FINAL REPORT

Characterization of Contaminant Migration Potential Through In-Place Sediment Caps

SERDP Project ER-1370

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ACRONYMS AND ABBREVIATIONS

ASTM	American Society of Testing and Materials
COC	contaminant of concern
CWA	Clean Water Act
DoD	Department of Defense
ELISA	Enzyme-Linked ImmunoSorbent Assay
EPC	electronic pressure controlled
ESB	equilibrium partitioning sediment benchmarks
GC/FID	gas chromatograph/flame ionization detector
GC/MS	gas chromatograph/mass spectrometer
GPS	global positioning system
ID	inner diameter
IS	internal standard
MSD	mass selective detector
NPL	National Priorities List
PAH	polycyclic aromatic hydrocarbon
PCB	polychlorinated biphenyl
ppm	parts per million
PSD	particle size distribution
rpm	rotations per minute
RSC	rapid screening characterization
SERDP	Strategic Environmental Research and Development Program
SIM	selective ion mode
SOP	standard operating procedure
SPAWAR	Space and Naval Warfare Systems Center (San Diego, CA)
SPME	solid phase microextraction
TOC	total organic carbon
t-PAH	total polycyclic aromatic hydrocarbon
TPH	total petroleum hydrocarbons
UMBC	University of Maryland, Baltimore Campus
USACE	United States Army Corps of Engineers
U.S. EPA	United States Environmental Protection Agency

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EXECUTIVE SUMMARY

Field efforts were conducted at Eagle Harbor in June 2006. The efforts focused primarily on understanding potential freshwater upwelling within and around the cap boundary; understanding the potential contaminant migration through the sand cap by collecting and analyzing sediment cores; and evaluating the effectiveness of rapid screening approaches in the field to develop real-time data for field decision purposes and ultimately accurate and less expensive approaches to total polycyclic aromatic hydrocarbon (t-PAH) analysis. Additionally, sediment and cap materials were collected and shipped to the University of Maryland, Baltimore County (UMBC) for polycyclic aromatic hydrocarbon (PAH) and particle size characterization and to develop column transport experiments.

Freshwater upwelling at the site was investigated using underwater divers who recorded conductivity measurements. The conductivity survey verified the presence of freshwater in the intertidal region, but further investigation is necessary to quantify the extent to which upwelling occurs since this study focused on the capped area and the intertidal region is adjacent to the cap. In-field observations made by the research staff that indicated freshwater permeation on the beach at low tide further verified the presence of freshwater in this region.

A total of 13 cores were collected during this initial investigation and all cores were sectioned and processed into segments that started from approximately 55 cm below the sediment-cap interface to the cap surface (cap-water interface). All segments were analyzed using in-field rapid screening analysis (RSC) techniques, which were later confirmed with gas chromatograph/mass spectrometer (GC/MS) analysis for select core segments. There appeared to be some migration pattern or mixing of PAH-contaminated sediments within the cap profile and some indication that there may be other anthropogenic sources contributing to the t-PAH concentration on the cap surface. While potential migration patterns may exist, additional laboratory analyses may provide valuable insight into the mechanisms by which PAH translocation in the cap profile is taking place. The collective results of particle size distribution analyses of select core segments, particle specific sorption isotherm studies, and laboratory column transport experiments have improved the understanding of the sedimentary translocation of PAH contaminants.

1.0 OBJECTIVE

By isolating contaminated sediments from overlying bodies of water, capping can effectively reduce ecosystem exposure to contaminants and minimize the possibility of contaminant transport into the food chain (Magar, 2001; Palermo et al., 1998; USACE, 1998). However, because contaminated sediments are left in place, caps generally require long-term monitoring, and the risks of contaminant transport or sediment resuspension persist. Many contaminated marine sediment sites reside in shallow, coastal areas that are often impacted by advective processes (i.e., groundwater flow, tidal pumping, and wave pumping), sorption controlled diffusive processes, and bioturbation. These forces contribute to the flux of contaminants through sediments and, ultimately, through a sediment cap. A theoretical foundation for contaminant transport through surface sediments exists (Medine and McCutcheon, 1989), but remains untested for sediment caps exposed to advective forces. The scientific and engineering principles of capping need to be improved by testing and validating this theoretical foundation, and by establishing design criteria that account for processes governing vertical contaminant migration through sediment caps.

The overall objective of this project is to enhance the scientific understanding of contaminant migration through sediment caps in areas with significant groundwater potential or tidal fluctuations. Specific objectives include the following:

(1) Examine contaminant mobility over time through an existing sediment cap;

(2) Measure the influence of porewater flux via groundwater advection and tidal pumping;

(3) Quantify aqueous contaminant mobility in the laboratory;

(4) Evaluate the fundamental mechanisms contributing to polycyclic aromatic hydrocarbon (PAH) sorption and retention in the laboratory.

To obtain the data necessary to meet the specific objectives listed above, a combination of field and laboratory studies were designed and implemented to examine the fate and transport of hydrophobic contaminants at a sediment-capped site. The information expected to be gained from these studies will build on current knowledge of contaminant transport phenomena and provide insight into the hydraulic and chemical mechanisms affecting migration of contaminants at capped sites.

This final report presents the results from activities conducted to date at the Wyckoff/Eagle Harbor Superfund Site in Bainbridge Island, Washington (referred hereinafter as the “Wyckoff/Eagle Harbor Site” or the “Eagle Harbor Site” or the “Site”). The Eagle Harbor Site is operated by the U.S. Environmental Protection Agency (U.S. EPA) in coordination with the U.S. Army Corps of Engineers (USACE), Seattle District. The contaminant of concern (COC) at the Eagle Harbor Site is PAH compounds due to historic use of creosote for wood preservation activities at this site. The potential for vertical migration of contaminants exists at

the Eagle Harbor Site because of a steep hydraulic gradient in the underlying groundwater aquifer and because of the potential for large tidal fluctuations, approximately 10 feet.

2.0 BACKGROUND

Due to potentially negative impacts of contaminated sediments on aquatic environments and food resources, there is an urgent need to understand how the fate and transport of toxic substances in contaminated sediments is governed by the aforementioned forces of advection, sorption and bioturbation. This work aims to improve the understanding of the fate and transport of persistent organic contaminants under a sediment cap that has been in place since 2000-2001.

2.1 Site History

The former Wyckoff wood-treatment facility operated on Eagle Harbor from the early 1900s until its closure in 1987. During its operation, large quantities of creosote were used, resulting in PAH contamination of Eagle Harbor sediments. Eagle Harbor is a shallow marine embayment of Bainbridge Island, Washington. The island is located approximately 10 miles due west of Seattle, Washington. The Wyckoff/Eagle Harbor Site was placed on the National Priorities List (NPL) in 1987 as a Superfund site. PAH sediment contamination originating from creosote use at the wood treatment facility has been extensively characterized (Stout et al., 2001; Brenner et al., 2002). Furthermore, a passenger/car ferry operation with service between Bainbridge Island and Seattle has been in existence for more than 50 years on the west side of Eagle Harbor. The presence of a passenger/car ferry introduces an additional non-point source of PAHs into the site.

The site has been capped to control PAH migration into the water column and surrounding sediments (Figure 2-1). This site was capped in 1993-1994 with approximately 275,000 yds^3 of dredge material, ultimately covering approximately 52 acres, with an average cap thickness of 3 ft. This cap was placed in an effort to prevent contaminants within the sediments from migrating within the harbor and also to protect sensitive ecological systems. Due to a lack of source-control, the 1993-1994 cap did not cover the sediments proximal to the Wyckoff facility. This area was later capped between November 2000 and February 2001.

The Wyckoff/Eagle Harbor Site was selected for this study for the following reasons:

- The site employed a conventional sediment cap, which is the most universally applied cap type.
- The site was contaminated with PAHs, which are ideal hydrophobic contaminants for study. Results based on the hydrophobic properties of PAHs can be extrapolated to other hydrophobic contaminants of concern, such as polychlorinated biphenyls (PCBs).
- The site is known to have groundwater advective flows and high tides. Virtually all sites have an advective component and those in areas of high tides are likely to be tidally influenced.

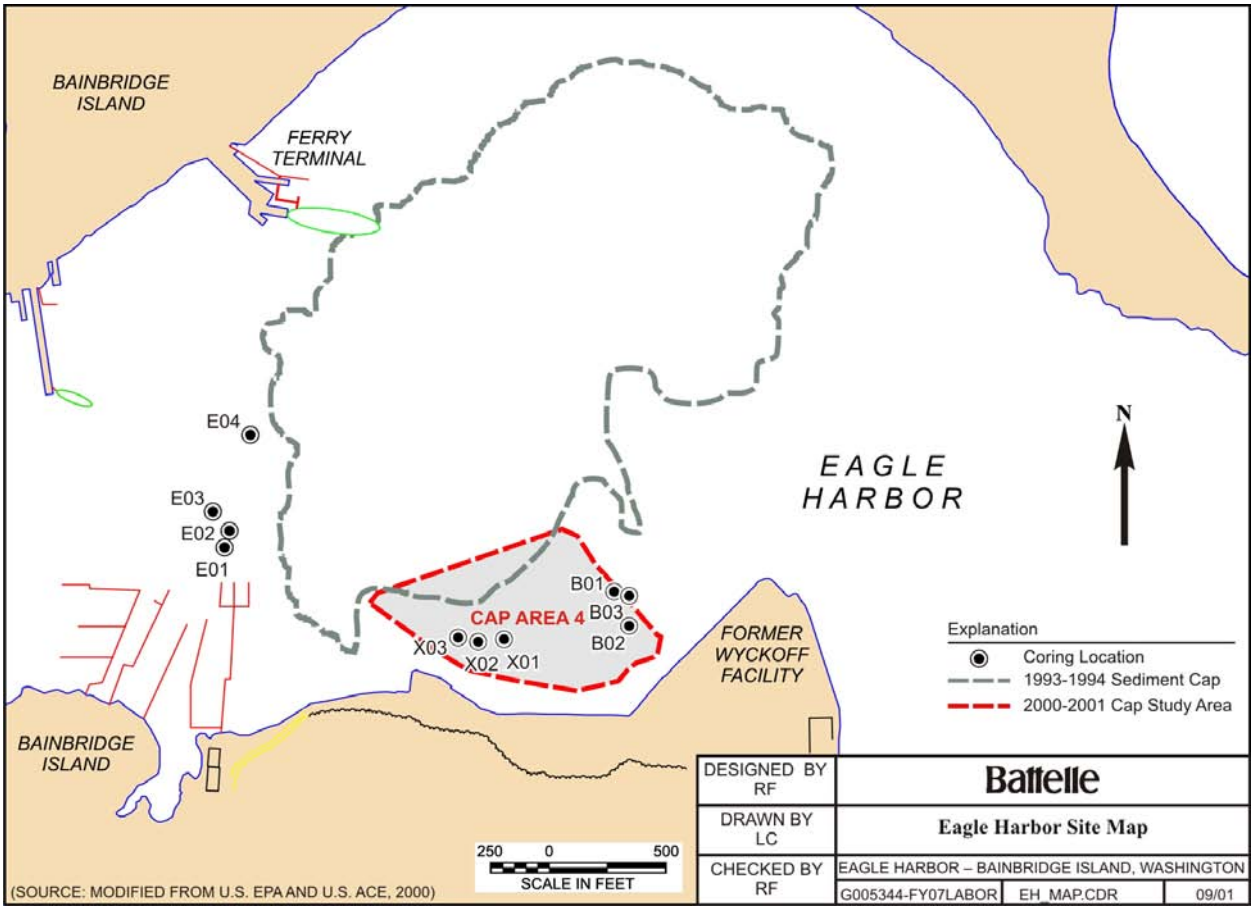

Figure 2-1. Eagle Harbor Original Cap Placement (1993-1994) Shown Relative to the Present Area of Study

2.2 Technical Approach

The field component of the research was designed to measure in situ hydrodynamic forces via freshwater upwelling in the cap area, and contaminant migration in the buried sediment and the in-place cap. A plan to measure contaminant transport phenomena by collecting sediment cores and analyzing the sediments for the COC, using rapid screening characterization (RSC) tools and gas chromatography/mass spectroscopy (GC/MS) techniques, was included in the approach. Also included in the original design was a plan to measure hydrodynamic forces using vertically-aligned piezometers at varied sediment depths; however, this component of the original work plan was not undertaken.

The laboratory study design included column testing and particle-scale analyses to evaluate the fundamental mechanisms contributing to and controlling contaminant sorption and retention in sediments and in the sediment cap material. The columns were designed to simulate and accelerate field conditions using contaminated and clean sediment and cap materials, respectively, from the site. The particle-scale analytical methods include those developed for PAHs and PCBs for other SERDP projects by members of this research team.

The tasks accomplished at the Wyckoff/Eagle Harbor site in 2006 are summarized herein and discussed in more detail in the following sections.

- **Task 1** consisted of electrical resistivity measurements that were collected at varying depths in the sediment cap and were used to identify areas where fresh groundwater may be entering the marine environment (freshening).

- **Task 2** consisted of cap and sediment coring activities. Thirteen continuous cores were collected using a vibracoring technique in areas where freshening was measured and where no freshening occurred.

- **Task 3** consisted of sectioning the core samples in centimeter-thick segments and conducting a PAH profile by depth using an in-field rapid screening technique called Enzyme-Linked ImmunoSorbent Assay (ELISA).

- **Task 4** consisted of conducting GC/MS analyses on specific core segments of interest as identified using ELISA in Task 3.

- **Task 5** was conducted at the University of Maryland Baltimore County (UMBC) using sediment collected from the Eagle Harbor Site. At UMBC, laboratory scale columns were constructed to simulate the vertical flux of contaminants. Solid phase microextraction (SPME) was used to measure low PAH concentrations in milliliter-size samples.

3.0 MATERIALS AND METHODS

3.1 Field Studies

Field activities for this investigation were previously described in a site-specific work plan that was prepared prior to the commencement of work in the field (Battelle, 2006; included as Appendix A of this report)). Of these activities, Tasks 1 through 4 were conducted in 2006 as previously described in Section 2.1, with the exception of the piezometer study.

Data from the field conductivity survey, combined with on-site and off-site physical and chemical characterization of the existing sediment cap and native sediment material, were used to determine the potential for vertical PAH migration in the sediment cap, and the relative influences of groundwater upwelling and tidal fluctuations on contaminant transport. The following sections describe in detail the field methods that were used to conduct the preliminary portion of this investigation.

3.1.1 Field Conductivity Survey. In 2006, a field conductivity survey was conducted immediately prior to coring activities to supplement the data that were collected in May 2005 and to identify locations where cores would be collected during the June 2006 field sampling event. The May 2005 data were plotted using EarthVision® software and were used to identify areas of potential upwelling. Figure 3-1 shows the 2005 plot with upwelling within the cap boundary. These data were used to design the sampling grid for the June 2006 activities.

In 2006, a similar survey strategy was designed and implemented. The objective of the survey was to map the conductivity of a broad area of the cap and to identify locations of measurable groundwater upwelling and locations of minimal or no groundwater upwelling. The results of these measurements were also plotted using global positioning system (GPS) and EarthVision® software to allow a three-dimensional determination of conductivity across the cap. To the extent possible, the field conductivity survey was conducted during low-tide periods to optimize the potential to detect groundwater upwelling. The field conductivity survey was conducted as follows.

Deployment of Electrical Conductivity Probes

Divers were deployed along two of the three transect lines that were pre-established in the work plan. Electrical conductivity transects 1 and 3 (ECT1 and ECT3) are shown in Figure 3-2. Figure 3-2 shows the coordinates that were anticipated for use in the June 2006 survey and defines the transect locations overlain with grid lines on even 50 foot increments (shown in state plane WA North NAD 83). ECT1 and ECT3 extended from the shore (from the west beach) northward and were approximately 160 m long beginning at the -10 foot reference to mean sea level contour line.

Divers were deployed at 10 m increments along ECT1 and ECT3. They inserted a probe into the sediment cap that was incrementally driven into the sand cap using a hand sledgehammer. Electrical conductivity measurements were recorded in the water column

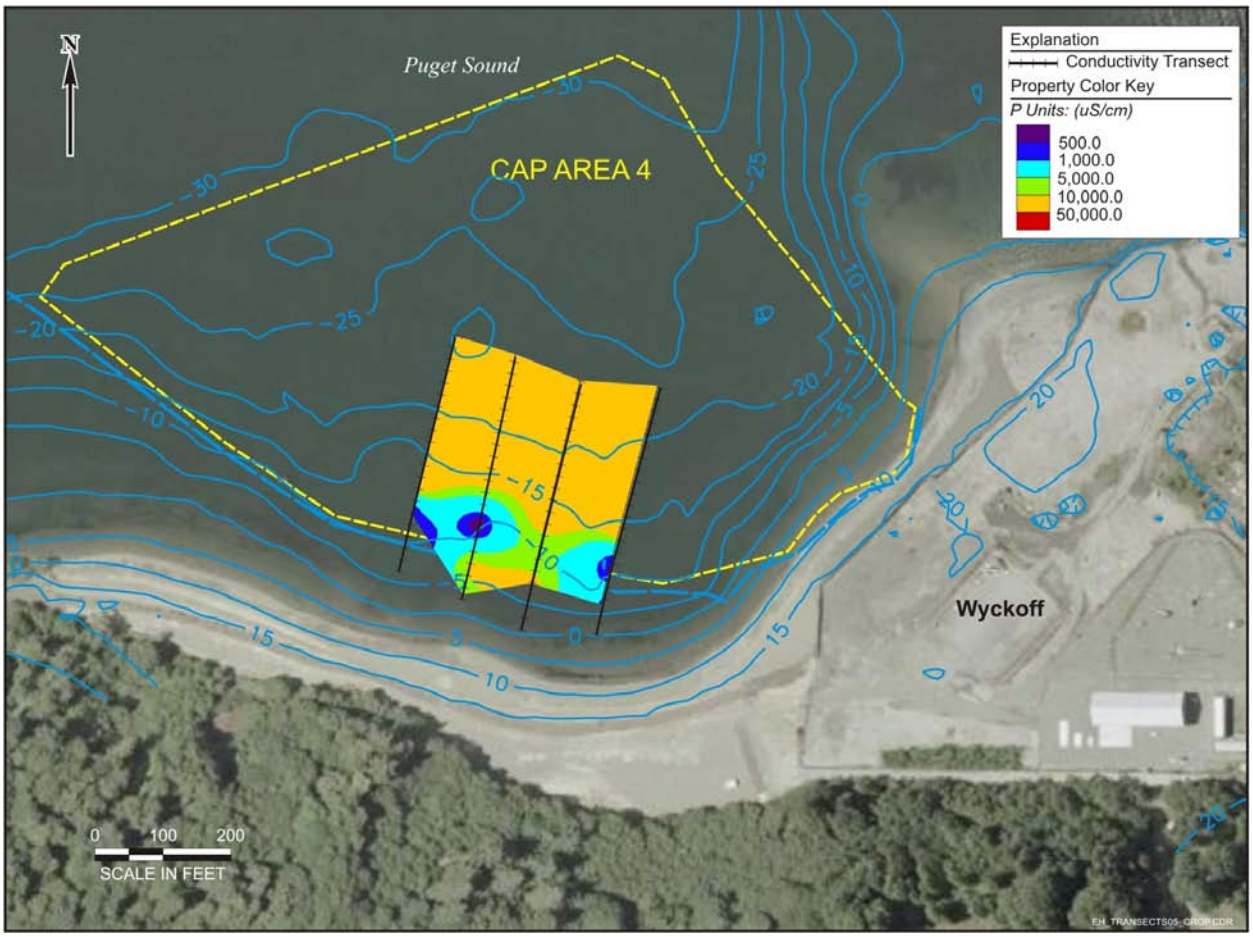

Figure 3-1. May 2005 Conductivity Survey Conducted at Eagle Harbor Shown Relative to the Cap Placement

approximately 2 m above the sediment cap and in the sand cap at 10 cm depth increments, starting at a depth of 10 cm and ending at a depth of ~100 cm or as far as the divers could reasonably penetrate the sediment cap and still retrieve the probe. Once the probe had reached the 100 cm depth or refusal, the probe was removed by hand and moved to the next grid position.

After determining an area of potential upwelling based on real-time analysis of the conductivity data, the divers advanced laterally away from the transect line to further delineate the areal extent of freshening. Additional conductivity measurements were made in the shallower regions by extending the length of the conductivity probe so that it could be manually deployed from onboard the research vessel. The need for more or less spatial resolution was determined in the field. Additional areas were surveyed based on the results obtained in the field.

Figure 3-3 shows a schematic of the conductivity probe and ancillary equipment used in the field for the survey. The device used to measure conductivity was a modified resistivity probe originally designed by Geoprobe (Manhattan, KS). The probe consisted of a conductivity

array (SC-300) connected to two segments of drive rod and a drive/pull cap. The probe was instrumented via cabling to a control box and a laptop computer at the water surface.

