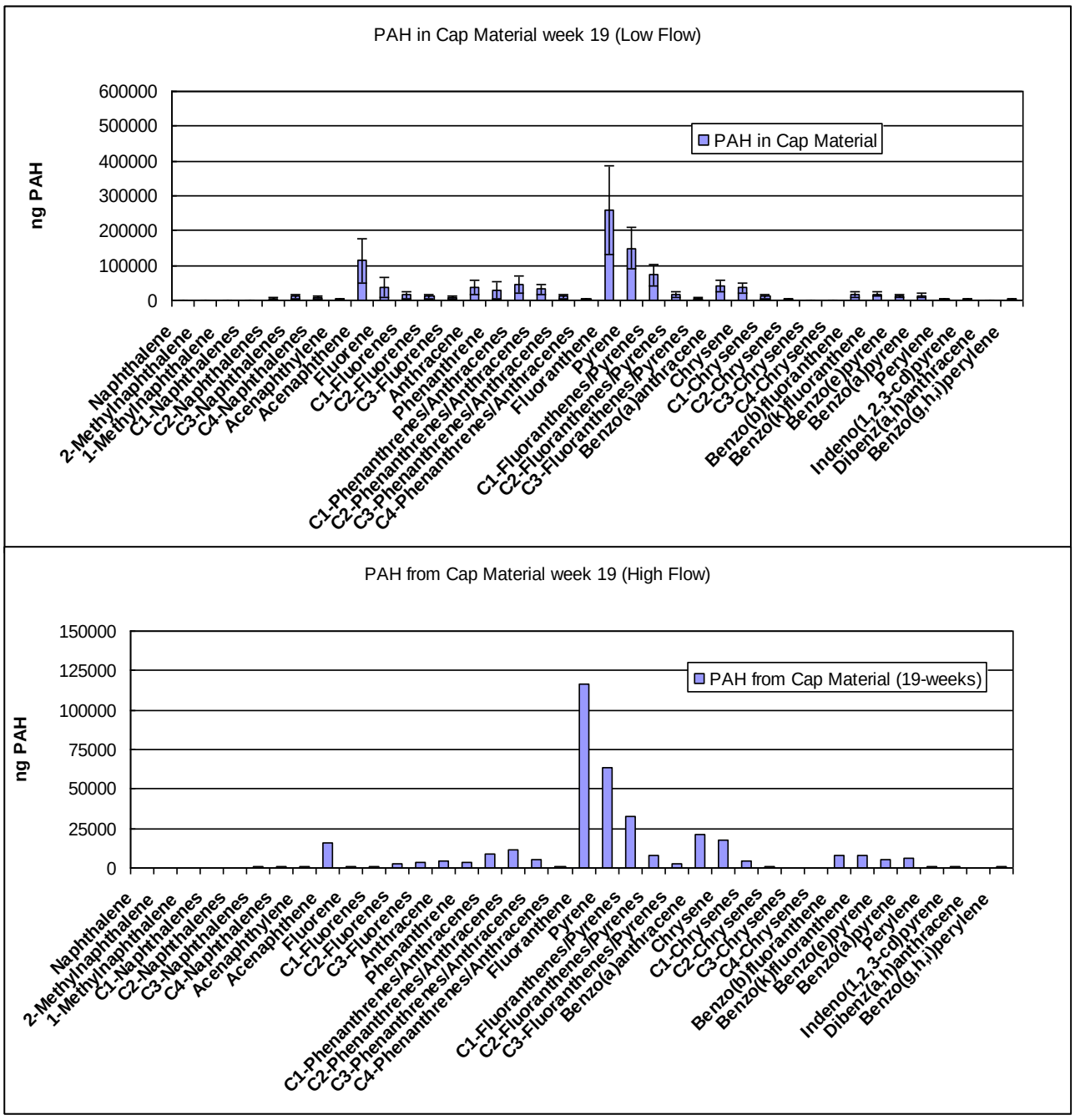


Figure 3-12. Eagle Harbor Cap Material at Low Flow 6.5 ml/min (upper graph) and High Flow