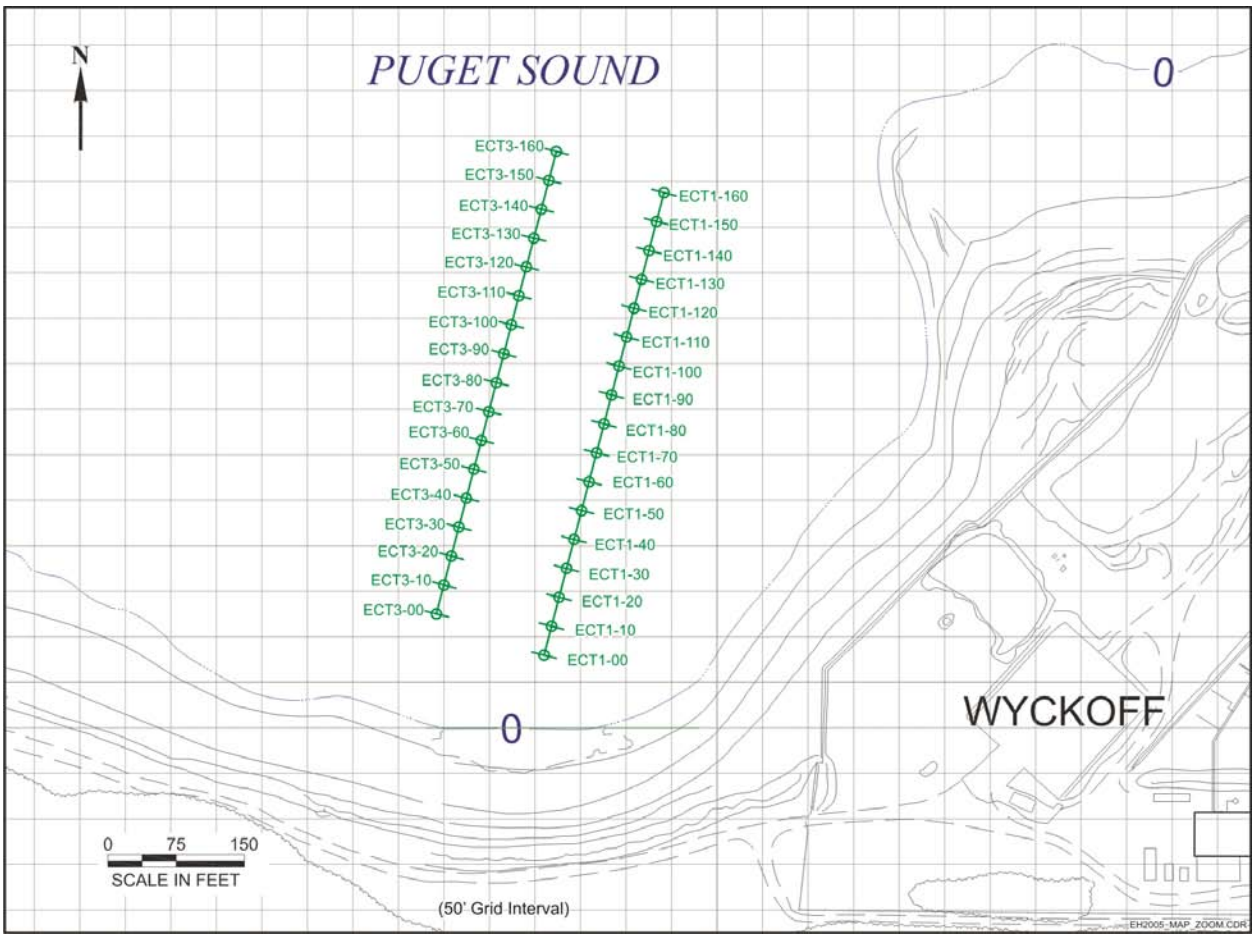

Figure 3-2. Field-Ready Map for June 2006 Conductivity Survey

3.1.2 Sediment Coring. The data collected from the conductivity survey were reviewed in the field and were used to identify areas of potential upwelling and core collection. Coring activities commenced using a contracted vessel with vibracoring capabilities (Figure 3-4). Cores of a 3-inch diameter were collected using thick-walled aluminum sleeves.

Core Layout

A total of 13 cores were collected to characterize the sediment cap and native sediments within and outside of the groundwater upwelling areas. Since the greatest interest was within the cap-sediment interface, the core depth was targeted for full penetration of the sand cap (~3 ft or 90 cm) plus an additional 1 to 3 ft (30 to 90 cm) of native sediment. Cores that did not meet these depth criteria were rejected.

Core Transport to an On-site Staging Area

Cores were sectioned into 5-foot sections on board the coring vessel and then transferred onto another boat that transported the core sections to the beach. The core sections were off-loaded from the transport vessel and either hand carried or transported in the bed of a pickup truck to an on-site staging area, where they were logged and processed (Figure 3-5). Through the transporting process, each core section was maintained in vertical position (respective to bottom and top of core).

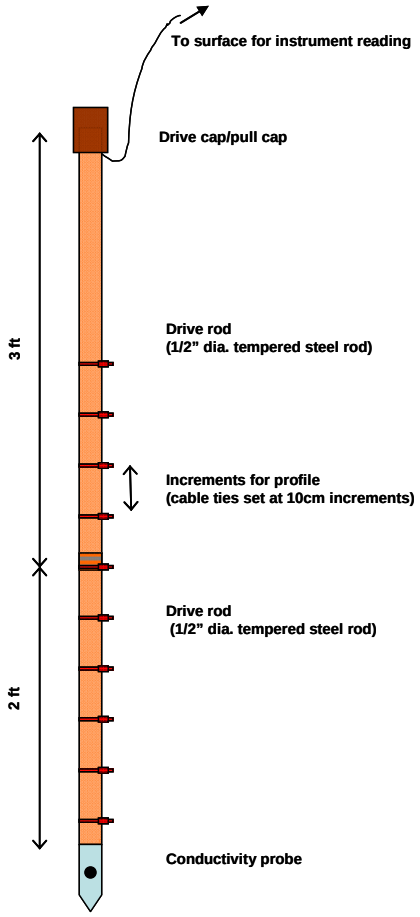

Figure 3-3. Detail of the Conductivity Probe Showing the 10 cm Increment Markings

Core Processing

Each core was analyzed on-site for porewater conductivity by tapping an intact vertical core with a drill to capture porewater before processing the core for total polycyclic aromatic hydrocarbon (t-PAH) analyses. In the vertical position, a series of small holes were drilled into the core tube starting at the top immediately above the sediment water interface and progressively downward until reaching the native sediment material. The electrical resistivity of the core porewater was measured on-site using a calibrated conductivity meter.

After porewater samples were collected, each core was placed horizontally onto a specialized rack equipped with a saw guide (Figure 3-6). The tube of the core was cut with a circular saw equipped with a collection system for capturing aluminum fines. The tube was cut on one side and then turned over to advance the saw such that the core could be cut in half.

Immediately upon opening the core, it was recorded by photograph and sediment characteristics were recorded into a field notebook which included the nature of the sediment material (e.g., sandy, silty, clayey, or variations of those characteristics), coloration (e.g., rusty,

Figure 3-4. Vibracoring Activity on the Cap at Eagle Harbor

Figure 3-5. Hand Transport of Cores from the Water to the On-Site Processing Area

Figure 3-6. Opening the Aluminum Core Tube for Sediment Core Processing Using a Circular Saw

anaerobic, etc.), and lengths of varying characteristics measured using a measuring tape (including the depth of the sediment cap measured from the cap/surface-water interface to the cap/native-sediment interface).

Core Sectioning

Contaminant distribution in the cap was determined through the analysis of discrete sections of each sediment core. The mixing zone and physical characteristics of the sediment-cap interface influenced the core sectioning performed on site. In general, each core was sectioned into increments above and below the cap/native-sediment interface. For each core, the entire cap was sectioned, along with two segments acquired from the native-sediment portion of the core. The samples were incremented to capture the length of each core, such that sample resolution would be finer near the cap/native-sediment interface and became coarser with distance from this interface and approaching the cap/surface-water interface (Figure 3-7). From each core, the surface 5 cm of the cap also was sectioned for analysis to characterize surface cap characteristics.

Sectioning began by measuring the total core length and the total cap length, and dividing the core into approximately 32 sections, which were measured to the nearest centimeter from the interface between the cap and native material. The interface was a common reference for all cores.

Next, core segments were collected using disposable wooden spatulas (e.g., medical tongue depressors) at predetermined intervals. The core was segmented into ten 1-cm intervals for the first 10 cm above the sediment-cap interface (i.e., 0 to +10 cm); ten 2-cm intervals from +10 cm to +30 cm, and twelve 5-cm intervals from +30 cm to +90 cm. Below the sediment-cap interface, the core was segmented into one 2-cm interval from -5 cm to -7 cm, and one 5 cm interval from -50 cm to -55 cm. Figure 3-7 shows the core segmentation protocol. This plan is summarized in Table 3-1. Figure 3-8 shows porewater sampling and core segmentation in the field. Core processing in this manner resulted in 34 segments per core. A majority (>80%) of the core segments were sub-sampled for in-field RSC using the ELISA method to measure t-PAH concentrations.

Results of the ELISA tests were used to profile the distribution of t-PAH in the sediment cores and to identify sediment core segments for further analysis off-site. The goal was to minimize spending project resources on the more expensive detailed PAH chemistry on portions of cores that would provide little new information on the distribution of hydrocarbon contaminants. Figure 3-9 shows ELISA tests being performed on core segments at the on-site processing area.

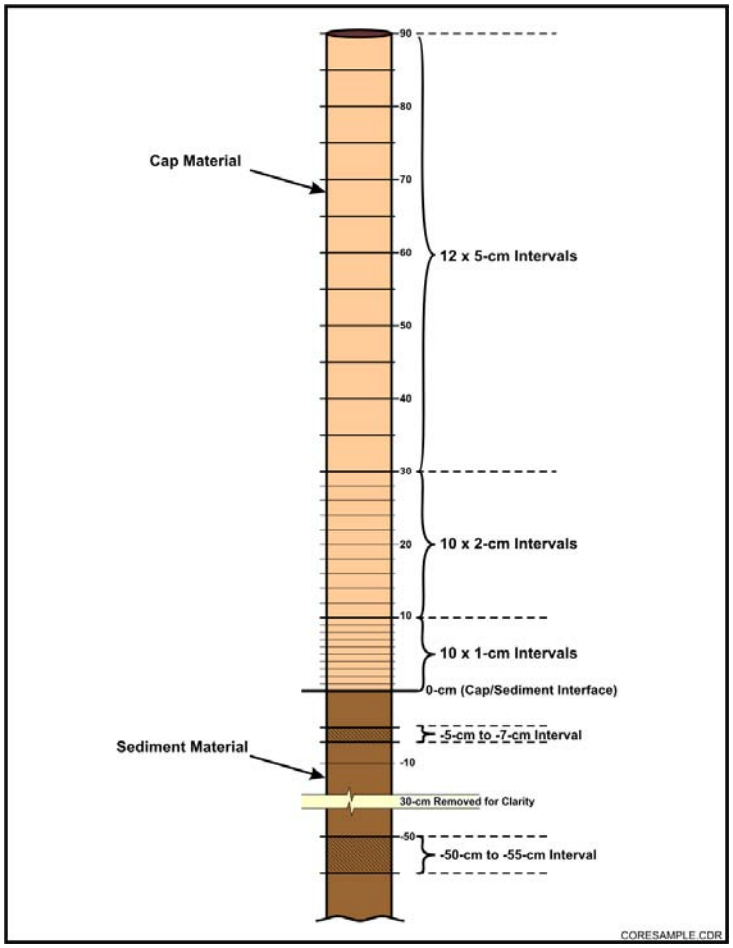

Figure 3-7. Sediment Core Processing Plan (Segmentation)

Table 3-1. Summary of Sediment Core Segments per Core for Rapid Screening Characterization

Depth Relative to Cap-Sediment Interface (cm)	Interval Thickness (Segment Thickness) cm	Number of Samples/Core
0 to +10	1	10
+10 to +30	2	10
+30 to +90	5	12
-5 to -7	2	1
-50 to -55	5	1
Total	**NA**	**34**

Figure 3-8. Porewater Sampling and Core Segmentation Processes in the On-Site Processing Area

Off-Site Sediment Measurements

Results of the RSC analyses were used to identify core segments for off-site analyses including 34 individual PAHs, total petroleum hydrocarbons (TPH), particle size distribution

(PSD) and total organic carbon (TOC) analyses. Sediments were selected for the presence of PAH and to characterize a range of t-PAH concentrations within each core. Non-detect t-PAH concentrations were also selected to bound the extent of migration, as appropriate. Of the 13 cores collected, four cores were identified for further analyses. From these four cores, a total of 26 core segments were submitted for additional analyses.

All core segments analyzed for PAH and TPH were also analyzed for TOC. Approximately 16 samples were selected for PSD analyses based on field observations and visual characterization. Approximately three segments from the cap and one from the native material per core were identified for PSD analysis.

Figure 3-9. Staff from SPAWAR Performing ELISA Analysis on the Core Segments in the On-Site Processing Area

3.1.3 Sample Collection for UMBC Column Tests. From the same 13 cores described previously, cap and native sediment materials were obtained and submitted to UMBC for column testing. Analytical data acquired from the field ELISA tests were used to determine those core sections that would be of appropriate concentration for laboratory tests. The samples were shipped from the field to the laboratory at UMBC and were homogenized and then stored under refrigeration upon receipt. Grab samples were obtained from two select sediment samples. Each grab sample was sub-sampled so that two aliquots (~2 grams wet weight) were collected from each grab and extracted for analysis. The 16 U.S. EPA priority pollutant PAHs were measured in the sediment samples after ultrasonic extraction (U.S. EPA method 3550B) and silica gel cleanup (U.S. EPA method 3630C). Calibration standards were used at seven levels ranging from 103 to 31,000 µg/L of 16 PAHs. Two internal standards (ISs), 1-fluoronaphthalene and p-terphenyl-d^{14}, were added to the GC vials prior to injection. Along with wet sample extraction, dry weights of sediment and cap samples were obtained from a portion (~5 grams wet weight) of each grab after overnight drying at 105^{o}C. Procedural blanks and mid-range calibration standards were run with samples to check background PAH levels and the initial calibration. For particle size dependent PAH distribution, wet sieving was performed on the sediments using standard sieve sizes 63 µm (mesh #230), 180 µm (mesh #80) and 1.7 mm (mesh #12), as described below. PAH extraction and analysis were performed for each of these sieved portions.

3.2 Laboratory Studies

3.2.1 Sediment Mass and PAH Distribution for Different Size Fractions. Wet sieving was performed on the Eagle Harbor sediments using standard sieve sizes 63 µm (mesh #230), 180 µm (mesh #80), and 1.7 mm (mesh #12). Approximately 100 g of wet sediment was placed on the three sieves and washed with deionized water to promote the separation. Particles less than 63 µm that collected in the bottom of the pan were allowed to settle down and the supernatant water was drained out. PAH extractions were performed for each of these sieved portions including fines collected in the pan (<63 µm).

3.2.2 Sediment-Water Equilibrium Partitioning Measurements. Batch equilibrium tests were conducted using whole and sieved fraction sediments. Approximately 1.5 grams of sediment was placed in 12 mL glass vials with Teflon® lined caps with a solution of 0.01M $CaCl_2$ and 100 mg/L sodium azide (NaN_3) in deionized water. 11 mL of solution was added to each of the vials. Twelve vials were placed in a plastic bottle and placed on a roller. The bottle was rolled slowly at 0.75 rotations per minute (rpm). Six of the 12 vials were removed from the roller after 16 days. Gravity settling was allowed to occur for one hour, and 9 mL of supernatant was removed from each of the six vials. Colloids in the water phase were removed by alum flocculation based on a method developed by Ghosh et al. (2000). The alum flocculation step involved the addition of 0.25 mL of 10% weight alum and two drops of 1 N NaOH to the supernatant. Sodium hydroxide was used to adjust the pH of the sample to neutrality. The supernatant was carefully mixed using a glass pipette for 1 min and allowed to sit overnight. The next day, a clear supernatant was seen at the bottom of the tube along with the settled colloidal particles. The supernatant was withdrawn using a glass pipette without disturbing the floc at the bottom. The bottom 2 to 3 mL of water was left in the tube to make sure no colloidal particles were removed with the sample water. The water phase was extracted three times with 2 to 3 mL of hexane.

3.2.3 PAH Extraction of Whole Sediment and Sediment Fractions. Extraction of PAHs from the sediments was performed according to U.S. EPA SW 846 Method 3550B. The sediment was dried by using anhydrous sodium sulfate which was purified at 100°C in a shallow tray for 4 hours. Enough sodium sulfate was added to the sediment so that a free flowing powder was formed. Any lumps of sediment were broken using a spatula. PAHs were extracted from the sediment using a 50:50 (v:v) mixture of pesticide grade hexane and acetone. Three volumes of 30 mL hexane/acetone were used for this purpose. The slurry was sonicated for three minutes at pulses of 30 seconds on and 30 seconds off. This process was repeated three times, and the extract was collected in a 250 mL flask. Whatman glass microfiber filter (GF/C 110 mmØ) was used to filter the extract. The volume of the extract was recorded; a portion of it was transferred to a vial and stored at 5°C. The rest of the extract was dumped in a waste container. The stored extract was used for further cleanup and analysis.

3.2.4 PAH Cleanup and Analysis. U.S. EPA SW 846 method 3630 was used for cleanup of sediment extracts. A required volume of extract was taken and solvent exchanged into 2 mL of cyclohexane. Glass wool was placed in a 10 mm inner diameter (ID) glass chromatography column. A slurry of 3 g activated chromatographic silica gel was prepared with methylene chloride and placed in the column. Silica gel was previously activated by baking overnight at 100°C. A 1 to 2 cm layer of anhydrous sodium sulfate was added in order to dry the extract. Then 15 mL of pesticide grade pentane was eluted through the column to drain out the methylene chloride. Two mL of the sample in cyclohexane was added to the column and allowed to elute. The transfer was completed by rinsing the sample vial with 1 mL cyclohexane and pouring it into the column prior to the exposure of sodium sulfate surface. Then 8 mL of pentane were eluted. All of the collected eluant was dumped in a waste container, and 15 mL of a methylene chloride:pentane (40:60, v:v) mixture was run through the column. The elutant was collected in a 40 mL vial, and concentrated to 10 mL under a nitrogen stream. One mL of this 10 mL cleaned sample was placed into a GC vial for injection into the GC/MS for PAH analysis.

An Agilent gas chromatograph (Model 6890) with a fused silica capillary column (HP-5, 30 m × 0.25 mm ID) and a mass selective detector (MSD) was used for analysis based on U.S. EPA method 8270 for PAHs. A standard mixture of 16 U.S. EPA priority pollutant PAH compounds obtained from Ultra Scientific was used for calibration.

3.2.5 Total Organic Carbon Analysis. TOC analysis was performed using a Shimadzu TOC analyzer with a solids sample module (TOC-5000A and SSM-5000A). The sediment TOC analysis followed an operating procedure recommended by the manufacturer. The sediment sample was first homogenized to a powder in a clean ceramic mortar. Two 0.5 g sub-samples of the homogenized sediment were placed in ceramic combustion boats. Inorganic carbon was removed from the homogenized samples by adding 1 mL of concentrated hydrochloric acid to each sample in the boats. After 1 hour of reaction and evolution of carbon dioxide, the boats were placed in an oven at 105°C for 10 hrs to remove the remaining hydrochloric acid before TOC measurement. Carbon in the sample was combusted to form carbon dioxide, which was detected by a non-dispersive infrared gas analyzer. The TOC instrument was calibrated using pure naphthalene standards.

3.2.6 Laboratory Column Studies. Laboratory columns were constructed and operated to simulate the vertical flux of contaminants in Eagle Harbor sediments. Six glass columns were fabricated in the UMBC glass shop based on the design shown in Figure 3-10. The columns were made of 2 inch diameter glass tubes with six sampling ports at 6 inch intervals to allow sampling of porewater at different elevations in the column. Each side port was closed with a Teflon® end cap and valve that allowed sampling of porewater using a syringe. The two end caps of the column are designed to hold screens to support the column contents. A programmable peristaltic pump was used to maintain water flow through the column (average flow rate of 25 mL/hr). A layer of glass beads and glass wool was placed over the bottom screen. The Teflon® liner, glass beads, and glass wool together were approximately 1.25 cm high in the column (under the sediment layer). Before the sediment was added, the influent tube and lower portion of the column was filled with synthetic groundwater. Sieved contaminated sediment was added to the top until it reached 20 cm of depth (above port 1, but below port 2). The side walls of the glass column were rinsed and the overlying water was drained. About 5 cm of wet capping material was then sprinkled down over the sediment. More groundwater was added (by pumping through the bottom inlet and adding from the top). The remainder of the cap material was allowed to settle through the synthetic groundwater. The cap material was 50 cm deep and ended at port 5 (above port 5 for column 2). Typical operating conditions were — flowrate: 25 mL/hr; synthetic groundwater: 0.01 M ionic strength with calcium chloride (sodium nitrate was used for the first trial column); and sample collection interval of 1 to 2 times per week. A picture of the column setup in the laboratory is shown in Figure 3-11. Biological activity in the sediment columns was minimized by adding 100 mg/L of sodium azide to the influent.

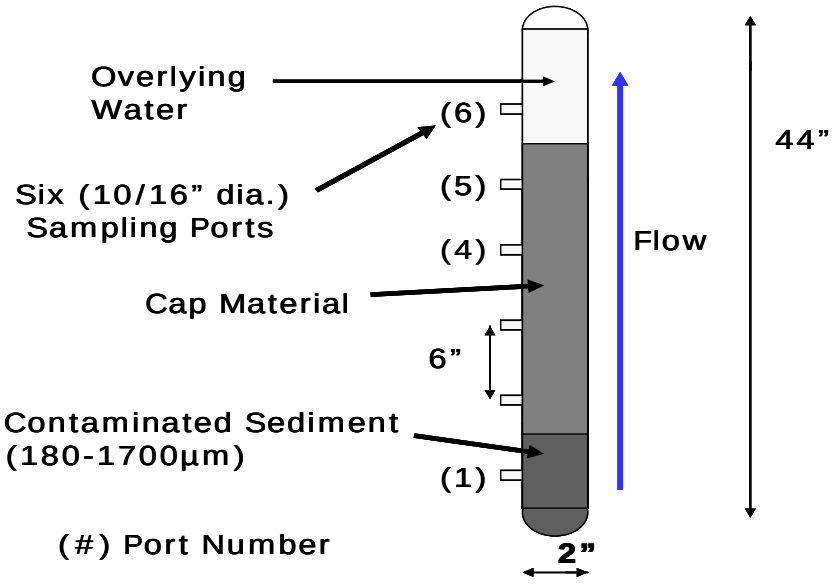

Figure 3-10. Column Design and Dimensions

3.2.7 PAH Measurement by Solid Phase Microextraction. Due to the extremely low aqueous solubility of high molecular weight PAHs, several hundred milliliters of sample volume

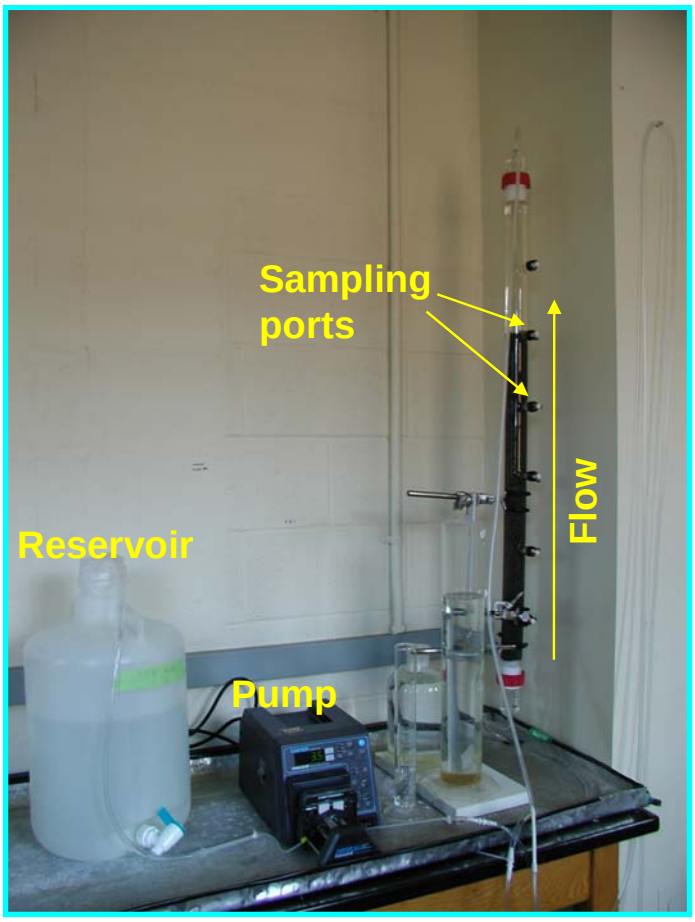

Figure 3-11. Laboratory Column Transport Study Setup Showing a Glass Column Containing PAH Contaminated Sediment in the Bottom and Clean Cap on the Top

is required to achieve reasonable detection limits in a liquid-liquid extraction scheme. A major challenge in analysis of PAHs in the water phase sampled from an experimental sediment column is the sample volume requirement. Physical models of contaminant transport are typically operated close to low groundwater velocities and extraction of large volumes of water through side sampling ports may significantly disrupt the nature of the fluid flow inside the column. Thus, alternate methods of porewater sample analysis were explored. Several methods have been used in the past for the measurement of organic contaminants in porewater, however a major challenge has been the availability of enough quantity of porewater necessary for low detection limits. A new method under development is SPME for ultra low level detection of sparingly soluble organic compounds in the water phase (Hawthorne et al., 2005). The method involves equilibration of a fiber coated with a suitable sorbent to a small volume (1 to 2 mL) of water sample. The analytes and added deuterated analytical standards partition into the fiber. The fiber is then introduced into a heated gas chromatograph injection port. The volatile analytes are desorbed into the chromatography column and detected by mass spectrometry. A major advantage of this method is that all of the sampled analytes are quantitatively transferred

to the gas chromatograph leading to very low detection limits (in the range of nanograms per liter) using a few milliliters of water sample.

In this work, the SPME fiber was exposed to a 1.5 mL water sample for 30 minutes; then the fiber was manually injected into the GC/MS for 5 minutes at 320^{o}C. The fiber was cleaned by exposing it to a nitrogen gas stream at 320^{o}C for 10 minutes. The PAH concentration was determined using an isotope dilution technique. Seven deuterated standards were used for the 10 PAHs measured as shown in Table 3-2. The calibration curve for each PAH was linear with correlation coefficient (r) values greater than 0.998 (see examples in Figure 3-12). The SPME method was compared with liquid-liquid extraction (Figure 3-13). PAH concentration measurement by both methods is in good agreement as can be seen in Figure 3-13.

3.3 Testing and Measurement Protocols

3.3.1 Sediment Sample Labeling Procedures. The platforms that were used for the conductivity survey and the coring activities were each equipped with an onboard GPS unit to determine longitudinal and latitudinal coordinates for each sampling location. Prior to the GPS being used at the study site, it was checked against a reference location's coordinates. Each sampling location was identified by GPS coordinates and a sample location identification number.

The time of day at each sampling location was recorded before and after collecting each sediment core. When the sediment cores were brought to the surface, they were visually inspected and assigned a location number. The GPS coordinates, date and time, and any observations associated with the sampling at that location were noted in the field notebook.

Sediment core samples were identified with the information listed below.

- *Sample Location Identification Number*: This was the primary sample identifier.
- Cap versus Native Sediment: "C" was used for cap material above the cap/native sediment interface, and "NS" was used for native sediment below the cap/native sediment interface.
- *Core Segment Code*: This identifier was included to identify the depth represented by the core segment relative to the cap/native sediment interface.
- *Date/Time*: The date and time of sample collection were documented.
- *Sampler Initials*: The initials of the person responsible for filling out each sample label and preparation of samples for shipment were identified
- *Sample Destination*: The sample destination was identified.

Table 3-2. List of PAH Compounds and Corresponding Deuterated Standards Used for SPME Analysis (The list of 10 PAH Compounds were Chosen Based on Their Observed Abundance in Aqueous Samples.)

Deutrated ISTD	Target analyte
Naphthalene-d8	Naphthalene
Acenaphthylene-d10	Acenaphthylene Acenaphthene
Fluorene-d10	Fluorene
Phenanthrene-d10	Phenanthrene Anthracene
Fluoranthene-d10	Fluoranthene
Pyrene-d10	Pyrene
Chrysene-d12	Benz(a)anthracene Chrysene

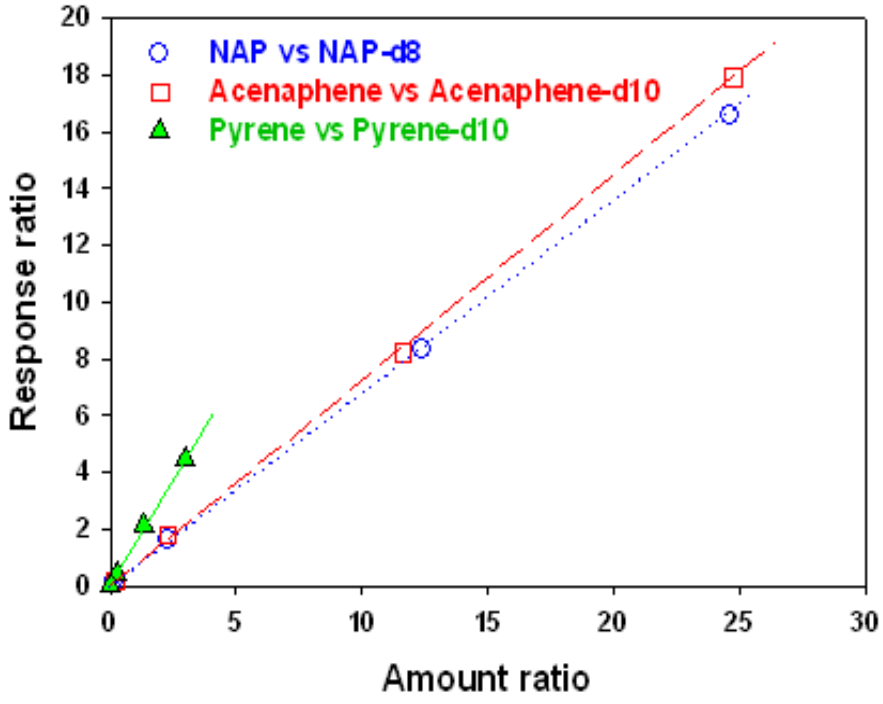

Figure 3-12. Example SPME Calibration Curves

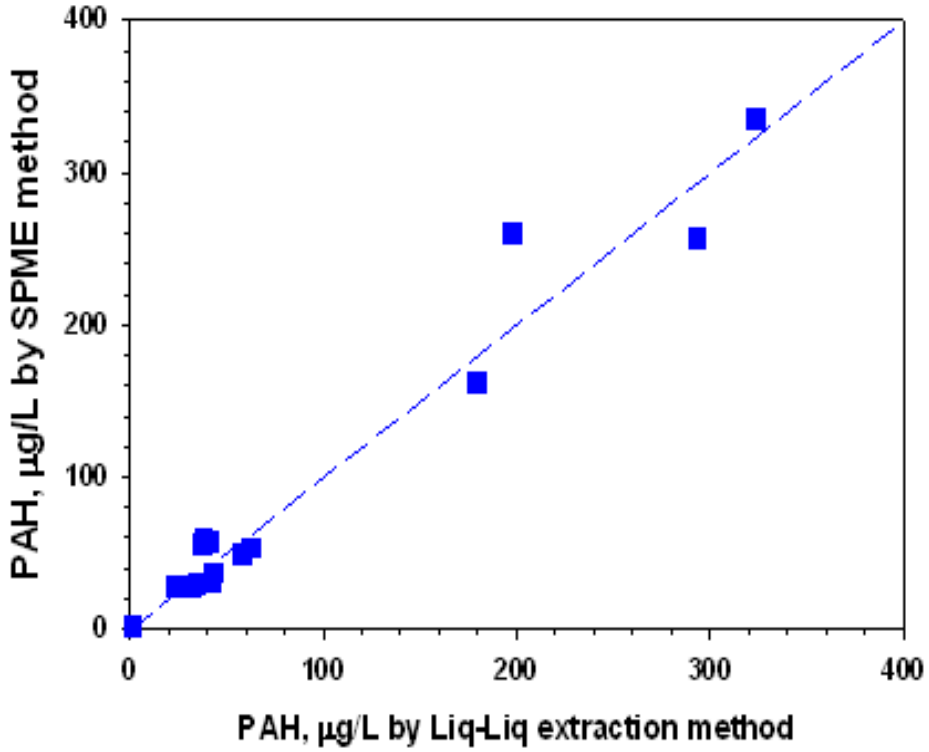

Figure 3-13. Comparison of Liquid-Liquid Extraction and Solid Phase Micro-Extraction

3.3.2 Sediment Sample Preservation and Shipping. Table 3-3 outlines the methods of analysis, sample volume requirements, sample preservation, and holding times for each of the analyses that were conducted for this study.

3.3.3 In Situ Electrical Conductivity. The probe itself had no calibration adjustments that could be made other than during factory maintenance. Therefore, a calibration correction was developed to calibrate the probe to a series of known solutions. The probe was calibrated in the laboratory prior to deploying it to the field. The probe was also fully calibrated or a calibration check was performed each time it was brought to the surface during use in the field by using a five-point calibration curve developed in the range of 0 to 50,000 parts per million (ppm) saline solution. In addition, the probe was maintained in the field by using a fine grit sand paper (200 grit) to remove the oxidation that occurred during exposure to salt water. The unit was checked for damage to the array itself, as well as the cabling connecting the probe to the instrumentation box. The visual inspection included an accuracy check of the incremental markings for depth that were on the unit.

3.3.4 Core Porewater Conductivity Measurements. Sediment porewater samples were obtained as previously described from vertical cores prior to core processing and were measured for conductivity on-site using a portable Orion Model 96-78-00 conductivity probe and meter. The meter was calibrated prior to use according to the manufacturer's instructions.

Table 3-3. Sample Methods, Volumes, Preservations, and Holding Times Wyckoff/Eagle Harbor Site Bainbridge, Washington

Analyte	Matrix	Method	Wet Weight or Liquid Volume	Container Type	Preservation	Holding Time
Off-Site Laboratory Analyses						
TPH in sediment	Sediment	Modified SW-846 8015	50 g (wet[a])	Amber glass with Teflon®-lined cap	Cool, 4°C	14 days
PAHs in sediment	Sediment	Modified SW-846 8270	50 g (wet[a])	Amber glass with Teflon®-lined cap	Cool, 4°C	7 days/ 40 days[b]
Particle Size Distribution	Sediment	ASTM D-422	100 g	Plastic	NA	28 days
Moisture Content	Sediment	Gravimetric Method (modified ASTM D2216)	300 g	Glass with Teflon®-lined cap	Cool, 4°C	14 days
TOC	Sediment	U.S. EPA 415.1	20 g	Whirl-Pak™ bags	Cool, 4°C	28 days
Field Analyses						
RSC	Sediment	EPA Method 4035	NA	NA	NA	Immediately
Conductivity	Sediment	Conductivity meter	NA	NA	NA	Immediately

(a) A single extraction was conducted for both TPH and PAH analyses, requiring a total of 50 g sediment for both analyses.
(b) Extractions must be complete within 7 days, and GC/MS analysis must be complete within 40 days.
TPH = total petroleum hydrocarbons
ASTM = American Society of Testing and Materials
NA = not applicable

3.3.5 In-Field Assay ELISA. ELISA was conducted by field staff from SPAWAR using the standard operating procedure (SOP) presented in Appendix B of the May 2006 work plan (Battelle, 2006; Appendix A). The sample (with the *unknown contaminant concentration*; ex. PAH) was analyzed by the addition of an enzyme conjugate (labeled PAH). This was followed by addition of paramagnetic particles with antibodies specific to known PAHs. In relatively proportional concentrations, both the sample PAH and the "labeled" PAH (conjugate) competed for the binding sites on the magnetic particles. After an incubation period, a magnetic field was applied to hold (in-place) the magnetic particles having the sample PAH and its "labeled" PAH analog to bind with the antibodies. Any unbound reagents were decanted and washed repeatedly. PAHs in the mixture were detected with the addition of an enzyme substrate (color solution) containing a chromagen, which specifically reacts to the "labeled" PAH. After another incubation, the reaction was stopped and stabilized by addition of acid (stopping solution). Since the labeled PAH and sample PAHs are in competition (proportionally) with the binding sites, the color developed at the end of reaction was inversely proportional to the PAH concentration in the sample. This color response was measured by a spectrophotometer (450 nm) and compared to the responses taken from a calibrated series of known PAH standards (kit-supplied) to determine the equivalent PAH concentration of the sample.

3.3.6 PAH Analysis. Parent PAHs and their alkylated derivatives were analyzed by Battelle using a modified SW-846 8270 method. The method employed high-resolution capillary GC/MS with analysis according to BOS SOP 5-157, *Identification and Quantitation of Polynuclear Aromatic Hydrocarbons (PAH) by Gas Chromatography/Mass Spectrometry* (Battelle, 2006 [Appendix C in the Work Plan]). The analytical system was comprised of a Hewlett Packard 6890 GC, equipped with an electronic pressure controlled (EPC) inlet and an HP 5973 MSD operating in the selected ion monitoring (SIM) mode. A minimum of a five-point response factor calibration was run with analyte concentrations in the standard solutions ranging from approximately 0.005 ng/μL to approximately 10 ng/μL. The samples were bracketed by passing continuing calibration checks analyzed at the beginning and end of each 12 hr period and at the completion of the sequence.

Quantification of individual compounds was performed by the method of ISs using the deuterated PAH internal standards. Total PAH was determined as the sum of the individual PAH and alkylated PAH analytes. The homologous series of alkylated PAH (multi-component analytes) was quantified using the response factor of the parent PAH or most appropriate alkyl PAH available in calibration standards. Target analytes are listed in Table 3-4.

3.3.7 TPH Analysis. Sample extracts were also analyzed for TPH at Battelle using a BOS SOP 5-202, *Determination of Low-Level Total Petroleum Hydrocarbon and Individual Hydrocarbon Concentrations in Environmental Samples Using GC/FID* (Battelle, 2006 [Appendix D]). This method, a modification of SW-846 Method 8015D, employed high-resolution capillary gas chromatography with flame ionization detection (GC-FID). TPH was measured on an Agilent 5890 GC, equipped with an EPC inlet and dual FID detectors. A successful linear calibration using a minimum of five calibration levels ranging from approximately 1 μg/μL to approximately 200 μg/μL individual saturated hydrocarbons was run before the analysis of samples. The samples were bracketed by passing continuing

Table 3-4. List of Target Analytes for Standard PAH Analysis Wyckoff/Eagle Harbor Site Bainbridge, Washington

Analyte/Analyte Group	Abbr.	Ring #	Analyte/Analyte Group	Abbr.	Ring #
Naphthalene*	**N0**	2	C_3-dibenzothiophenes	D3	3
C_1-naphthalenes*	N1	2	C_4-dibenzothiophenes	D4	3
C_2-naphthalenes*	N2	2	**Fluoranthene***	**FL**	4
C_3-naphthalenes*	N3	2	**Pyrene***	**PY**	4
C_4-naphthalenes*	N4	2	C_1-fluoranthenes/pyrenes*	FP1	4
Biphenyl	Bph	2	C_2-fluoranthenes/pyrenes	FP2	4
Acenaphthylene*	**Acl**	3	C_3-fluoranthenes/pyrenes	FP3	4
Acenaphthene*	**Ace**	3	**Benz(a)anthracene***	**BaA**	4
Dibenzofuran	DdF	3	**Chrysene***	**C0**	4
Fluorene*	F0	3	C_1-chrysenes/benzantracenes*	C1	4
C_1-fluorenes*	F1	3	C_2-chrysenes/benzantracenes*	C2	4
C_2-fluorenes*	F2	3	C_3-chrysenes/benzantracenes*	C3	4
C_3-fluorenes*	F3	3	C_4-chrysenes/benzantracenes*	C4	4
Anthracene*	**AN**	3	**Benzo(b)fluoranthene***	**BbF**	5
Phenanthrene*	**P0**	3	**Benzo(k)fluoranthene***	**BkF**	5
C_1-phenanthrenes/anthracenes*	P1	3	Benzo(e)pyrene*	BeP	5
C_2-phenanthrenes/anthracenes*	P2	3	**Benzo(a)pyrene***	**BaP**	5
C_3-phenanthrenes/anthracenes*	P3	3	Perylene*	Per	5
C_4-phenanthrenes/anthracenes*	P4	3	**Indeno(1,2,3-c,d)pyrene***	**ID**	6
Dibenzothiophene	D0	3	**Dibenz(a,h)anthracene***	**DA**	5
C_1-dibenzothiophenes	D1	3	**Benzo(g,h,i)perylene***	**BgP**	6
C_2-dibenzothiophenes	D2	3	--	--	--

Bold = 16 PAH priority pollutants identified in the Clean Water Act (CWA)
* = 34 PAHs identified in *Procedures for the Derivation of Equilibrium Partitioning Sediment Benchmarks (ESBs) for the Protection of Benthic Organisms: PAH Mixtures* (U.S. EPA, 2003)

calibration checks analyzed at the beginning and end of each 12 hr period and at the completion of the sequence.

TPH was defined as resolved plus unresolved hydrocarbons and included gasoline range, diesel range, and higher molecular weight hydrocarbons in the C_8 through C_{40} volatility range. TPH quantification was performed by the method of internal standards. D_{42}-eicosane and d_{62}-triacontane served as the ISs and were present at ~50 µg/mL in all calibration solutions and sample extracts. TPH concentrations were corrected for the amounts of IS and surrogate internal standards added to each sample. The TPH method detection limit was approximately 4 mg/kg.

3.3.8 Sediment Moisture Content/Dry Weight Analysis. Moisture content of each sediment sample was determined by Battelle during analytical extraction using a modified version of American Society for Testing and Materials (ASTM) Method D2216. The method

was modified as follows: approximately 5 to 10 g of sediment was placed in a pre-weighed, aluminum weighing pan. The weight was recorded (initial weight), and the pan was placed in a drying oven at 110 ± 5°C. The sample was dried to constant weight (overnight), cooled in a desiccator for at least 30 minutes, and weighed again (dry weight). The sediment moisture content was calculated as [1-(dry weight/initial weight)] × 100%. The percent dry weight was calculated as (dry weight/initial weight) × 100%.

3.3.9 Particle Size Distribution and Total Organic Carbon Analyses. PSD was determined for at least one sediment segment and one cap material segment per each core. PSD was conducted at Applied Marine Sciences, Inc. (Ft. Worth, TX), using ASTM D422-*Standard Method for Particle-Size Analysis of Soils*. Data were reported as weight percentages of gravel (>4.74 mm diameter), sand (4.75 to 0.74 mm diameter), silt (0.74 to 0.005 mm diameter), and clay (<0.005 mm diameter).