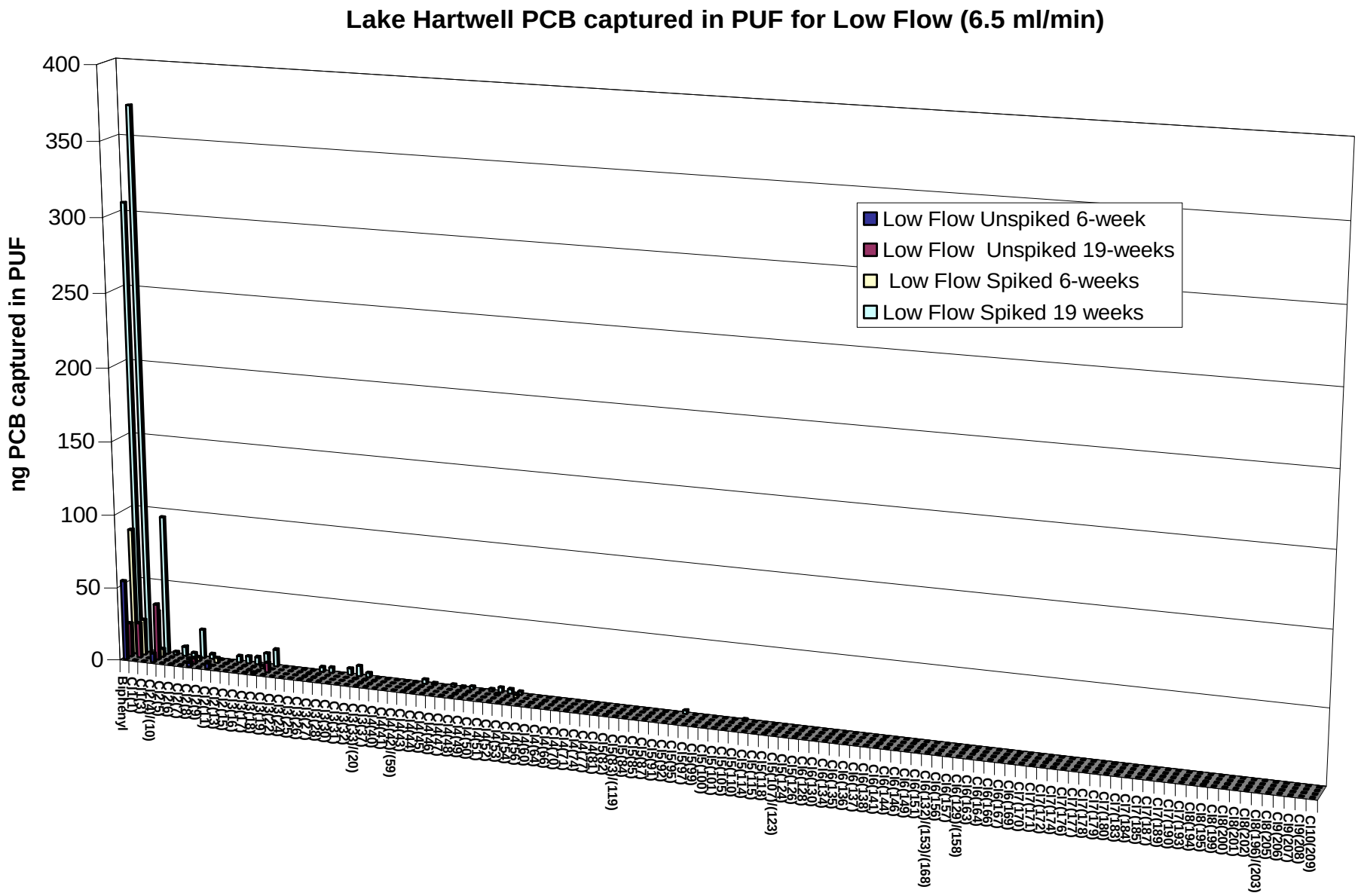


Figure 3-13. Comparison of PCBs at Low Flow (6.5 ml/min) for Spiked and Unspiked Lake Hartwell Sediment