TOC was determined for each sediment segment that was analyzed for PAHs conducted by the UMBC. TOC was determined according to U.S. EPA Method 9060-*Total Organic Carbon*.

4.0 RESULTS AND ACCOMPLISHMENTS

4.1 Field Conductivity Measurements

Figure 4-1 shows the results from the in-field conductivity survey that was conducted in June 2006. The survey was conducted immediately preceding the coring activities and the data from the survey were used to identify coring locations of interest. Initially, the divers sampled along ECT3 to a depth of approximately 100 cm below the cap-water interface as described in Section 3.1.1. Additional sampling occurred along ECT1 after the ECT3 sampling activities were completed.

The results from the survey indicated that there was limited or no detectable freshwater upwelling on ECT3 and ECT1 inside the capped area. The most notable upwelling appeared to be occurring in the inter-tidal zone along the southern cap boundary.

Additional sampling was conducted along the southeastern boundary of the cap and closer to shore and also to the north and northeast of the cap where upwelling was evident in past investigations. The data acquired in the field were plotted using EarthVision® geospatial modeling software using a two dimensional gridding algorithm approach. The entire data set, where each sample point was unique in depth and location, was contoured to develop the isoconcentration surface map shown in Figure 4-1. The two-dimensional plot shows the lack of detectable freshwater upwelling in the cap boundary.

4.2 Sediment Core Profiles

Figure 4-2 shows the core locations and transects that were developed due to the core positions. The new transects were identified as TR1, TR4, TR5 and TR6. Each core was processed in the field as described in Section 3.1.2 and independent core segments were analyzed for t-PAHs using the RSC procedure. The RSC results were used to select specific core segments that were shipped to Battelle's laboratory for GC/MS analysis of 34 analyte PAHs. Those results, shown in Table 4-1, compare results from RSC and GC/MS methods. RSC results are expressed in t-PAHs per segment, where GC/MS data are expressed as the sum of the individual 34 analyte PAHs. In addition, TPH analyses were performed on each segment, results of which are also included in Table 4-1.

The RSC method proved to be a useful in-field tool for rapid analysis of the core samples and provided valuable information that could be used to select specific core segment samples for the more expensive and time consuming GC/MS analysis. In general, the RSC method compared well with the detailed GC/MS results for t-PAHs. Greater variations between the two methods occurred at higher concentrations, indicating that the RSC method may perform more accurately at lower t-PAH concentrations. One anomaly was observed in Core TR1-10 at 19 cm above the sediment-cap interface. Here, the results indicated an order of magnitude difference between the two methods (14,114 mg/kg vs. 4,182 mg/kg, for RSC vs. GC/MS, respectively). This anomaly remains unexplained, but may have been the result of a heterogeneous sample or may have been due to compound/matrix interferences.

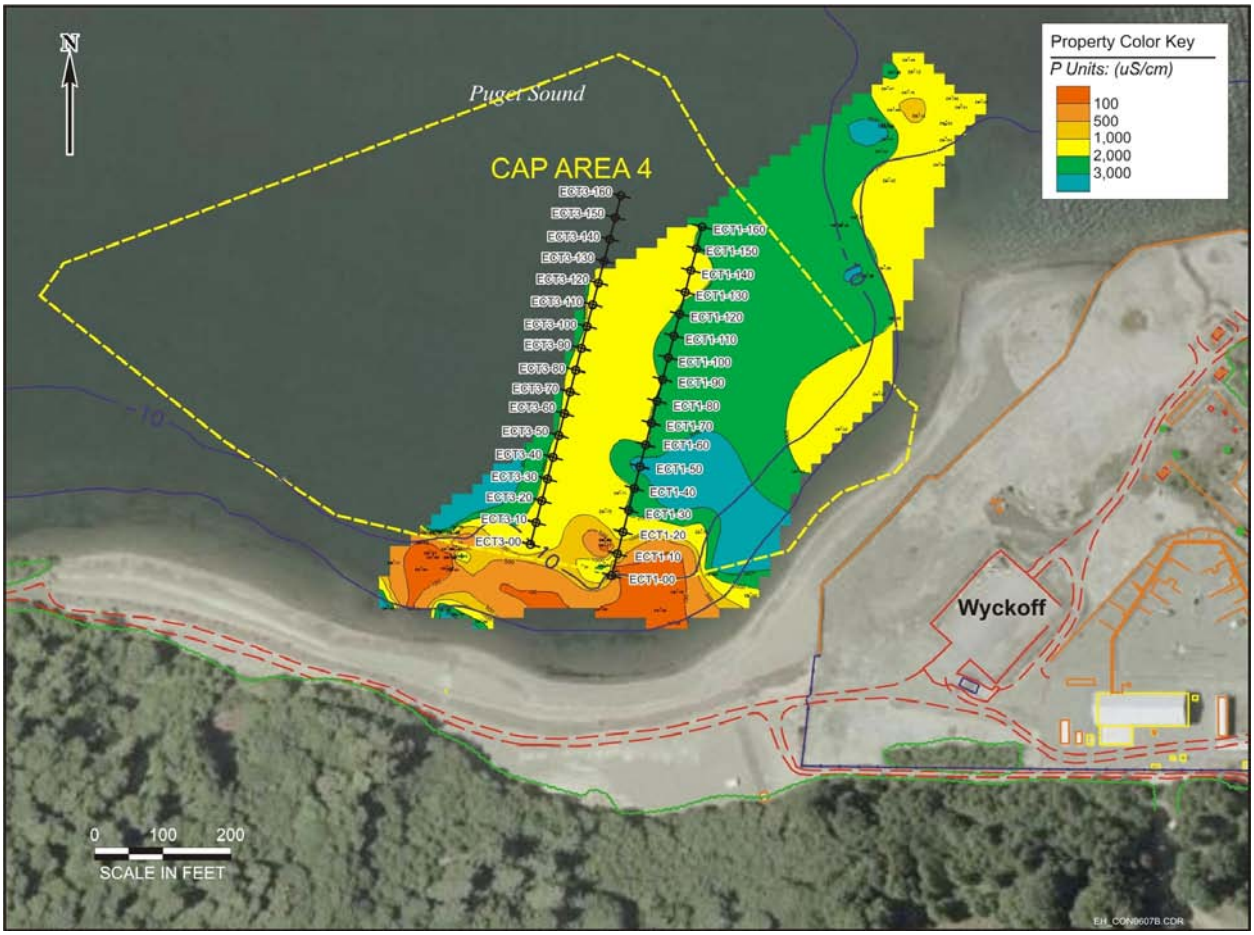

Figure 4-1. Freshwater Upwelling in the Surficial Cap Layer at the Eagle Harbor Site

TPH values were relatively high in all cores ranging from approximately 5 ppm (i.e., 5,000 µg/kg) to over 1,000 ppm in some core segments. The TPH concentration profile corresponded with increasing and decreasing concentrations relative to the t-PAH concentration profile.

Figures 4-3 through 4-5 show cross-sectional views of the primary transects created by the coring effort — TR1, TR4 and TR5. The figures also show the t-PAH and TPH concentration as a function of depth for select cores. For each core, the t-PAH profile results for the RSC are shown. The GC/MS results for the t-PAH and TPH for select segments of cores are adjacent to the RSC data.

A more detailed forensic analysis of the core data is underway; however, preliminary evidence indicates that some cores exhibited a potential migration pattern or some distribution has occurred within the cap profile possibly due to mixing during the capping event. In all cores reported, mixing at the cap-sediment interface appeared to be insignificant. The interface layer

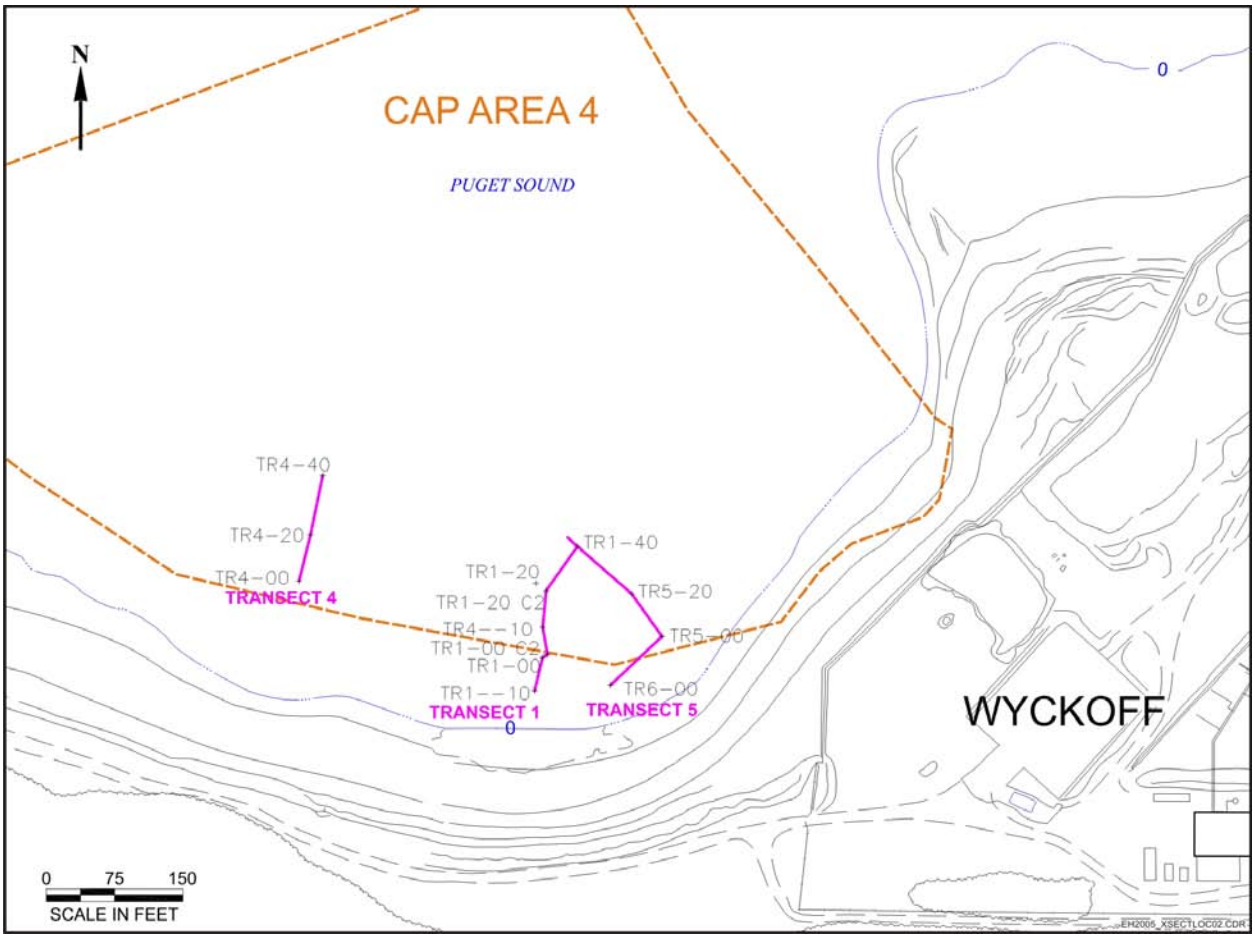

Figure 4-2. Core Locations and Transect Lines, TR1, TR5, TR6 and TR4

was easily defined and material mixing appeared to have occurred within the top 6 cm or less of the cap material. Core TR1-10 (shown in Figure 4-3) showed an increasing t-PAH concentration trend moving away from the sediment-cap interface and peaking at approximately 30 cm above the sediment-cap interface at a t-PAH concentration of approximately 13.4 ppm, before decreasing in the upper layers.

In core TR1-40 (Figure 4-3), there was an abrupt t-PAH increase at approximately 97 cm above the sediment-cap interface (2.5 ppm). Core logging data that were recorded during core processing indicated that this segment was characteristic of the cap material and that there were no observations to suggest a physical or material change in the cap consistency at this location. Above 97 cm and moving towards the cap-water interface, t-PAH concentrations decreased to 0.4 ppm in the top 5 cm of the cap surface (or 155 cm above the sediment-cap interface). It is unclear if the apparent t-PAH concentration increase at the cap surface is due to chemical migration emanating from native material or to other anthropogenic sources that have accumulated since the placement of the cap.

In core TR5-20 (Figure 4-5), a substantial increase in t-PAH concentration was observed at approximately 50 cm above the sediment-cap interface. Concentrations at this point in the profile were approximately 4.6 ppm t-PAH and decreased to 0.1 ppm in the top 5 cm of the cap surface. However, at 50 cm above the sediment-cap interface, a characteristically clay-fine material was observed which may have resulted in a selectively adsorptive layer midway in the cap profile.

Table 4-1. Total PAH and TPH Profile in the Cap at Eagle Harbor Using RSC and GC/MS Analysis Techniques

Sample ID	Average Distance Above the Sediment-Cap Interface (cm)	PAH Rapid Screening (µg/kg)	Total PAH (µg/kg)	TPH (µg/kg)
TR1- (-10)	-1	NA	74,105	854,326
	11	1,292	1,748	29,344
	19	14,114	4,182	57,652
	30	19,786	13,477	127,109
	42	4,032	2,733	27,071
	62.5	2,315	3,181	43,869
TR1- 40	-1	NA	53,717	974,711
	26	40	9	20,613
	58	16	4	15,951
	97.5	5,535	2,499	33,730
	155	638	425	16,841
TR5-20	-1	NA	73,690	1,197,370
	3	610	956	24,566
	7	14	48	14,521
	26	81	94	15,892
	34	243	372	16,407
	50	6,838	4,664	47,335
	67.5	1,576	477	13,047
	87.5	627	918	17,995
TR5-00	-1	40,618	52,440	1,073,443
	7	3,503	5,574	40,628
	19	1,921	2,967	32,556
	34	8	39	4,921
	58	13	35	4,922
	77.5	1,171	739	14,799
	97.5	314	458	11,348

NA = Sample not analyzed using this method

In core TR5-00 (Figure 4-5), there was a migratory trend observed immediately above the sediment-cap profile and then again in the top 5 to 8 cm of the cap. At approximately 77 cm above the sediment-cap interface a t-PAH concentration of 1.1 ppm was observed.

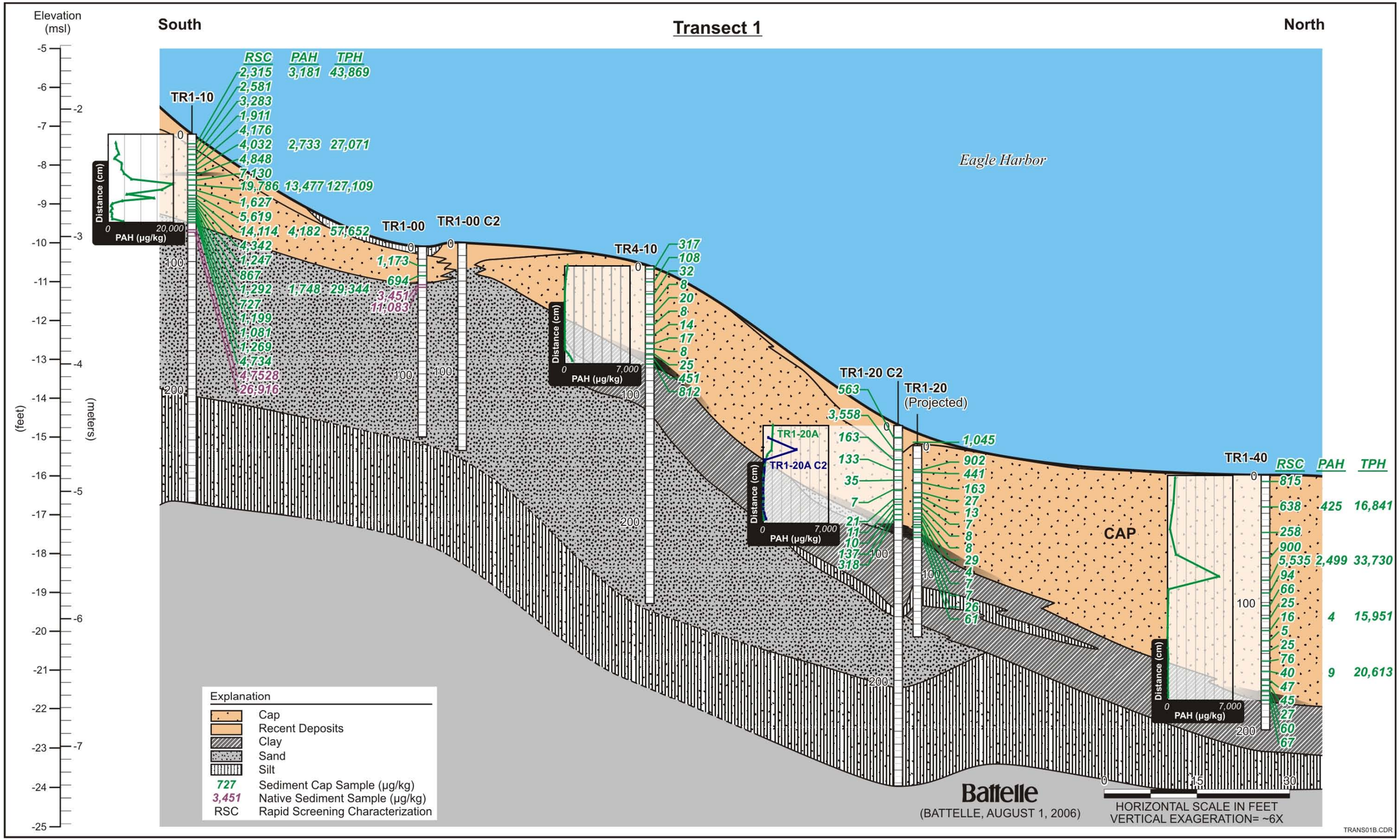

Figure 4-3. Cross Sectional View of Transect 1 with PAH and TPH Profile by Depth for Select Cores

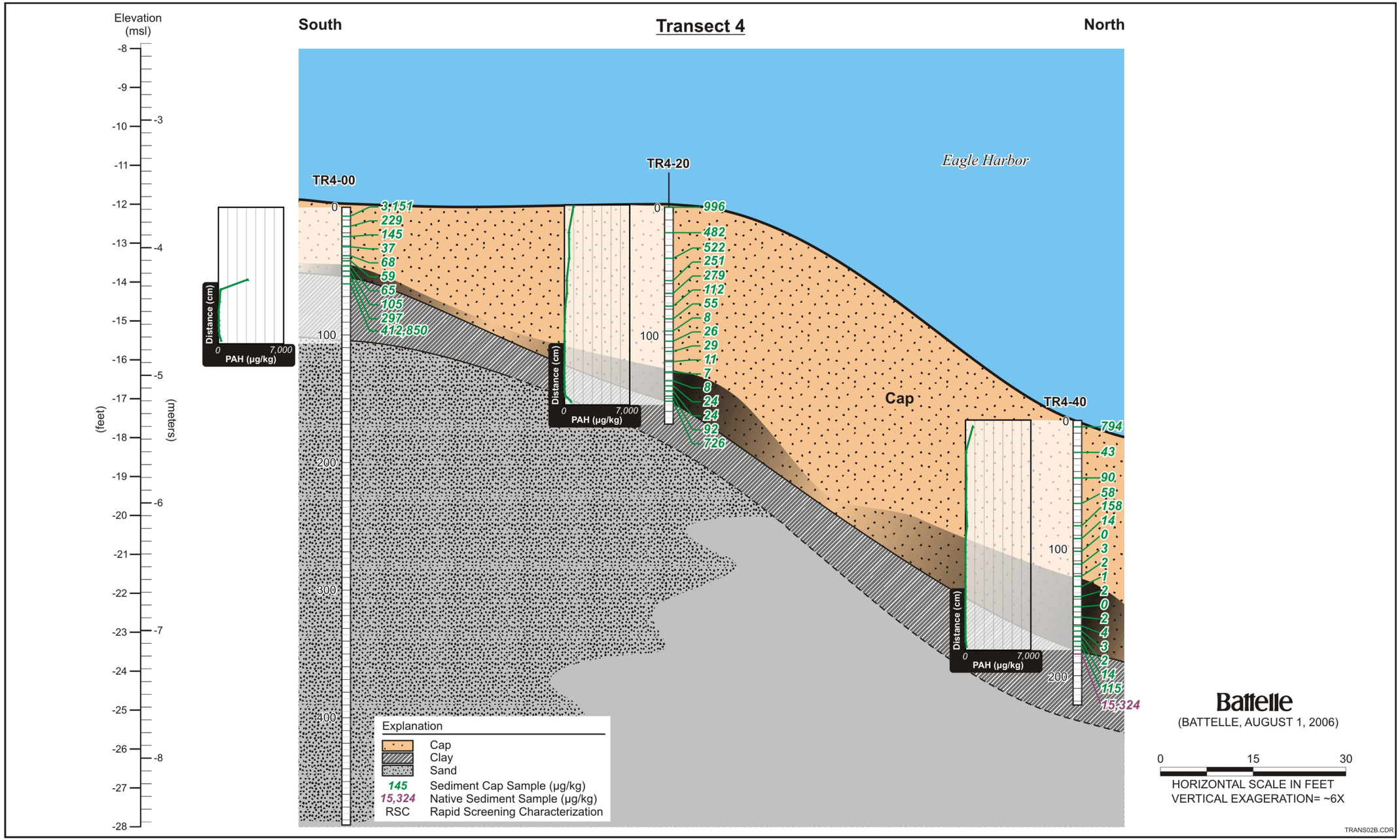

Figure 4-4. Cross Sectional View of Transect 4 with PAH and TPH Profile by Depth for Select Cores