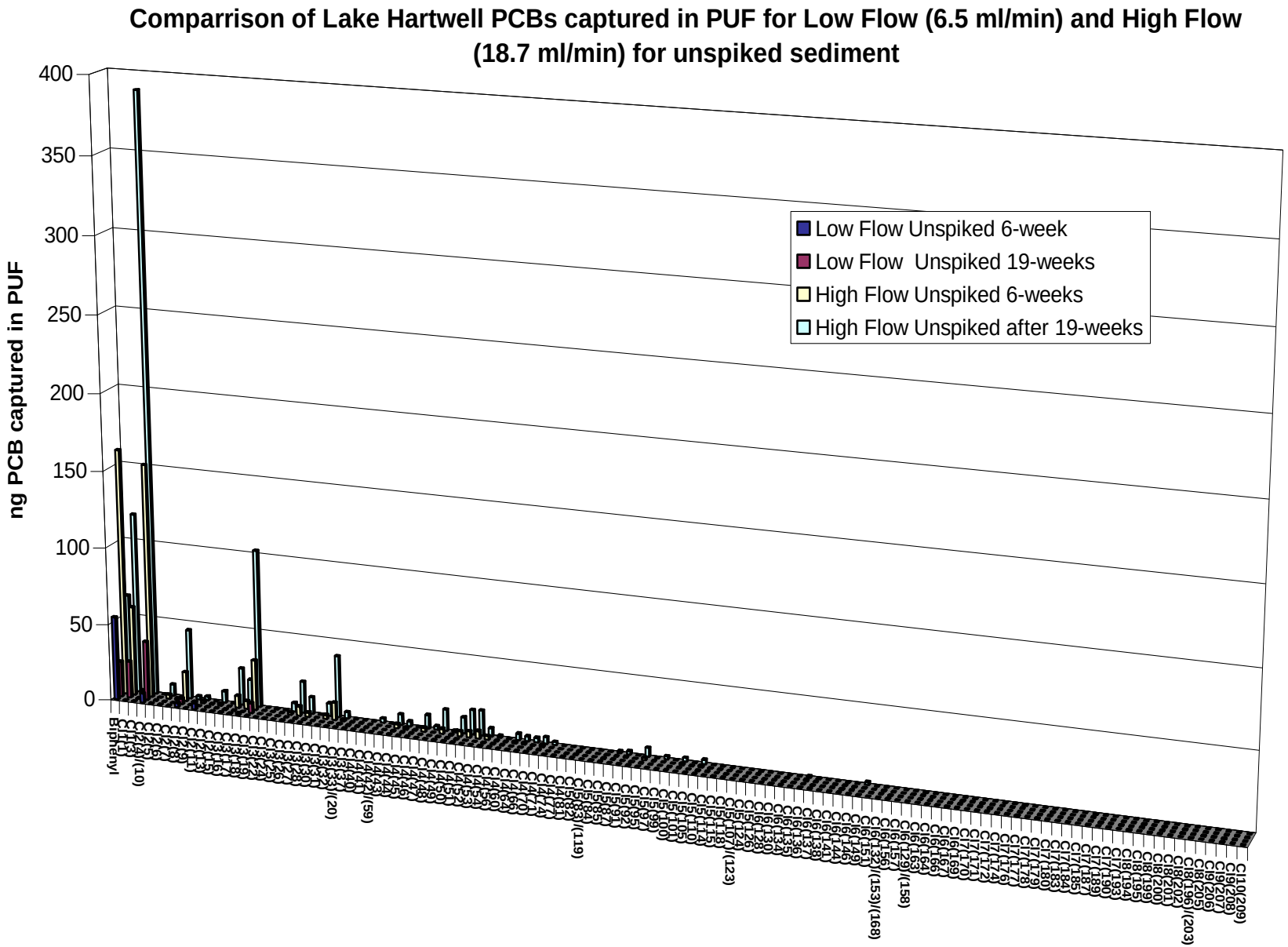


Figure 3-14. Comparison of PCBs at Low Flow (6.5 ml/min) and High Flow (18.7 ml/min) for Unspiked Lake Hartwell Sediment

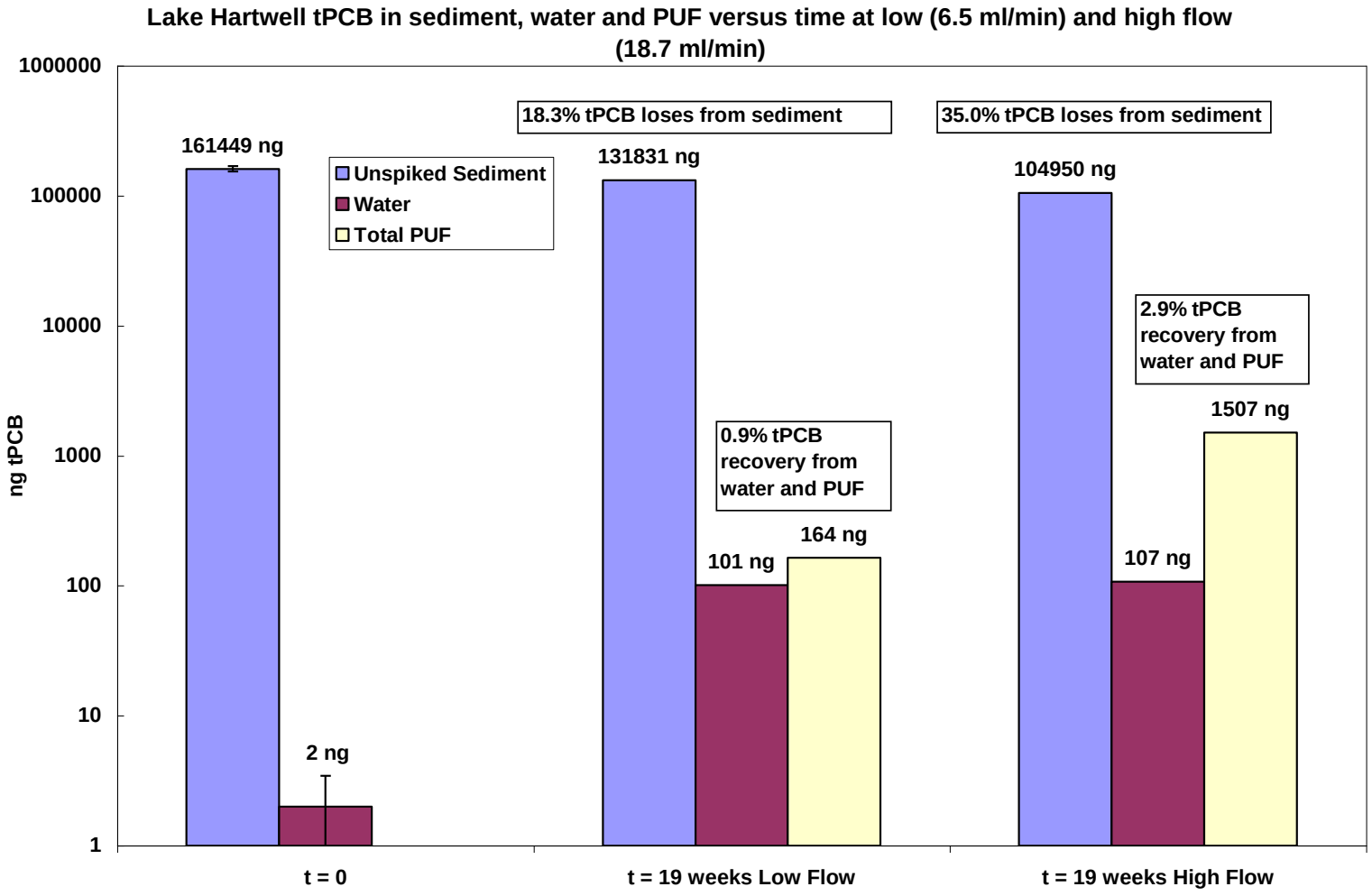


Figure 3-15. Lake Hartwell tPCB Comparison Initially and After 19-weeks for Unspiked Sediment at Low Flow (6.5 ml/min) and High Flow (18.7 ml/min)