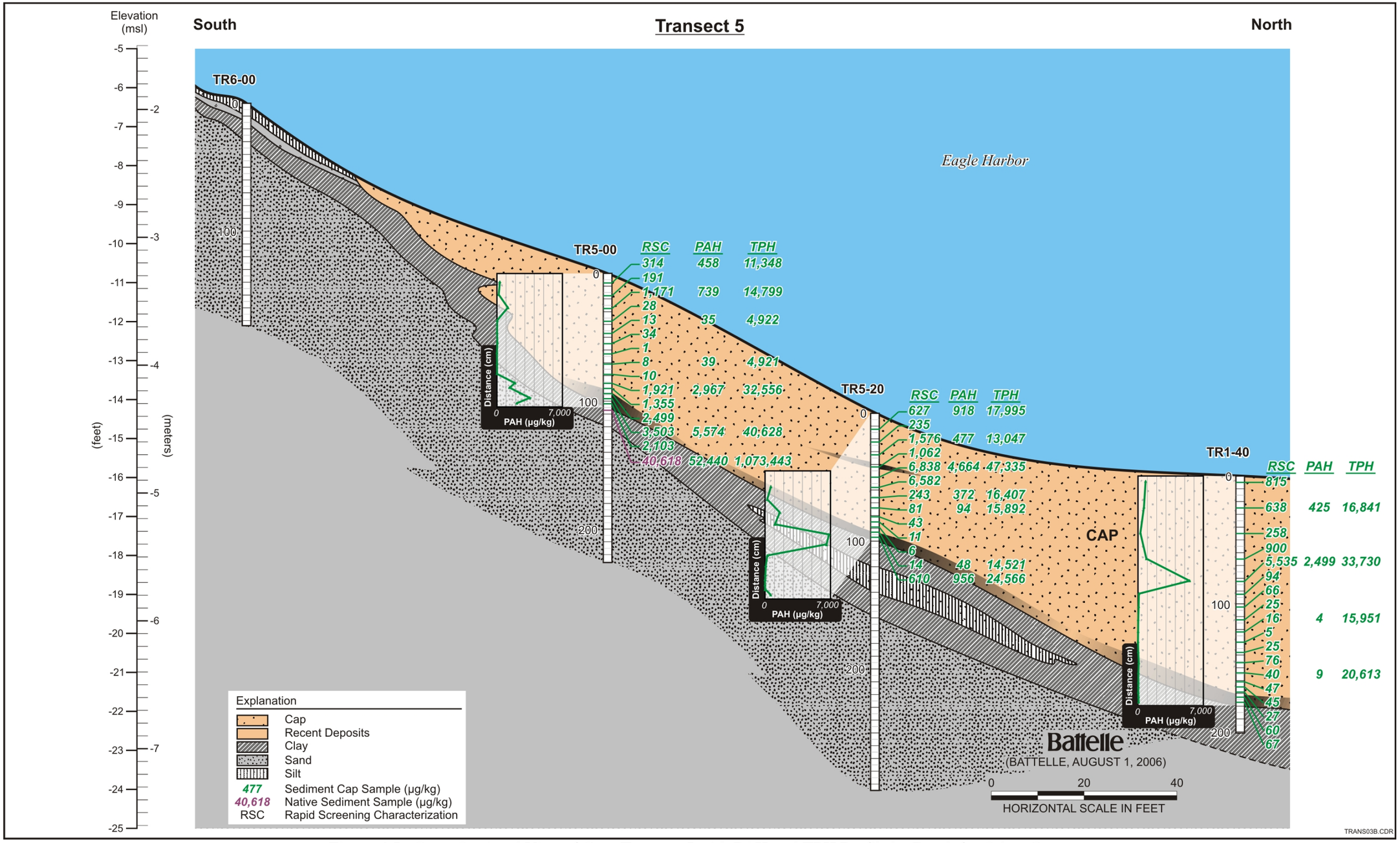

Figure 4-5. Cross Sectional View of Core Transect 5 with PAH and TPH Profile by Depth for Select Cores

4.3 Laboratory Column Experiments

4.3.1 Sediment and Cap Characterization. In preparation of laboratory column experiments, initial PAH characterization was conducted on sediment and cap material samples that were collected prior to the field coring event. The total concentration for 16 U.S. EPA priority pollutant PAHs in the sediment was 1162 ± 108 µg/g. (Concentrations of individual PAHs for bulk sediment and cap material are shown in Figure 4-6). The two to three ring PAHs dominated the distribution in Eagle Harbor sediment. The total PAH concentration in cap material was lower by four orders of magnitude (0.098 ± 0.012 µg/g). The PAH distribution in the cap material was different with more higher molecular weight PAHs present compared to the Eagle Harbor sediments. The Eagle Harbor sediment TOC was found to be 3.40 ± 0.01 % (w/w). Organic carbon concentration of the sand cap (along TR1) was found to be 0.075 ± 0.03 % (w/w). The low TOC and high PAH content of sediment raises an interesting observation — the retention of PAHs by Eagle Harbor sediments may exceed monolayer coverage if an adsorptive mechanism was responsible for PAH retention in these sediments. For tar-impacted manufactured gas plant sites, Hawthorne et al. (2006) showed that the priority pollutant PAHs comprise about 40% of the total PAHs including the major alkylated homologs (a total of 34 PAHs). In this present example, the 16 priority pollutant PAHs comprise approximately 3% of the sediment TOC. While this is significantly lower that the 40% observed by Hawthorne et al. (2006), this observation may indicate that retention of creosote onto Eagle Harbor sediments is not principally dominated by partitioning to an organic matter phase in the sediment. In the absence of a sorbent organic matter phase, the PAH mixture may be present as a separate oil phase that coats the sediment inorganic particles, much like what may be expected from a creosote-contaminated sediment.

Additional evidence of a creosote coating on particles is seen in the data for PAH distribution by particle size class. The distribution of PAHs in different size fractions of the Eagle Harbor sediment and cap are shown in Table 4-2. As shown in Table 4-2, the PAH concentration is higher in the smaller particle sizes indicating a surface coating or surface adsorption phenomenon. The highest PAH concentration of 34,690 µg/g is observed in the smallest particle size range (<63 microns).

Table 4-2. PAH Distribution in Four Size Fractions of Eagle Harbor Sediment

Grain size µm	Weight fraction %	Total PAH µg/g	PAH fraction % by total
> 1700	5	969	2
170 – 1700*	**77**	**846**	**32**
63 - 170	15	2,039	15
< 63	3	34,690	51

*Used for column experiment; TOC content: 3.4 ± 0.01 % by wt.

4.3.2 Sediment-Water Equilibrium Measurement. Batch equilibrium tests were conducted using whole and sieved (180-12 mesh) sediment. As shown in Figure 4-7, the whole

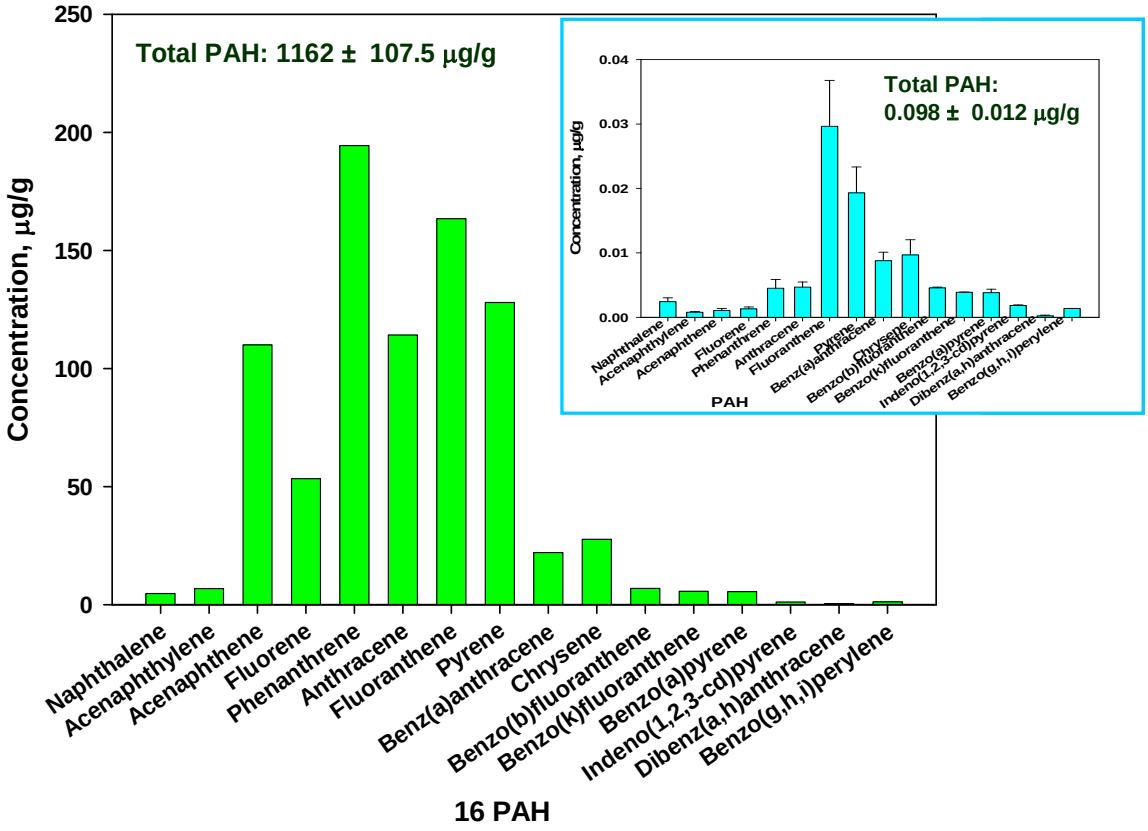

Figure 4-6. The Individual PAH Concentration for Bulk Sediment and Cap Material (inserted)

and sieved sediments gave nearly identical aqueous PAH concentrations. The most abundant PAH in the aqueous phase was acenaphthene followed by phenanthrene and fluorene. The concentration of PAHs larger than chrysene was barely detectable in the aqueous phase. As shown in Figure 4-8, the sieved and bulk TOC normalized solid-water distribution ratios (log K_{TOC}) ranged from 4.3 to 7.1, and were close to the literature values (Mackay et al., 1992).

4.3.3 Sediment Column Studies. Custom made glass columns were constructed for monitoring contaminant transport through sediment and in-place cap material. Initial studies with bulk Eagle Harbor sediment indicated challenges in maintaining uniform flow through the column due to clogging from the clayey fraction. A column composed of the portion of contaminated Eagle Harbor sediment retained on the 180 µm sieve (80 mesh), but passing though the 1.7 mm sieve (12 mesh) was prepared with native overlying cap material. As shown earlier, this sediment size fraction comprised 77% of the sediment mass and gave identical aqueous PAH concentrations as the bulk sediment. Thus, the use of this sediment fraction is not expected to impact the PAH column transport study. Liquid samples were taken from six evenly spaced ports along the column. Typically, these samples were 1.5 mL in volume and placed directly in silanized GC vials using a glass syringe. Prior to collecting a sample, 2 mL of column water was purged to avoid measuring a stagnant pool near the port. Samples were

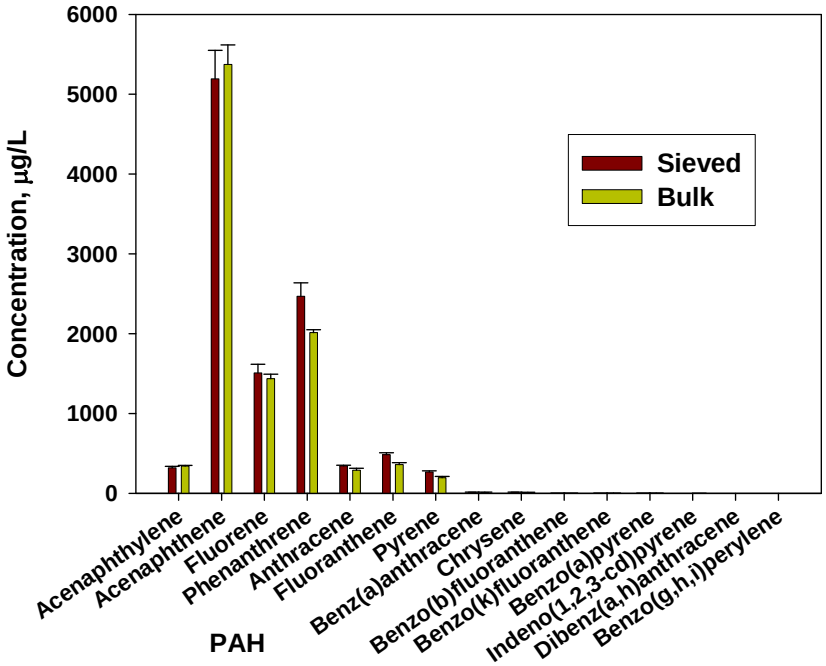

Figure 4-7. Equilibrium Aqueous PAH Concentration for Bulk and Sieved Fraction of PAH Contaminated Eagle Harbor Sediment

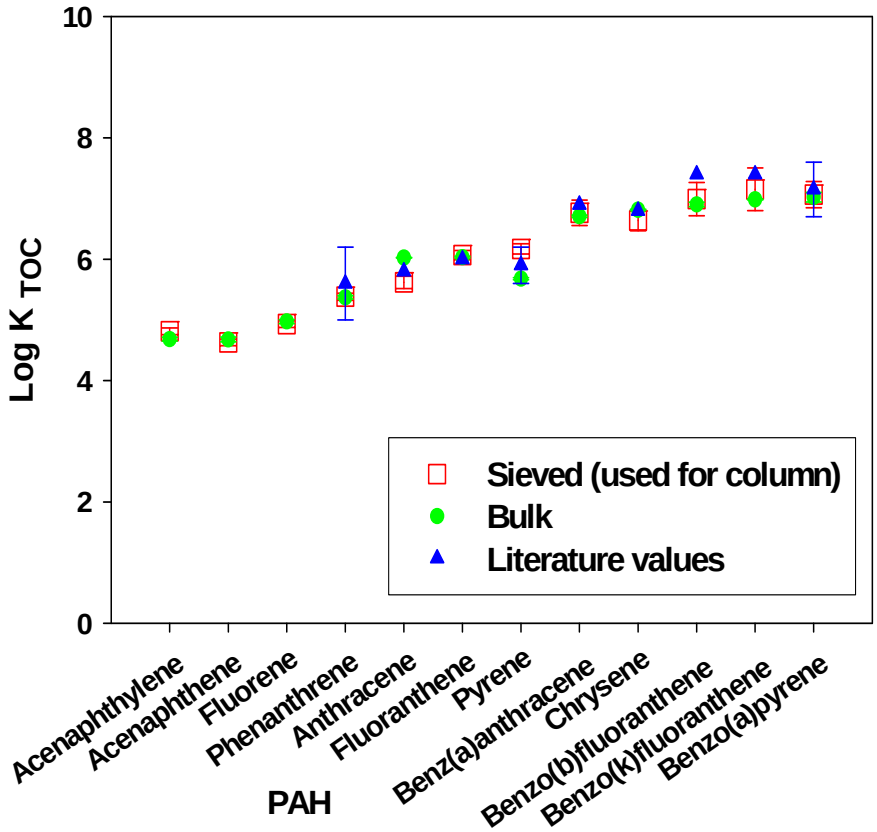

Figure 4-8. TOC Normalized Solid-Water Distribution Ratios (log K_{TOC}) of PAH

sometimes diluted 10 times (so measurements would fall in the linear range of the calibration) or treated using alum flocculation if the sample had a tinted color from suspended fine particles.

SPME was then used to measure 10 PAHs (naphthalene though chrysene). The average flow though the column was about 25 mL/hr over a period of eight weeks. Figures 4-9 and 4-10 show the results of the column tests for PAHs over an 8 week operation period. The results in Figure 4-9 show four orders of magnitude range in concentrations for the different PAH compounds. As observed in the aqueous equilibrium studies, the most abundant PAH in the sediment-cap porewater at the beginning of the study was acenaphthene. The acenaphthene concentration fell by nearly two orders of magnitude over the 8-week period of operation. The apparent rapid breakthrough of all PAHs is possibly due to very low organic matter content and PAH retardation of cap material. Figure 4-10 shows that the concentration of relatively high molecular weight PAH (e.g., chrysene) decreased with increasing height in the cap. Monitoring of the trial column was continued for three months before setting up of additional column studies. A second sediment column was started to evaluate if the process of filling the column with sediments may have resulted in contamination of the upper regions of the column. In the second column setup the contaminated sediment was placed carefully at the bottom using a second tube inserted in the glass column. This process prevented any contact of the sediment with the inner walls of the upper portion of the column during filling. The cap material was also placed carefully with minimum disturbance. Monitoring of the second column is ongoing.

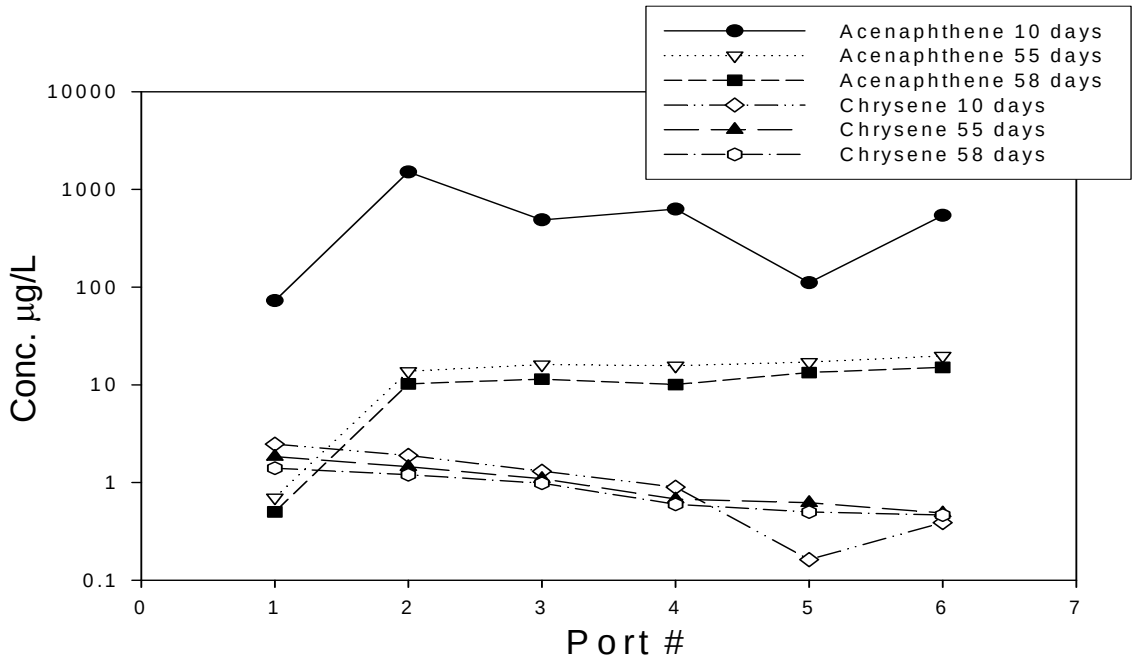

Figure 4-9. Operation Time Dependent PAH Concentration

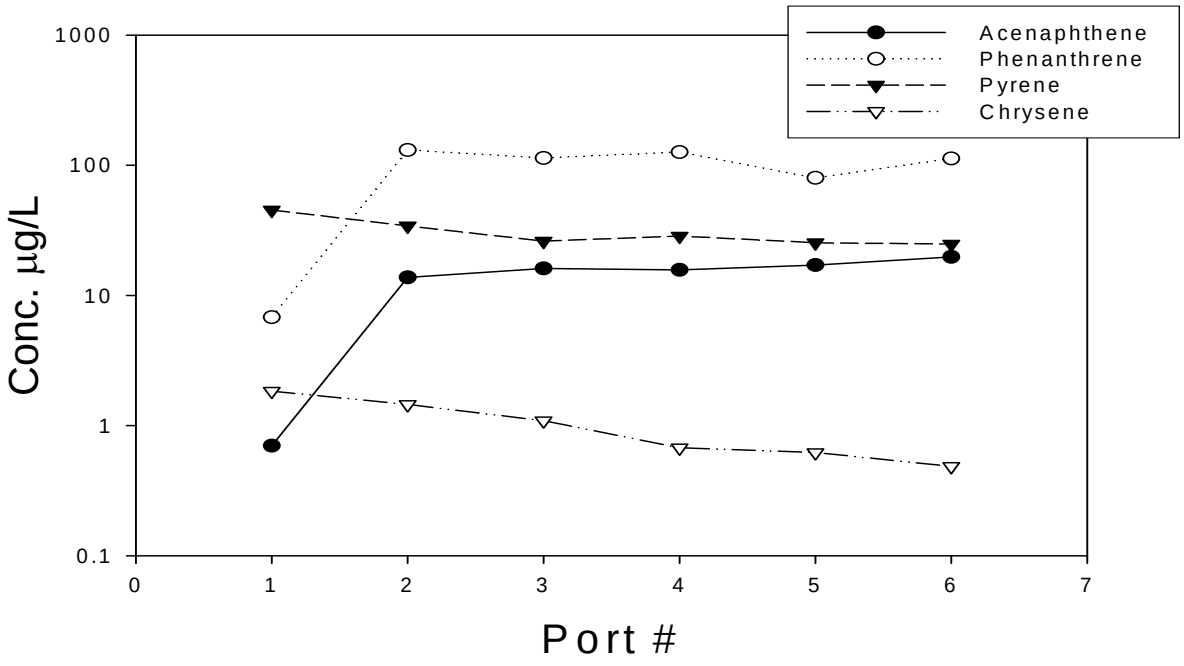

Figure 4-10. PAH Concentration at 55 Days of Operation

5.0 CONCLUSION

With the initial field effort completed, much has been learned about the cap at Eagle Harbor. Initially, it was thought that the engineered cap extended well into the intertidal zone and formed the near shore portion of the beachfront. Through on-site work and further on-site communications with U.S. EPA and USACE and the U.S. EPA's on-site contractor, it was learned that the near shore boundary of the cap occurs near the -10 ft mean sea level contour line at a significant distance from the beachfront. The beachfront is composed of a coarse sand mixture that has distributed broadly across the intertidal zone and seems to form the upper several centimeters of the cap boundary in that area.