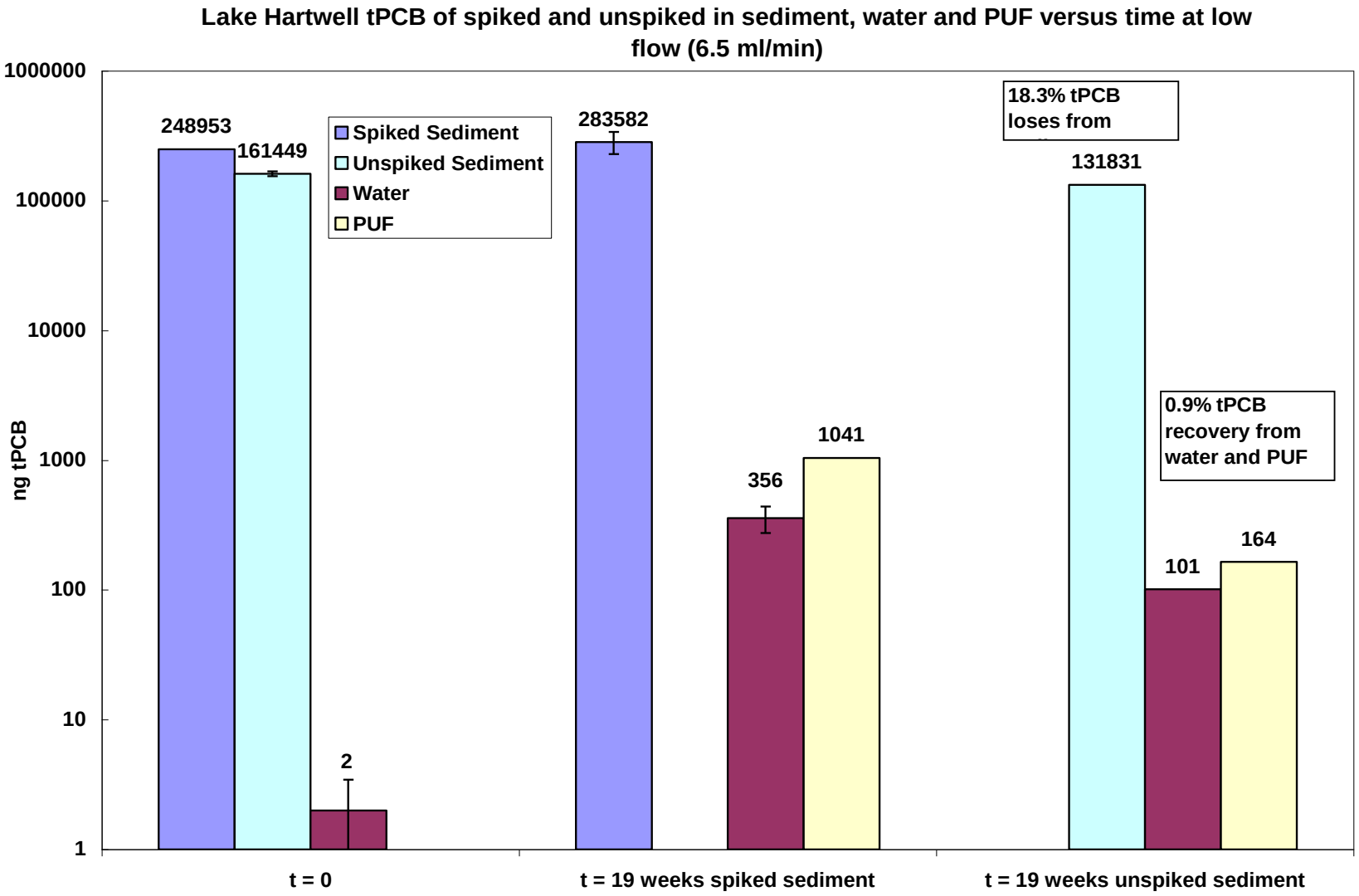


Figure 3-16. Lake Hartwell tPCB Comparison Initially and After 19-weeks for Spiked and Unspiked Sediment at Low Flow (6.5 ml/min)

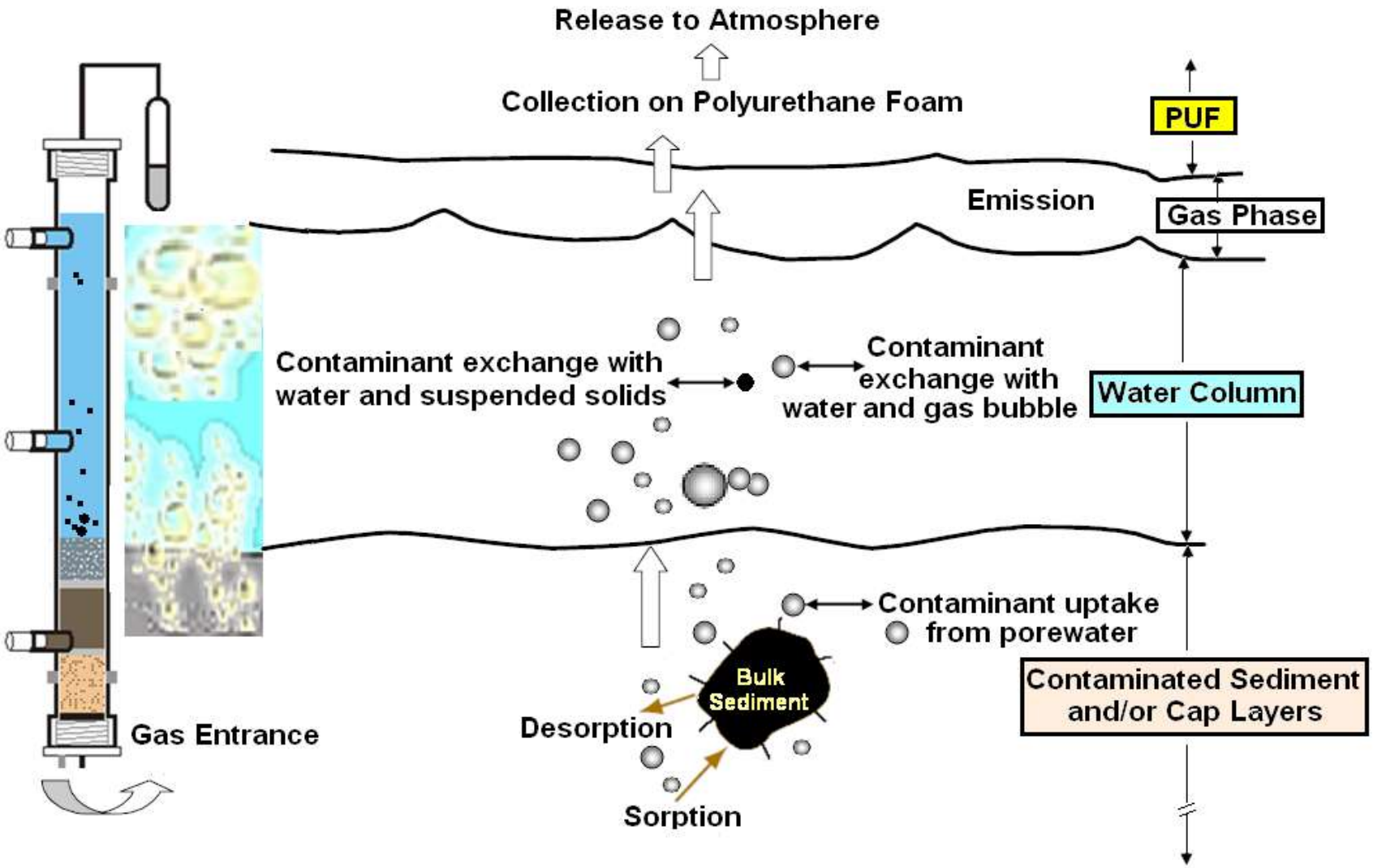


Figure 3-17. Conceptual Diagram of Gas Ebullition and Contaminant Migration through the Sediment-Water-Gas phases (Chattopadhyay, 2006)

Section 4.0 SUMMARY

The results of the microcosm experiments are summarized below.

- The pH of water in the serum bottles containing Eagle Harbor sediment varied between 7.3 and 8.3 and ORP of the same varied between -210 to -240 mV after 19 weeks of incubation. The killed control bottles had an oxidizing environment (ORP = 130 mV) more than the other bottles. The pH of the water in the serum bottles containing Lake Hartwell sediment varied between 6.4 and 6.9, and the ORP of the same varied between -25 mV and -110 mV. The killed control bottles maintained the reducing environment (negative ORP value) like the sample serum bottles containing Lake Hartwell sediment.

- Higher percentages of methane and carbon dioxide were present in the headspace of the Lake Hartwell serum bottles than the Eagle Harbor samples at 37 °C. No detectable level of gas (methane or carbon dioxide) was measured at lower temperatures (10 °C and 25 °C) for either sediments (Eagle Harbor or Lake Hartwell). Detectable amounts of gases were measured at all time intervals for both Eagle Harbor and Lake Hartwell sediments at 37 °C.

- The serum bottles containing sediment and water from Eagle Harbor and Lake Hartwell were incubated at 10°C, 25 °C (room temperature) and 37°C. These serum bottles were analyzed for 38-priority PAHs (Eagle Harbor samples) or PCBs (Lake Hartwell samples) after 90-days of incubation. Higher concentrations of PAHs (ng/g) were observed in the Eagle Harbor sediment as the temperature increased from 10 °C to 37 °C. This type of trend was observed from low and high molecular weight compounds of PAHs. An inverse relationship was observed in the case of the incubated Eagle Harbor water. The concentration of PAH (ng/L) in the water decreased from low temperature (10 °C) to higher temperature 37°C.