The conductivity survey conducted by the dive team verified that there was freshwater upwelling in the intertidal region, but further investigation is necessary to quantify the extent to which this occurs or if there is significant contamination migration in this area, as core collection and analysis efforts were not focused in this area once the cap boundary was identified. Further verifying near-shoreline effects were in-field observations made by the research staff that indicated freshwater permeation on the beachfront at low tide.

A total of 13 cores were collected during this initial investigation and all cores were sectioned and processed into segments starting from approximately 55 cm below the sediment-cap interface and working upwards to the cap surface (cap-water interface). All segments were analyzed using in-field RSC techniques. The RSC method proved to be a successful approach for quantifying the sediment t-PAH profile in real-time, making it an effective decision tool for locating additional core samples. The results from the RSC method paralleled the results produced from the more detailed GC/MS method, and may provide a cost-effective alternative for continued analysis at this site or for future work at the next site.

In selected cores, there appeared to be potential migration or mixing patterns and some indication that there may be other anthropogenic sources contributing to the t-PAH concentration on the cap surface. While potential migration patterns may exist, additional analyses being performed in the lab may provide valuable insight into the mechanisms under which this distribution in the cap profile is taking place. Particle size distribution analyses of select core segments and particle specific sorption isotherm studies, as well as the laboratory column experiments, will be used to further the understanding of the existing data and to develop a numerical model.

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APPENDIX A

Work Plan for “Characterization of Contaminant Transport Potential Through In-Place Sediment Caps” May 2006

WORK PLAN

FOR

CHARACTERIZATION OF CONTAMINANT TRANSPORT POTENTIAL THROUGH IN-PLACE SEDIMENT CAPS

Submitted to:

Strategic Environmental Research
and Development Program

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May 2006

Work Plan Approval Sheet

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Upal Ghosh, UMBC Co-Principal Investigator (UMBC co-PI)

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Brenda Bachman, USACE Coordinator

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ACRONYMS AND ABBREVIATIONS

ASTM	American Society of Testing and Materials
CCV	continuing calibration verification
DCM	dichloromethane
DQC	data quality control
DUP	duplicate
ENVIRON	ENVIRON International Corporation
EPC	electronic pressure controlled
HP	Hewlett Packard
GC/FID	gas chromatograph/flame ionization detector
GC/MS	gas chromatography with mass spectrometry
GPS	Global Position System
K-D	Kuderna-Danish
LCS	laboratory control sample
MDL	method detection limits
MS	matrix spike
N-Evap	nitrogen evaporation
NA	not applicable
NIST	National Institute of Standards and Technology
NPL	National Priorities List
NRMRL	National Risk Management Research Laboratory
NS	native sediment
ORD	Office of Research and Development
ORP	oxidation-reduction potential
PAH	polycyclic aromatic hydrocarbon
PB	procedural blank
PCB	
PI	Principal Investigator
POC	point of contact
PSD	
QA	quality assurance
QC	quality control

RF	response factor
RIS	Recovery Internal Standard
RL	reportable limit
RPD	relative percent difference
RSD	relative standard deviation
SERDP	
SIM	selected ion monitoring
SLN	Sample Location Number
SM	Standards Methods for the Examination of Water and Wastewater
SOP	standard operating procedure
SPAWAR	
t-PAH	total PAH
TOC	total organic carbon
TPH	total petroleum hydrocarbons
TS/VS	total solids/total volatile solids
UMBC	University of Maryland Baltimore
USACE	US Army Corps of Engineers
US EPA	U.S. Environmental Protection Agency

1.0. PROJECT DESCRIPTION AND OBJECTIVES

This Work Plan has been prepared for the field activities that will be performed to examine fate and transport of creosote-based contaminants over time through an existing sediment cap by analyzing sediment cores extracted from the sediment cap at the Wyckoff/Eagle Harbor Superfund Site in Bainbridge Island, Washington (the "Wyckoff/Eagle Harbor site"). The site location is shown on Figure 1-1.

1.1. General Overview

Due to potentially negative impacts of contaminated sediments on aquatic environments and food resources, there is an increasing need to understand their fate and transport, and to identify, develop, and improve sediment management practices that reduce risks to human and environmental receptors. By isolating contaminated sediments, capping can effectively reduce exposure to contaminants and the possibility of contaminant transport into the food chain (Magar, 2001; Palermo et al. 1998; USACE, 1998). However, because contaminated sediments are left in place, caps generally require long-term monitoring, and the risks of contaminant transport or sediment resuspension persist. Many contaminated marine sediment sites reside in shallow, coastal areas that are often impacted by advective processes (i.e., groundwater flow, tidal pumping, and wave pumping), sorption controlled diffusive processes, and bioturbation. These forces contribute to the total flux of contaminants through sediments and ultimately through a sediment cap. A theoretical foundation for contaminant transport through surface sediments exists, but remains untested for sediment caps exposed to advective forces. The scientific and engineering principles of capping need to be improved by testing and validating this theoretical foundation, and by establishing design criteria that account for processes that govern vertical contaminant migration through sediment caps.

To address the above data needs, the following tasks are planned:

1. Measure the influence of porewater flux via groundwater advection and tidal pumping, using continuously monitored piezometers and seepage meters.

2. Examine contaminant mobility over time through existing sediment caps by analyzing sediment cores extracted from existing capped sites.

3. Quantify aqueous contaminant mobility and processes that govern vertical contamination transport through caps using laboratory sediment columns exposed to simulated advective conditions in the field.

4. Evaluate the fundamental mechanisms that contribute to contaminant desorption and transport using particle scale analyses and measurements of aqueous partition coefficients.

5. Evaluate the role of natural organic matter caps and test effectiveness of amending capping materials with sorbents (e.g., activated carbon/charcoal).

6. Use state-of-the art modeling techniques to evaluate transport mechanisms using field and laboratory data and develop a model into an engineering tool for cap evaluation and design.

The field tasks (Tasks 1 and 2) will be conducted at two sites, to study more than one geological condition and more than one contaminant type. The laboratory studies (Tasks 3 through 5) will focus on one cap condition, and will be configured to include contaminants and sediments from each of the first site included in this investigation. The modeling task (Task 6) also only will be applied to the first site using field and laboratory data.

This work plan has been prepared for the Task 2 activities that will be performed to examine the fate and transport of hydrophobic contaminants through a sediment cap at the Wyckoff/Eagle Harbor site. (At later dates, a subsequent work plan will be prepared to address Task 1 field activities, and to address Task 3 through 5 laboratory activities.) This work plan will serve as a guideline for conducting field and laboratory activities. This work plan encompasses all phases of Task 2 to ensure that the specified materials and methods are acceptable and conducive to the production of meaningful test results.

Specifically, this work plan focuses on Task 2 implementation at the Wyckoff/Eagle Harbor Site (Bainbridge Island, WA), identified as Site 1 in the original SERDP proposal. This task will involve measurement of in situ contaminant transport through sediments buried underneath the Eagle Harbor in-place cap through sediment coring and vertical contaminant profiling within selected sediment cores.

1.2. Environmental System

The former Wyckoff wood-treatment facility became operational in the early 1900s. During its operation, large quantities of creosote were used resulting in PAH contamination of Eagle Harbor sediments. Eagle Harbor is a shallow marine embayment of Bainbridge Island, Washington. The island is located approximately 10 miles due west of Seattle, Washington. The Wyckoff/Eagle Harbor site was placed on the National Priorities List (NPL) in 1987 as a Superfund Site. PAH sediment contamination originating from creosote use at the wood

treatment facility has been extensively characterized. The site has been capped to control PAH migration into the water column and surrounding sediments (Figure 1-2).

The Wyckoff/Eagle Harbor site was selected primarily because of its universal properties:

- The site employed a conventional sediment cap, which is the most universally applied cap type.
- The site was contaminated with PAHs which are ideal hydrophobic contaminants for study. The hydrophobic properties of PAHs can be applied to other hydrophobic contaminants of concern, such as PCBs.
- The site is known to have groundwater advective flows and high tides. Virtually all sites have an advective component and those in areas of high tides are likely tidally influenced.

1.3. Study Objectives

The primary objective of this task will be to examine historical contaminant transport at the Wyckoff/Eagle Harbor site and to quantify aqueous PAH transport within the existing sediment cap.

2.0. PROJECT ORGANIZATION

Battelle will be responsible for conducting the field activities associated with this work plan with support from the project team including ENVIRON International Corporation (ENVIRON), University of Maryland Baltimore Campus (UMBC), U.S. Environmental Protection Agency (USEPA), and US Army Corps of Engineers (USACE). This will include sample collection and related field activities, laboratory analyses, data validation and reduction, and preparation of field and laboratory data. The key personnel that will be involved in these efforts, including their responsibilities, are described below. Table 2-1 summarizes the key personnel, their affiliations and responsibilities.

Table 2-1. List of Technical Personnel and Project Responsibilities Wyckoff/Eagle Harbor Site Bainbridge, Washington

Personnel	Location	Phone Number	Project Responsibility(ies)
Dr. Bruce Sass	Battelle, Columbus, OH	(614) 424-6424	Battelle PI
Dr. Victor Magar	ENVIRON, Chicago, IL	(312) 853-9430	ENVIRON PI
Dr. Upal Ghosh	UMBC, Baltimore, MD	(410) 855-4665	UMBC Co-PI
Dr. Marc Mills	U.S. EPA Cincinnati, OH	(513) 569-7322	USEPA Project Coordinator
Ms. Brenda Bachman	USACE, Seattle, WA	(206) 764-3524	USACE Coordinator
Mr. Eric Foote	Battelle, Columbus, OH	(614) 424-7939	Battelle Senior Research Scientist
Ms. Elizabeth Cutie	Battelle, Columbus, OH	(614) 424-4899	Battelle QA Officer

NRMRL = National Risk Management Research Laboratory
PI = Principal Investigator
USACE = United States Army Corps of Engineers

Dr. Bruce Sass *Battelle Principal Investigator (PI).* Dr. Sass will be responsible for work implementation and technical coordination in conjunction with Dr. Victor Magar. Dr. Sass will maintain regular telephone communications with the project team inform the team, including SERDP and USEPA, of technical progress, identify problems that may impede performance, and develop corrective actions to respond to any problems and is responsible for Battelle's performance of the work conducted. Dr. Sass will manage the coordination of all field and analytical work from Battelle's Columbus office (Battelle-Columbus) to ensure that samples are collected, processed, analyzed, and reported in accordance with this work plan. Dr. Sass also is responsible for the final report to be prepared based on the results of this study. Dr. Sass will be assisted by Mr. Eric Foote, who will be primarily responsible for field activity coordination.

Dr. Victor Magar *ENVIRON PI.* Dr. Magar will be responsible for test design and field implementation in conjunction with Dr. Bruce Sass and Eric Foote of Battelle. Dr. Magar will maintain regular telephone communications with the project team inform the team, including SERDP and USEPA, of technical progress, identify problems that may impede performance, and develop corrective actions to respond to any problems and is responsible for Battelle's performance of the work conducted.

Dr. Upal Ghosh *UMBC.* Dr. Ghosh will provide technical input and support throughout the field effort. Dr. Ghosh also will receive sediment materials for Task 3-5 laboratory studies to be conducted at UMBC. Dr. Ghosh is responsible for ensuring that the field activities complement the Task 3-5 laboratory studies, and vice versa.

Dr. Marc Mills *USEPA Project Technical Lead.* Dr. Mills will represent the USEPA Office of Research and Development (ORD). He will oversee efforts concerning the project, coordinate activities with all USEPA staff and will serve as the USEPA point-of-contact (POC) for this work. Dr. Mills also will coordinate activities with USEPA Region 10.

Ms. Brenda Bachman *USACE Coordinator.* Ms. Bachman will assist with site management. She will provide on-site coordination and up-to-date information on the status of the sediment cap. She also will provide expertise in sediment caps and assist with technology transfer. Ms. Bachman also will work with Dr. Mills to coordinate activities with USEPA Region 10. It will be imperative that USACE and USEPA Region 10 concur with the proposed work plan prior to field implementation.

Mr. Eric Foote *Project Field Coordinator* Mr. Foote will be responsible for assisting the Battelle PI with management and coordination of all field and analytical activities. Mr. Foote will assist with sample collection, processing, and shipment of samples from the field to the appropriate laboratory for analysis.

Ms. Elizabeth Cutie *Battelle QAO.* Ms. Cutie will review the analytical data and audit the critical data to ensure that they meet the quality assurance (QA) objectives stated in this work plan. To ensure continuity in the project, Ms. Cutie's QA review will include a review of the critical data reported from all project participants including the various Battelle Laboratories in Columbus, OH and Duxbury, MA, and U.S. EPA field data. Data developed by the UMBC will be the subject of a later work plan or addendum.

3.0. EXPERIMENTAL APPROACH

Table 3-1 identifies both critical and non-critical measurements that will be made during the course of this study, focusing on Task 2. The goal of this task will be to measure the amount of contaminant mass that migrates vertically upward into the sediment cap and the extent of transport toward the cap/water interface, over time. Areas of potential freshwater upwelling will be determined by conducting a field survey consisting of porewater measurements by electrical resistivity. Areas of low conductivity will be considered potential areas of fresh water upwelling. Additional monitoring will be conducted via sediment coring; analysis of cores for porewater conductivity; and contaminant concentration profiling of the core with emphasis placed on profiling within the cap material and the cap-sediment interface.

Table 3-1. Critical and Non-Critical Measurements Wyckoff/Eagle Harbor Site Bainbridge, Washington

Measurement	Method
Critical Measurements	
TPH in sediment	Modified SW-846 8015
PAHs in sediment	Modified SW-846 8270
Particle Size Distribution	ASTM D-422
Bulk Density	ASTM D2937
Moisture Content	Gravimetric Method (modified ASTM D2216)
Noncritical Measurements	
TOC (aqueous)	U.S. EPA 415.1
Total Solids	SM 2540G
Total Volatile Solids	SM 2540G
Porosity	Calculated
Conductivity	Conductivity meter

TPH = Total Petroleum Hydrocarbons
PAH = Polycyclic Aromatic Hydrocarbon
ASTM = American Society of Testing and Materials
TOC = Total Organic Carbon
SM = Standard Methods for the Examination of Water and Wastewater

Sediment coring and solid-phase analyses will be employed to understand the long-term vertical contaminant distribution and transport potential into the cap. Sediment cores will be extracted and segmented into predetermined intervals for total contaminant concentration analyses. Coring locations will be determined based on the porewater survey results and emphasis will be placed on coring in those areas that show potential fresh water upwelling and also in areas where there is no evidence of upwelling. The later may indicate potential migration effects due to tidal influences only.

Once these study areas are established, work will commence to locate and install a piezometer array to monitor advective pore water effects over the period of one-full year. Data will be acquired remotely or by physical downloads from data acquisition points in the system. This will be the emphasis placed on Task 1, which is not included in this work plan. A modified work plan or work plan addendum will be developed for this work as stated previously.

3.1. Field Conductivity Survey

Areas of potential fresh water upwelling will be defined by conducting an in-field survey. Divers will be deployed along three transect lines that will be established in the harbor and will extend from the beach-side to the north (see Appendix B). Each transect will consist of approximately 160 m and will begin at the -10 foot reference to mean sea level contour line. Figure 3-1 shows the three transect locations relative to the beach and historic conductivity contour data captured in previous investigations by EPA (May 2005). Figure 3-2 shows the transect locations in a field-ready version of the same map that will be used for the conductivity survey scheduled to occur June 2006. In Figure 3-2, the site of interest is overlain with a grid that contains state plane (WA North NAD 83) gradations on even 50 foot increments for field use. Conductivity survey sampling locations are shown in Table 3-2 for each of the transect intervals that will be sampled during the survey. These are shown in both state plan and geographical format.

Divers will advance at 10 m increments along the first transect line and electrical resistivity measurements will be recorded in the sand cap at 10 cm depth increments starting at a depth of 10 cm and ending at a depth of 80 cm. The resistivity probe will be advanced into the cap by use of a sledge. Measurements will be recorded along the transect line for the full 160 m. Points along the transect that show evidence of potential fresh water upwelling will be further delineated on the north and south boundary of the transect using 10 m increments. Further delineation of the transect line will be determined if deemed necessary by investigators in the field. After the north and south boundaries of the upwelling area have been established, the divers will advance to the east and west of the transect line to further delineate the extent of the freshening plume. The east and west boundaries will be advanced on 10 m intervals and further refined if deemed necessary.

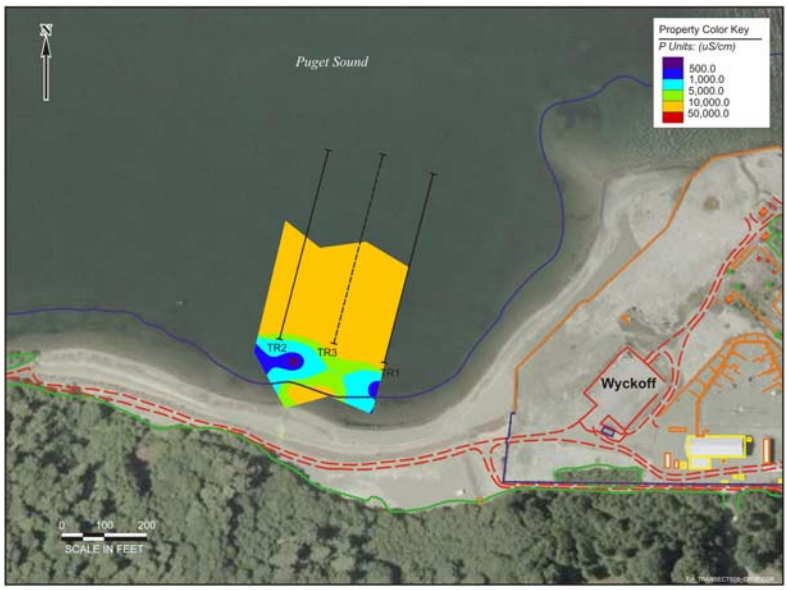

Figure 3-1. Transect Locations for Electrical Resistivity Survey

This procedure will be repeated for the second and third transects if necessary. The goal of the survey is to establish one area of potential upwelling and one area where there is no evidence of upwelling for future study objectives. If these areas are established on the first transect, it may not be necessary to conduct the survey for the remaining two transects. However, if these areas can not be defined on the first attempt, divers will progress to transect 2 and 3. It is envisioned that this survey will take approximately three full dive days to complete.

3.2. Sediment Coring

Once the two study areas have been identified from the field survey as described above, coring activities will commence using an experienced coring contractor familiar with the Eagle Harbor site. Currently, it is envisioned that the coring contractor will be Marine Sampling Technologies, Inc.