- The concentrations of PCBs (ng/g) in the serum bottles containing Lake Hartwell sediment with an incubation temperature of 10 °C were higher than those bottles incubated at 25 °C and 37 °C. However, the PCB concentrations in water (ng/L) increased as the incubation temperature increased from 10 °C to 37 °C. However, this trend was reversed for the higher molecular weight PCBs in sediment, where the concentration decreased from low to high temperature. The PCBs in the Lake Hartwell sediment partitioned into the water phase more strongly at a higher temperature than lower temperature.

The results of the simulated gas ebullition column experiments are summarized below.

Eagle Harbor

- The total amount (combination of 6 and 19 weeks) of tPAH captured by the PUFs connected to the uncapped Eagle Harbor columns at a low gas flow rate (6.5 mL/min) was 1283042 ng, which was significantly more than the capped column (350,077 ng). The uncapped PUFs also recovered higher molecular weight PAHs, which were not detected in the capped PUF. The uncapped Eagle Harbor sediment lost 55.4% of the tPAH after 19-weeks of gas sparging with respect to the tPAH concentration in the sediment inside the column prior to the gas sparging. The sediment from the column containing both sediment and cap material lost 42.0% tPAH. The water and PUFs recovered 2.8% of the tPAH losses from the sediment for the uncapped column. The water, cap material and PUF recovered 3.9% of the lost tPAH from the capped column.