Table 3-2. Summary of Conductivity Survey Points in State Plane and Geographic Coordinates

ID	Washington State Plane (North - NAD 83 ft)		Geographic (NAD 83)	
	Easting	Northing	Lat	Long
TR1-00	1228259.985	229329.826	47 36 59.14282	122 30 16.43586
TR1-10	1228268.220	229361.584	47 36 59.45794	122 30 16.32576
TR1-20	1228276.456	229393.342	47 36 59.77306	122 30 16.21564
TR1-30	1228284.691	229425.100	47 37 00.08818	122 30 16.10553
TR1-40	1228292.926	229456.858	47 37 00.40331	122 30 15.99542
TR1-50	1228301.162	229488.616	47 37 00.71843	122 30 15.88530
TR1-60	1228309.397	229520.374	47 37 01.03355	122 30 15.77519
TR1-70	1228317.632	229552.132	47 37 01.34867	122 30 15.66508
TR1-80	1228325.868	229583.890	47 37 01.66379	122 30 15.55496
TR1-90	1228334.103	229615.648	47 37 01.97892	122 30 15.44485
TR1-100	1228342.338	229647.406	47 37 02.29404	122 30 15.33474
TR1-110	1228350.574	229679.164	47 37 02.60916	122 30 15.22461
TR1-120	1228358.809	229710.922	47 37 02.92428	122 30 15.11450
TR1-130	1228367.044	229742.680	47 37 03.23940	122 30 15.00439
TR1-140	1228375.280	229774.438	47 37 03.55452	122 30 14.89427
TR1-150	1228383.515	229806.196	47 37 03.86965	122 30 14.78416
TR1-160	1228391.750	229837.954	47 37 04.18477	122 30 14.67404
TR2-00	1228013.885	229385.522	47 36 59.63961	122 30 20.04483
TR2-10	1228022.120	229417.280	47 36 59.95474	122 30 19.93473
TR2-20	1228030.355	229449.038	47 37 00.26986	122 30 19.82463
TR2-30	1228038.591	229480.796	47 37 00.58498	122 30 19.71451
TR2-40	1228046.826	229512.554	47 37 00.90011	122 30 19.60441
TR2-50	1228055.062	229544.312	47 37 01.21523	122 30 19.49429
TR2-60	1228063.297	229576.071	47 37 01.53036	122 30 19.38419
TR2-70	1228071.532	229607.829	47 37 01.84548	122 30 19.27409
TR2-80	1228079.768	229639.587	47 37 02.16061	122 30 19.16397
TR2-90	1228088.003	229671.345	47 37 02.47573	122 30 19.05387
TR2-100	1228096.238	229703.103	47 37 02.79085	122 30 18.94376
TR2-110	1228104.474	229734.861	47 37 03.10598	122 30 18.83364
TR2-120	1228112.709	229766.619	47 37 03.42110	122 30 18.72354
TR2-130	1228120.944	229798.377	47 37 03.73622	122 30 18.61343
TR2-140	1228129.180	229830.135	47 37 04.05134	122 30 18.50331
TR2-150	1228137.415	229861.893	47 37 04.36647	122 30 18.39321
TR2-160	1228145.650	229893.651	47 37 04.68159	122 30 18.28310
TR3-00	1228141.697	229375.135	47 36 59.56453	122 30 18.17639
TR3-10	1228149.932	229406.893	47 36 59.87965	122 30 18.06629
TR3-20	1228158.167	229438.651	47 37 00.19477	122 30 17.95618
TR3-30	1228166.403	229470.409	47 37 00.50990	122 30 17.84606
TR3-40	1228174.638	229502.167	47 37 00.82502	122 30 17.73596
TR3-50	1228182.873	229533.925	47 37 01.14014	122 30 17.62585
TR3-60	1228191.109	229565.683	47 37 01.45526	122 30 17.51573

ID	Washington State Plane (North - NAD 83 ft)		Geographic (NAD 83)	
	Easting	Northing	Lat	Long
TR3-70	1228199.344	229597.441	47 37 01.77039	122 30 17.40563
TR3-80	1228207.579	229629.199	47 37 02.08551	122 30 17.29552
TR3-90	1228215.815	229660.957	47 37 02.40063	122 30 17.18540
TR3-100	1228224.050	229692.715	47 37 02.71575	122 30 17.07529
TR3-110	1228232.286	229724.473	47 37 03.03088	122 30 16.96517
TR3-120	1228240.521	229756.231	47 37 03.34600	122 30 16.85506
TR3-130	1228248.756	229787.989	47 37 03.66112	122 30 16.74495
TR3-140	1228256.992	229819.747	47 37 03.97624	122 30 16.63483
TR3-150	1228265.227	229851.505	47 37 04.29136	122 30 16.52472
TR3-160	1228273.462	229883.264	47 37 04.60650	122 30 16.41461

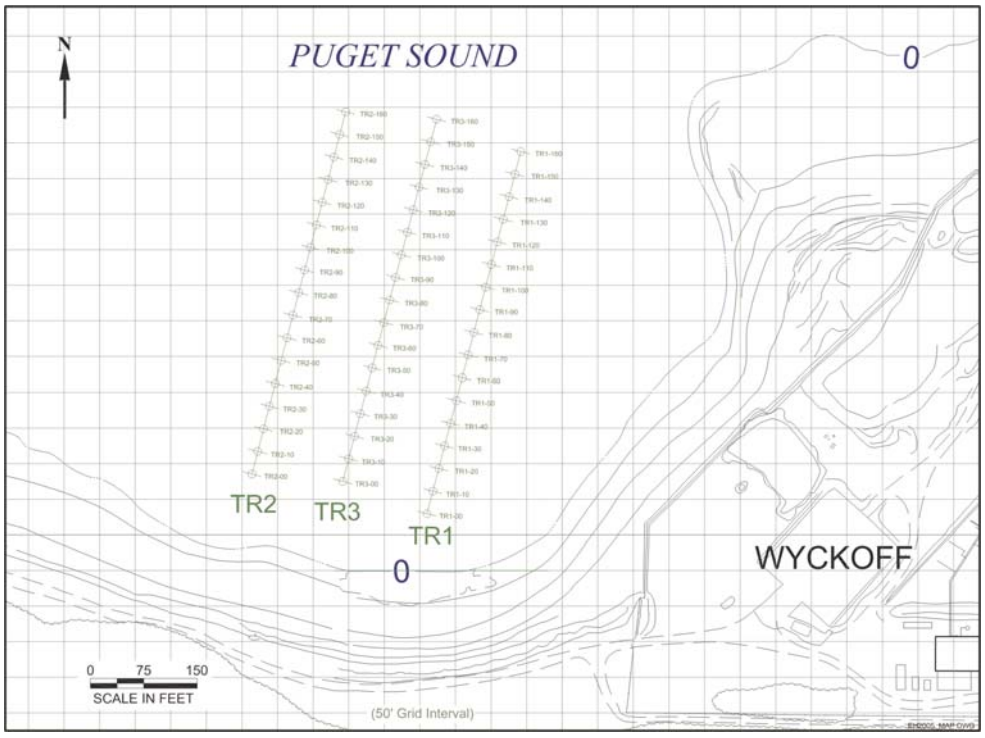

Figure 3-2. Field-Ready Map for June 2006 Conductivity Survey

Sediment cores will be collected in up to three locations in the area of upwelling and in the area with no upwelling (Figure 3-3). The three locations in the area of upwelling will be established from the electrical resistivity data and will be located along the upwelling gradient. A total of two sediment cores will be collected in close proximity to each other (approximately 3 m distance) at each of the three coring locations for a total of six sediment cores in the upwelling study area.

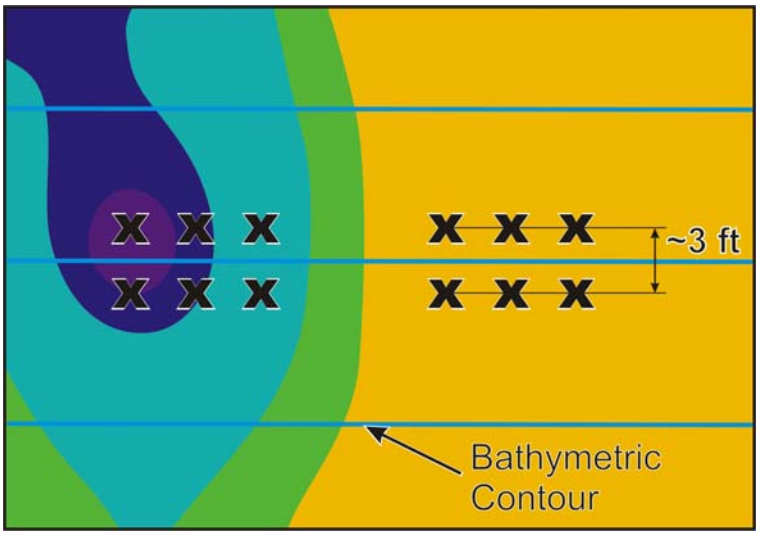

Figure 3-3. Conceptual Plan for Sediment Coring Locations

Likewise, six sediment cores will be collected from the study area devoid of upwelling. Sediment core locations in this area will be modeled of similar distances described above, since there will be no upwelling gradient to contour in this area. All twelve samples will be collected at similar bathymetric contour to avoid variability due to water depth.

Coring through the sand cap will require a vibratory coring device. Penetration through as much as 3 ft (180 cm) of sand plus 1 to 2 ft (30 to 60 cm) of native sediment will be required. It is the goal during sampling to collect cores that intersect the cap/sediment interface.

A Global Positioning System (GPS) on the coring vessel will be used to define longitudinal and latitudinal coordinates for each sampling location. Prior to the GPS being used at the study site, it will be checked against a reference location's coordinates. Acceptable GPS performance readings will be based on the reported accuracy of the instrument. Each sampling location will be identified by GPS coordinates and a unique Sample Location Number (SLN). The sediment sampling locations will start with SLN-01 and increase numerically until all sampling locations have been identified. If a core is pulled but not used because the sediment core was deemed unsuitable for the study, the SLN identifier for that location will still have its unique coordinates but no sediment core. It will therefore be possible to have SLNs greater than the total number of cores collected for analysis.

The time of day and water depth at each sampling location will be recorded before and after collecting each sediment core. When the sediment cores are brought to the surface, they will be inspected. The sample location number, GPS coordinates, date and time, depth of the water column, and any observations associated with the sampling at that location will be made in the field notebook.

Dr. Magar and Dr. Sass will make the decision, with consultation from the other team members, on the acceptability of the sediment cores. If a core is collected that does not intersect the cap/native sediment interface, it will be returned to the sediment cap, providing that no native material is present within the core. On the other hand, if a core is collected and does intersect the cap/native sediment interface, but still is rejected, sediments cannot be returned to the harbor. Rejected cores that exhibit any indications of hydrocarbon contamination will be disposed of at a designated on-site location.

3.3. Sediment Core Processing and On-Site Analyses

Sediment cores will be brought on shore to an on-site staging area that will be established at the former Wycoff-Eagle Harbor area. Each core will be held vertically through transit and processed immediately upon receipt. In vertical position, a series of small holes will be drilled into the core tube starting at the top immediately above the sediment water interface in an effort to drain head water. Following this the extraneous tube material will be removed.

Starting at a distance of 15 cm from the top of the core tube, and sequentially every 15 cm thereafter, a small hole will be drilled into the tube and tapped to drain and collect porewater from each increment. The electrical resistivity of the core porewater will be measured immediately using an on-site conductivity meter and recorded in a field notebook.

Once core porewater measurements are complete, the core will be laid horizontally into a prefashioned rack and the tube will be opened along the core length using a circular saw. The cap-sediment interface will be defined and the sediment phases will be defined and recorded in the field record book.

Cores that intersect the cap/sediment interface will be prepared for sectioning and placement into sampling containers. The goal of this study is to identify the extent of vertical migration of PAH into the sediment cap. It also must be recognized that sediment mixing zone likely exists at the cap/native sediment interface; this mixing zone may be several cm thick and may confound the interpretation of dissolved vertical PAH migration into the sediment cap at the interface. To better understand the mixing zone, photographs will be taken of the core before and after sectioning, focusing on the interface, and observations describing the interface will be recorded in the log book for each sediment core.

The mixing zone and physical characteristics of the interface will influence the core sectioning performed on site. In general, each core will be sectioned into increments above and below the cap-sediment interface. Since it is of most interest to determine contaminant portioning into the cap, the entire cap section will be sectioned. Approximately three total segments will be acquired from the sediment portion of the core. The samples will be incremented to capture the length of each core, such that sample resolution will be finer near the

cap-sediment interface and will become courser with distance from the interface and approaching the cap-water interface. At each location, the cap surface 5 cm also will be characterized and sampled to understand surface cap characteristics at the site.

Sediment segments will be collected using disposable wooden spatulas (e.g. sterile medical tongue depressors) at each predetermined interval; predetermined volumes/sediment mass will be placed into appropriately sized glass containers. In general, the sediment-cap interface will serve as the zero point of reference for core segmenting. The core will be segmented into ten 1-cm intervals for the first 10 cm above the sediment-cap interface (i.e. 0 to +10 cm); ten 2-cm intervals from the +10 cm to +30 cm, and twelve 5-cm intervals from the +30 cm to +90 cm range. Below the sediment-cap interface, the core will be segmented into one 2-cm interval from -5 cm to -7cm ; and one 5 cm interval from -50 cm to -55 cm. Figure 3-4 shows the planned core segmentation. This plan is summarized in Table 3-3. Core processing efforts will result in a total of 32 segments per core. Each segment will be submitted for in-field rapid screening characterization (RSC). RSC will be used to identify a total of 10 segments per core or 60 total segment samples that will be submitted to the laboratory for PAH and TPH analysis using gas chromatography/mass spectrometry (GC/MS). Details of these analyses are further described in Section 5.0 of this work plan.

The planned segmentation must be flexible and is subject to change in the field. Reasons for changing the segmentation include a deeper cap-native sediment mixing zone than anticipated, or the absence of PAHs in the cap sediment.

Core diameters will be as large as practicable for the coring contractor to core through the sand cap, and to ensure backfill and collapse of the cap after coring; tentatively 10-cm core diameters are planned. The larger core diameter provides more sediment sample material for the suite of analyses planed for each segment. A conservative bulk density for wet sediments is approximately 1.0 g/cm^3, and for dried sediments it is approximately 0.50 g/cm^3. Based on these bulk densities, and assuming a 9-cm nominal diameter (due to loss of the outer 1 cm), each 1-cm interval of sediment should contain approximately 63.6 cm^3 or grams of wet sediment or approximately 31.8 cm^3 or grams of dry sediment.

Core segments for PAH and TPH analysis will also be analyzed for total organic carbon (TOC), particle size distribution (one select cap material sample and one select sediment sample per core) and mineralogy analysis (one select cap material and one select sediment material per core).

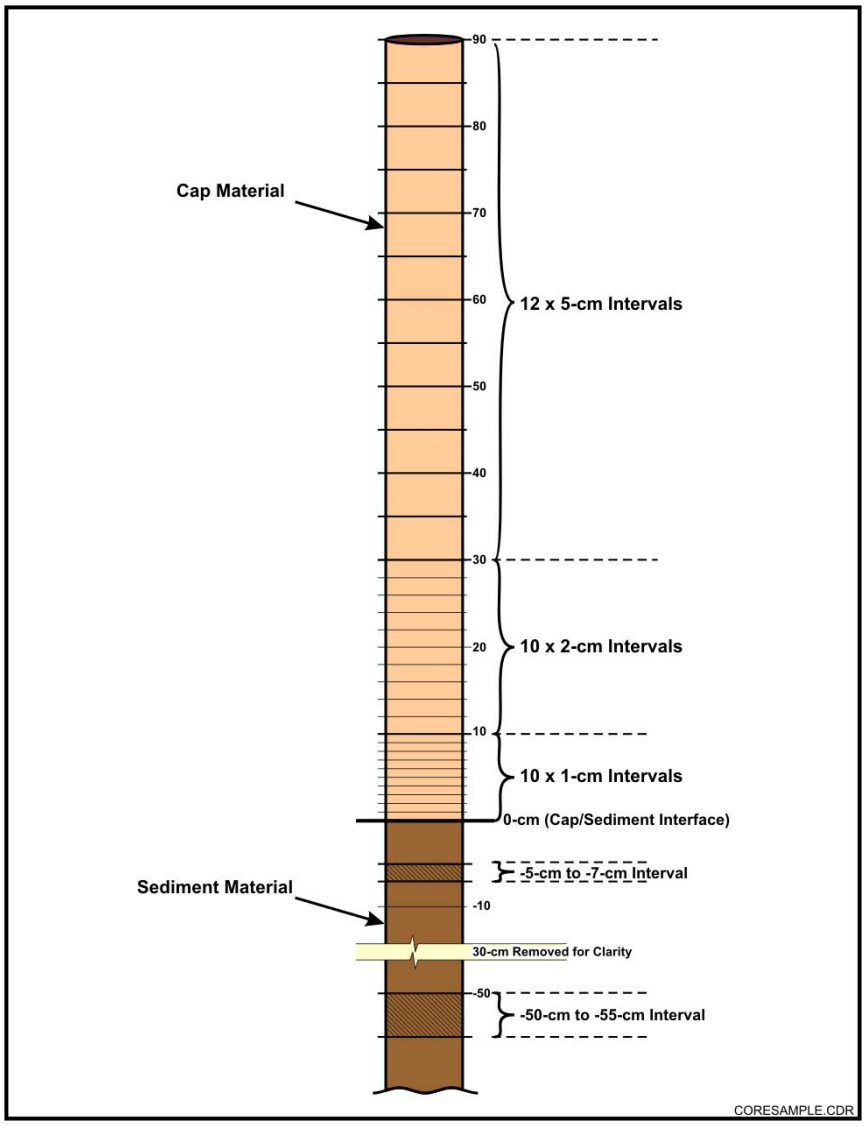

Figure 3-4. Sediment Core Processing Plan (Segmentation)

3.4. In-field Core Measurements

As mentioned previously, core porewater will be measured for electrical resistivity using an Orion Model 96-78-00 meter and electrical conductivity probe.

RSC will be conducted in the field and will be led by staff from the U.S. Navy Space and Naval Warfare Systems Center (SPAWAR). PAH screening will be conducted using Enzyme-Linked Immuno Sorbent Assay (ELISA) by EPA Method 4035. The ELISA kits for this work will be purchased from Scientific Diagnostics Inc. (SDI).

Table 3-3. Summary of Sediment Core Segments per Core for RSC

Depth Relative to Cap-Sediment Interphase (cm)	Interval Thickness (Segment Thickness) cm	Number of Samples/Core
0 to +10	1	10
+10 to +30	2	10
+30 to +90	5	12
-5 to -7	2	1
-50 to -55	5	1
Total	**NA**	**34**

3.5. Sampling Equipment Decontamination

Following the collection, inspection, and segmentation of a sediment core, the sampling equipment will undergo a decontamination process. The bulk of any sediment material that has adhered to the coring equipment will be scraped from the equipment into a containment bucket.

If the sediment displays any indication of hydrocarbon contamination, it will be held for proper disposal at the designated on-site location. Cap material that is not impacted by the native sediment will be assumed not to be contaminated and can be returned offshore to the cap surface.

Coring equipment will first be rinsed with harbor water to remove any remaining sediment. Next, the water-rinsed equipment will be cleaned with methanol to remove hydrocarbon contaminants. The methanol rinsate will be reserved for proper disposal. Finally, the equipment will be rinsed again with harbor water before it is used to collect the next sediment core. This saltwater rinsate will be reserved since it may contain residual methanol. This aqueous material will be included with the methanol rinsate for disposal. Any hand-held equipment used during core inspection or segmentation will undergo the same decontamination process, except for probes that may be damaged by direct contact with methanol. Such probes will be rinsed copiously with harbor water.

3.6. Summary of Sediment Sampling Activities

The sediment sampling activities are summarized in Table 3-4. Included in the table are the types of analyses to be performed, the number of analyses for each matrix associated with the task, and the frequency for performing the analyses.

Table 3-4. Summary of Sediment Analytical Activities for Wyckoff/Eagle Harbor Site Bainbridge, Washington

Measurement	Number of Samples/Event	Responsible Party
TPH in sediment	Ten samples per core	Battelle
PAHs in sediment	Ten samples per core	Battelle
PSD	Two samples per core (one in the cap material and one in the sediment)	UMBC
TOC	Ten samples per core	UMBC
Bulk Density	Ten samples per core	Battelle
Moisture Content	Ten samples per core	Battelle
Mineralogy	Two samples per core (one in the cap material and one in the sediment)	Battelle

TPH = Total Petroleum Hydrocarbons
PAH = Polycyclic Aromatic Hydrocarbon
PSD = particle size distribution
TOC = total organic carbon

4.0. SAMPLING PROCEDURES

This section describes sample handling procedures, including sample labeling, preservation, custody, shipping, and processing for PAH and TPH analyses.

4.1. Sediment Sample Labeling Procedures

Sediment samples will be identified with the information listed below. Labels will be attached to the sampling containers prior to their shipment. The label will include:

- *Sample Location Number (SLN)*: The SLN will be the primary sample identifier.
- Cap versus Native Sediment: "C" will be used for cap material above the cap/native sediment interface, and "NS" will be used for native sediment below the cap/native sediment interface.
- *Core Segment Code*: This identifier will include the SLN along with the depth above or below the cap/native sediment interface.
- *Date/Time*: The date and time of sample collection will be documented.
- *Sampler Initials*: The initials of the person responsible for filling out each sample label and preparation of samples for shipment will be identified
- *Sample Destination*: The sample destination will be identified.

Segments will be identified by depth beginning at the cap/native sediment interface, and by whether the material is in the cap (C) or the native sediment (NS). An example of a sediment identification code from the bottom of the core from SERDP-1 would be SERDP-1-C-0005 or SERDP-1-NS-0005 for 5 cm above or below the interface, respectively; mixing zones will be assumed to be part of the cap. For example, as segments are delineated, the sample identification would be SERDP-1-C-0005, SERDP-1-C-0015, SERDP-1-0250 for segments at 5 cm, 15 cm, and 250 cm above the interface and in the cap, and SERDP-1-NS-0005, SERDP-1-NS-0015 for sediments below the interface in the native sediment.

4.2. Sediment Sample Preservation and Shipping Requirements

Table 4-1 outlines the methods of analysis, sample volume requirements, sample preservation, and holding times for each of the analyses to be conducted for this study.