- At high gas flow rates (18.7 mL/min), the PUFs captured 3077520 ng tPAH for the uncapped sediment column while the PUFs from the capped column captured 2576017 ng tPAH. After 19-weeks of gas sparging operation, the PUFs for the capped column sorbed lower molecular weight PAH compounds, such as 1-methylnaphthalene and C1-naphthalenes, than the uncapped column. However, the PUFs from the uncapped column sorbed higher molecular weight PAH compounds than the capped column. The Eagle Harbor sediment without a cap lost 47.8% of the tPAH after 19-weeks of gas sparging with respect to the tPAH concentration in the sediment inside the column prior to the gas sparging at a high flow rate. The sediment from the column containing both sediment and cap lost 28.2% tPAH. The water and PUF recovered 7.1% of the tPAH losses from the sediment for the uncapped column. The water, cap material and PUF recovered 11.5% of the lost tPAH from the capped column.

- The possible reasons for the loss of the tPAH losses from the Eagle Harbor sediment could be:

  - ❒ PAH losses from the sediment occurred as the columns were packed at the beginning of the gas ebullition tests and as they were unpacked at the end of the tests.
  - ❒ The binding of PAHs on the PUF Tenex material may not be strong enough to prevent any volatilization losses. During the continuous operation of the columns under the ventilated hood, a portion of the PAH that sorbed on the PUFs could have volatilized.
  - ❒ The residence time of the PAH vapor through the PUF may not have been sufficient to achieve high sorption capacity.
  - ❒ A portion of the PAHs could have adhered to the stainless steel piping and the tygon tubing at the top of the column before entering the PUF.
  - ❒ The carbon dioxide and methane gas could have stripped sorbed PAHs onto the Tenex material as it traversed through the PUFs.

- The Eagle Harbor sediment (initial, uncapped and capped) and water (initial, uncapped and capped) have a similar distribution of PAH compounds. Though the magnitudes of the PAH concentrations were different, the pattern was consistent.

- The cap material sorbed more PAH at the lower gas ebullition rate. At high flow (18.7 ml/min), the cap material sorbed 360659 ng tPAH and at low flow (6.5 mL/min), the cap material sorbed 1030019 ng (i.e., 2.9 times more sorption).

Lake Hartwell

- The PUFs at the outlet of the columns containing Lake Hartwell spiked and unspiked sediment captured 1041 ng and 164 ng of tPCB, respectively, at low gas flow conditions. The PUFs were also captured at higher molecular weight PCBs (such as Cl5(110)) from the PCB spiked sediment.

- During high gas sparging, the PUFs sorbed 1507 ng from columns that were packed with unspiked Lake Hartwell sediment in comparison to the low flow columns which sorbed 164 ng. The transfer of PCBs from the sediment to the water column and thereafter to the air appeared to be more dependent on the sparging flow rate than the concentration of PCB in the sediment. Higher concentrations of PCBs (hydrophobic) could be sorbed in the sediment with a low risk of escape as long as the gas ebullition rate was low. Higher gas sparging also resulted in the release of higher molecular weight PCBs. For example, the PUFs detected Cl6 (149) at 18.5 mL/min for

unspiked Lake Hartwell sediment, whereas C13 (19) was the highest molecular weight compound detected at low flow.

- The sediment in the columns under low gas flow conditions lost 18.3% tPCB with respect to the tPCBs concentration in the unspiked Lake Hartwell sediment contained inside the column prior to the gas sparging at a high flow rate. The water and PUF recovered 0.9% of the lost tPCB. At high gas flow condition, the unspiked sediment lost 35.0% tPCB. The water and PUF recovered 2.9% of the lost PCB. The higher gas sparging flow rate resulted in higher transfer of PCBs from the sediment surfaces.

Section 5.0 REFERENCES

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