Table 4-1. Analyte Sample Methods, Volumes, Preservations, and Holding Times Wyckoff/Eagle Harbor Site Bainbridge, Washington

Analyte	Matrix	Method	Wet Weight or Liquid Volume	Container Type	Preservation	Holding Time
Off-Site Laboratory Analyses						
TPH in sediment	Sediment	Modified SW-846 8015	50 g (wet[a])	Amber glass with Teflon™-lined cap	Cool, 4°C	14 days
PAHs in sediment	Sediment	Modified SW-846 8270	50 g (wet[a])	Amber glass with Teflon™-lined cap	Cool, 4°C	7 days/ 40 days[b]
Particle Size Distribution	Sediment	ASTM D-422	100 g	Plastic	NA	28 days
Bulk Density	Sediment	ASTM D2937	300 g	Glass with Teflon™-lined cap	Cool, 4°C	14 days
Moisture Content	Sediment	Gravimetric Method (modified ASTM D2216)	300 g	Glass with Teflon™-lined cap	Cool, 4°C	14 days
TOC (aqueous)	Sediment	U.S. EPA 415.1	20 g	Whirl-Pak™ bags	Cool, 4°C	28 days
Total Solids	Sediment	SM 2540G	25 g	Glass with Teflon™-lined cap	Cool, 4°C	7 days
Total Volatile Solids	Sediment	SM 2540G	10 g	Glass with Teflon™-lined cap	Cool, 4°C	7 days
Field Analyses						
RSC	Sediment	EPA Method 4035	NA	NA	NA	Immediately
Conductivity	Sediment	Conductivity meter	NA	NA	NA	Immediately

(c) A single extraction will be conducted for both TPH and PAH analyses, requiring a total of 50 g sediment for both analyses.
(d) Extractions must be complete within 7 days, and GC/MS analysis must be complete within 40 days.
TPH = Total Petroleum Hydrocarbons
PAH = Polycyclic Aromatic Hydrocarbon
ASTM = American Society of Testing and Materials
NA = Not applicable.
TOC = Total Organic Carbon
SM = Standard Methods for the Examination of Water and Wastewater
RSC = Rapid screening characterization

4.3. Sediment Sample Custody

Chain-of-custody procedures will be implemented following the attached chain-of-custody standard operating procedure to track sample movements and to assign responsibility for all stages of sample handling. Chain-of-custody forms will be used for all samples that are submitted for off-site analyses. All fields will be completed appropriately to reflect the source of the sample, date and time of sample collection, sample matrix, and requested analyses.

4.4. Sediment Sample Shipments and Receipt

All sample containers will be labeled, and labels will be sealed with clear tape. Bottle containers will be wrapped in bubble wrap to reduce the potential for breakage before being placed into a cooler. The coolers will be packed with blue ice or equivalent. Loose ice will be packaged into plastic zip-lock bags to prevent spillage.

The completed chain-of-custody form will be placed in a zip-lock bag and taped to the inside top of the cooler. Coolers will be taped shut prior to shipment. Upon sample receipt, the Sample Custodian will verify that all samples indicated on the chain-of-custody form are included and intact. Sample label identifications will be checked against the chain-of-custody form and the samples will be logged into the laboratory sample receipt log. Any discrepancies will be noted by the sample custodian and the PIs will be notified immediately. The chain-of-custody record will remain with the sample from the time of preparation through analysis and final disposition. Upon arrival at each laboratory, the sample custodian will log in the samples, check for and resolve any discrepancies, and provide unique laboratory identifications. Samples will be stored at or below 4°C upon arrival.

4.5 Sediment Sample Processing and Extraction

Given holding time constraints, samples will be prepared and extracted within 14 days of their collection date. The extracts from each sample matrix will be analyzed for PAHs and TPH within 40 days of their extraction. General physical observations of the samples (e.g., color, visible grain size, and presence of plant/wood debris) will be made and recorded in the laboratory prep records.

Sediment samples will be prepared for analysis according to modified USEPA SW846 Methods 3550, 3611, and 3660 procedures described herein. The Battelle SOP 5-190-05 (*Tissue and Sediment Extraction for Trace Level Semi-Volatile Organic Contaminant Analysis)* for this extraction method is found in Appendix A. The method and any modifications are briefly described below.

Appropriate concentrations of surrogate internal standards (SIS) will be added to the sample to be extracted to allow accurate measurement of target organic compounds. The SIS compounds to be added are *o*-terphenyl, naphthalene-d_8, phenanthrene-d_{10}, and chrysene-d_{12}.

Anhydrous sodium sulfate will be added to absorb water from the samples and facilitate the extraction with an organic solvent. Additionally, activated copper will be added to sediment samples to complex any sulfur that may be present in the samples. The sediment homogenates will be shaken/tumbled for a minimum of 12 hours with 100 mL of dichloromethane (DCM). The sample/solvent will be centrifuged, and then the solvent will be decanted into a pre-cleaned, labeled, Erlenmeyer flask. The same sediment will have another 100-mL aliquot of DCM added, it will be again be shaken/tumbled for a period of at least one hour, and the solvent removed as before. A third and final 100 mL of DCM will be added to the sediment, and after another one-hour extraction, the sample will again be centrifuged and this solvent will be combined with the two previous aliquots. The combined extracts will be filtered and dried through a glass fiber filter containing sodium sulfate. The filtered/dried extract volume will be reduced to a final sample volume of 1 mL by using a Kuderna-Danish (K-D) concentrator at approximately 60-65°C and nitrogen evaporation (N-Evap) techniques.

An aliquot of the concentrated extract will be weighed and then processed through a 20-g alumina (2% deactivated F20) column to obtain a combined aliphatic and aromatic/unsaturated hydrocarbon fraction (F_1+F_2). The combined F_1 and F_2 fraction will be eluted from the alumina column with 100 mL of DCM. The combined F_1/F_2 fraction will be concentrated to 1 mL using the K-D and N-Evap techniques described above. The concentrated F_1/F_2 fraction will be treated once again with activated granular copper to complex any remaining sulfur, and then spiked with appropriate concentrations of Recovery Internal Standard (RIS) containing 5α-androstane, acenaphthene-d_{10}, fluorene-$d_{10,}$ and benzo[a]pyrene-d_{12} in preparation for TPH and PAH analysis.

The following quality control samples will be processed along with each batch of sediment samples:

1 laboratory control sample (LCS)
1 procedural blank (PB)
1 duplicate (DUP)
1 matrix spike (MS)

5.0. TESTING AND MEASURMENT PROTOCOLS

5.1. In-Field Assay (RSC)

RSC will be conducted using the SOP in Appendix A of this work plan. The sample (with the *unknown contaminant concentration*; ex. PCB) is analyzed by the addition of an enzyme conjugate (labeled PCB). This is followed by addition of paramagnetic particles with anti-bodies specific to "both" PCBs. In relatively proportional concentrations, both the sample PCBs and the "labeled" PCBs (conjugate) compete for the binding sites on the magnetic particles. After an incubation period, a magnetic field is applied to hold (in-place) the magnetic particles having the sample PCB and its "labeled" PCB analog to bind with the antibodies. Any unbound reagents are decanted and washed repeatedly. PCBs in the mixture are detected with the addition of an enzyme substrate (color solution) containing a chromagen which specifically reacts to the "labelled" PCBs. After another incubation, the reaction is stopped and stabilized by addition of acid (stopping solution). Since the labelled PCBs and sample PCBs are in competition (proportionally) with the binding sites, the color developed at the end of reaction is inversely proportional to the concentration of PCBs in the sample. This color response is measured by a spectrophotometer (set at 450 nm) and compared to the responses taken from a calibrated series of known PCB standards (kit-supplied) to determine the equivalent PCB (as Aroclor 1254) concentration of the sample.

5.2. PAH Analysis

Splits of the same sediment extracts will be analyzed for the concentration of 34 PAH analytes by Battelle-Duxbury using a modified SW-846 8270 method. This method employs high-resolution capillary gas chromatography with mass spectrometry (GC/MS) with analysis according to BOS SOP 5-157, *Identification and Quantitation of Polynuclear Aromatic Hydrocarbons (PAH) by Gas Chromatography/Mass Spectrometry*. The analytical system is comprised of a Hewlett Packard (HP) 6890 GC, equipped with an electronic pressure controlled (EPC) inlet and an HP 5973 MSD operating in the selected ion monitoring (SIM) mode. A minimum of a 5-point response factor calibration will be run with analyte concentrations in the standard solutions ranging from approximately 0.005 ng/μL to approximately 10 ng/μL. The samples will be bracketed by passing continuing calibration checks analyzed at the beginning and end of each 12-h period and at the completion of the sequence.

Quantification of individual compounds will be performed by the method of internal standards using the deuterated PAH internal standards. Total PAH will be determined as the sum of the individual PAH and alkylated PAH analytes. The homologous series of alkylated PAH (multi-component analytes) will be quantified using the response factor of the parent PAH or most appropriate alkyl PAH available in calibration standards. The biomarker (17α(H),21β(H)-hopane) will be included in the analysis in the event that it proves useful as a conservative internal marker compound. The available method detection limits (MDLs) for the PAH analytes in sediment and aqueous matrixes are listed in Appendix D.

5.3. TPH Analysis

Sample extracts will also be analyzed for the Total Petroleum Hydrocaarbons (TPH) at Battelle-Duxbury using a BOS SOP 5-202, *Determination of Low-Level Total Petroleum Hydrocarbon and Individual Hydrocarbon Concentrations in Environmental Samples Using GC/FID*. This method, a modification of SW-846 Method 8015D, employs high-resolution capillary gas chromatography with flame ionization detection (GC-FID). TPH will be measured on an Agilent 5890 GC, equipped with an electronic pressure controlled (EPC) inlet and dual FID detectors. A successful linear calibration using a minimum of five calibration levels ranging from approximately 1 μg/μL to approximately 200 μg/μL individual saturated hydrocarbons will be run before the analysis of samples. The samples will be bracketed by passing continuing calibration checks analyzed at the beginning and end of each 12-h period and at the completion of the sequence.

TPH is defined as resolved plus unresolved hydrocarbons and includes gasoline range, diesel range, and higher molecular weight hydrocarbons in the C_8 through C_{40} to volatility range. TPH quantification will be performed by the method of internal standards. D_{42}-eicosane and d_{62}-triacontane serve as the internal standards (IS) and are present in at ~ 50 μg/mL in all calibration solutions and sample extracts. TPH concentrations are corrected for the amounts of IS and surrogate internal standards added to each sample. The individual saturated hydrocarbon fingerprint can be used for product identification should it be useful. The TPH method detection limit is approximately 4 mg/kg.

5.4. Sediment Moisture Content/Dry Weight Analysis

The moisture content of each sediment sample will be determined by Battelle-Duxbury during analytical extraction using a modified version of American Society for Testing and Materials (ASTM) Method D2216. The method is modified as follows: approximately 5 to 10 g of sediment will be placed in a pre-weighed, aluminum weighing pan. The weight will be recorded (initial weight), and the pan will be placed in a drying oven at 110±5°C. The sample will be dried to constant weight (overnight), cooled in a desiccator for at least 30 minutes, and weighed again (dry weight). The sediment moisture content will be calculated as [1-(dry weight/initial weight)] × 100%. The percent dry weight will be calculated as (dry weight/initial wet weight) × 100%.

5.5. Particle Size Distribution and Total Organic Carbon Analyses

PSD will be determined for one sediment segment and one cap material segment per each core. TOC will be determined for each sediment segments from each sediment core. These analyses will be performed by UMBC. Zip-lock bags containing samples for PSD analysis and Whirl-Pak™ bags containing a homogenized aliquot of the sediment for TOC analysis will be shipped cold with chain-of-custody documentation.

PSD will be determined according to ASTM D422-*Standard Method for Particle-Size Analysis of Soils*. Data will be reported as weight percentages of gravel (> 4.74 mm diameter), sand (4.75-0.74 mm diameter), silt (0.74-0.005 mm diameter), and clay (< 0.005 mm diameter). TOC will be determined according to EPA Method 9060-*Total Organic Carbon*.

5.6. Field Measurements

5.6.1. Electrical Resistivity Survey

The performance of the conductivity probe will be determined in the field by checking readings in dionized water (~0 mS/cm) and in harbor water (~ 50mS/cm).

5.6.2. Core Porewater Conductivity Measurements. Sediment porewater samples will be obtained from vertical cores prior to core processing and will be measured for conductivity on site using a portable Orion Model 96-78-00 conductivity probe and meter. The meter will be calibrated prior to use according to the manufacturer's instructions.

6.0. PROCEDURES

As shown in Table 6-1, this project will have five critical measurements: TPH concentrations, PAH concentrations, particle size distribution, bulk density, and moisture content. The precision and accuracy of these critical measurements will be verified. Table 6-1 outlines the acceptance criteria for data quality objectives. Tables 6-2 through 6-4 describe the QC checks, methods, frequencies, acceptance criteria, and corrective actions for each of the five critical measurements. Table 6-5 presents the GC/FID and GC/MS calibration criteria. Acceptance criteria in these tables supersede the acceptance criteria stated in the SOPs appended to this work plan.

For analysis of TPH and PAHs, analytical precision will be performed through the analysis of sample duplicates, and accuracy will be quantified through the analysis of LCS, SIS, PB, and MS samples. QC samples will be prepared at a frequency of 1 per 20 or fewer authentic samples. The quantification of accuracy for soil moisture content will be determined by a balance calibration check. The quantification of sediment dating will be determined by analyses of LCS, a reference material and duplicates.

Table 6-1. QA Objectives for method Detection Limits, Precision, Accuracy, and Completeness Wyckoff/Eagle Harbor Site Bainbridge, Washington

Analyte	Matrix	Units	Method Detection Limit	Precision	Accuracy	Completeness
TPH in sediment	Sediment	mg TPH/kg dry sediment	1.11 mg/kg	See Table 6-2		80%
PAHs in sediment	Sediment	mg PAH/kg dry sediment	See Appendix D	See Table 6-3		80%
Particle Size Distribution	Sediment	%	See Method ASTM D-422	See Table 6-4		80%
Bulk Density	Sediment	g dry sediment/mL sample	Instrument Sensitivity, 0.0001 g	NA		80%
Moisture Content	Sediment	%	Instrument Sensitivity, 0.0001 g	Specified by Outside Laboratory		80%

TPH = Total Petroleum Hydrocarbons; PAH = Polycyclic Aromatic Hydrocarbon; ASTM = American Society of Testing and Materials
NA = Not applicable

Table 6-2. Summary of TPH Sediment Sample QC Checks Wyckoff/Eagle Harbor Site Bainbridge, Washington

Matrix	QC Check	Method	Frequency	Acceptance Criteria	Corrective Action
Sediment	Surrogates	Spiking[(a)]	All samples and all blanks	40 to 120% recovery OTP	In case of occasional violation of acceptance criteria, the violating data will be flagged. The Work Assignment Leader will decide whether to re-extract/re-analyze sample. In the case of frequent violation (>10% samples), the problem will be investigated, and the whole sample set will be rerun.
Sediment	Duplicate	Split homogenized sample at analytical lab prior to processing	One per batch (no more than 20 samples)	±30% RPD if concentration >5× MDL	
Sediment	Matrix spike	Spiking[(a, b)]	One per batch (no more than 20 samples)	40 to 120% recovery if amount spiked > 5× background	Investigate problems, evaluate data for usability, re-analyze matrix spike or blank.
Sodium sulfate, Ottawa Sand, and extraction solvent	Laboratory Control Sample (LCS)	Spiking[(a, b)]	One per batch (no more than 20 samples)	40 to 120% recovery	
Sodium sulfate and extraction solvent	Procedural Blank	Spiking[(a)]	One per batch (no more than 20 samples)	No target analytes >5 × MDL	Investigate problem, evaluate data for usability.

(a) Surrogate-spike solution includes o-terphenyl (OTP).
(b) Matrix- and LCS-spike solution includes selected n-alkanes and isoprenoids from C8-C44.
TPH = Total Petroleum Hydrocarbons; QC = Quality Control; RSD = Relative Standard Deviation; MDL = Method Detection Limit

Table 6-3. Summary of PAH Sediment Sample QC Checks Wyckoff/Eagle Harbor Site Bainbridge, Washington

Matrix	QC Check	Method	Frequency	Acceptance Criteria	Corrective Action
Sediment	Surrogates	Spiking[(a)]	All samples and all blanks	40 to 120% recovery	In case of occasional violation of acceptance criteria, the violating data will be flagged. The Work Assignment Leader will decide whether to rerun sample. In the case of frequent violation (>10% samples), the problem will be investigated, and the whole sample set will be rerun.
Sediment	Duplicate	Split homogenized sample at analytical lab prior to processing	One per batch (no more than 20 samples)	±30% RPD if concentration > 5 × MDL	
Sediment	Matrix spike	Spiking[(a, b)]	One per batch (no more than 20 samples)	40 to 120% recovery if amount spiked > 5× background	Investigate problems, evaluate data for usability, re-analyze matrix spike.
Sodium sulfate, Ottawa Sand, and extraction solvent	Laboratory Control Sample (LCS)	Spiking[(a, b)]	One per batch (no more than 20 samples)	40 to 120%	
Sodium sulfate and extraction solvent	Procedural Blank	Spiking[(a)]	One per batch (no more than 20 samples)	No target analytes >5 x MDL	Investigate problem, evaluate data for usability.

(a) Surrogate-spike solution includes d8-naphthalene, d10-acenaphthene, d10-pehnanthrene, d12-benzo[a]pyrene, and d12-benzo[b]fluoranthene.
(b) Matrix- and LCS-spike solutions include the 16 priority pollutant PAHs in addition to other selected target PAH compounds and representative alkylated PAH isomers.

PAH = Polycyclic Aromatic Hydrocarbon; QC = Quality Control; MDL = Method Detection Limit.

Table 6-4. Summary of Sediment Moisture Content QC checks Wyckoff/Eagle Harbor Site Bainbridge, Washington

Matrix	QC Check	Method	Frequency	Acceptance Criteria	Corrective Action
Sediment	Precision	Duplicate - split at laboratory	One per batch (no more than 20 samples)	RPD <20%	Data will be flagged; the Work Assignment Leader will decide whether to rerun sample set.
Sodium sulfate and extraction solvent	Accuracy	Use of NIST professionally (annually) calibrated balance	Calibration check using NIST Class 1 weight prior to sample analysis	± 5 mg	Check leveling of the balance, clean and recalibrate balance. Service balance if necessary and use a different working balance for samples in the meantime.

QC = Quality Control; RPD = Relative Percent Difference; NIST = National Institute of Standards and Technology

Table 6-5. GC/FID and GC/MS Calibration Criteria Wyckoff/Eagle Harbor Site Bainbridge Washington

QC Check	Method	Frequency	Acceptance Criteria[(a)]	Corrective Action
GC/FID initial calibration	Appendix C; Section 3.2.1	5-point; prior to analysis of samples	%RSD for each analyte <15% of the average RF	Recalibrate.
GC/FID calibration verification (ICV)	Appendix C; Section 3.2.2	Immediately after initial calibration	RF for each analyte <25% difference from average RF for 90% of analytes; <35% difference for remaining 10% of analytes.	Reanalyze mid-level check standard; check integrity of the check standard, recalibrate if necessary.
GC/FID performance check (CCV)		At beginning of each analytical sequence and every 10 samples		
GC/MS initial calibration	Appendix D; Section 3.2.1	5-point; prior to analysis of samples	%RSD for each analyte <25% of average RF	Recalibrate.
GC/MS calibration verification (ICV)	Appendix D; Section 3.2.2	Immediately after initial calibration	25% RPD individual analyte	Reanalyze mid-level check standard; check integrity of the check standard, recalibrate if necessary.
GC/MS performance check (CCV)		At the beginning and end of each analytical sequence and every 10 samples	15% RPD average of all analytes	

(a) The acceptance criteria in this table supersede the criteria in Battelle SOPs attached as appendices.
GC/FID = Gas Chromatograph/Flame Ionization Detector
GC/MS = Gas Chromatograph/Mass Spectrometer
QC = Quality Control
RSD = Relative Standard Deviation
RF = Response Factor
ICV = Initial Calibration Verification

7.0. DATA REDUCTION, VALIDATION, AND REPORTING

7.1. Data Reduction

Dr. Magar and Dr. Sass will have lead responsibility for preparing a data report that will include a description of the experimental methods, any observations of note, and the analytical data resulting from all of the analyses described in the plan. All team members will contribute to the technical report and interpretation. The analytical data will be presented in tabular form. Data will be reported on a dry weight basis. Laboratory duplicates will be reported individually. All the QC data will be reported with the data quality statistics. The completeness and validity of the data with respect to the quantitative QA objectives will be discussed. The data validation process is discussed in Section 7.2. Invalid data or data reported below the MDL will be flagged and the implications discussed in the accompanying text. Units reported will be consistent with those defined in Table 6-1. If contamination (unexplained values of the parameters measured) is discovered in the blanks, the implications will be discussed in the data report. However, data will not be blank-corrected.

7.2. Data Validation

The QAO will be responsible for overall review of the data, including valid and invalid results, and for compliance with the QA objectives. Additional comments on data validity may be made as the QAO sees fit. After this QA procedure is complete, the valid data will be incorporated into the data report.

Data validation is the process of evaluating data and accepting or rejecting it on the basis of the data quality objectives shown in Tables 6-1 through 6-5. QA personnel will use the data quality criteria outlined in Section 6.0. Validation procedures accomplish the following:

- Ensuring close adherence to the specified sampling, preparation, and analysis procedures
- Ensuring the use of properly calibrated and maintained equipment and analytical instrumentation
- Examining the precision, accuracy, and other QC aspects of the data generated during the project.

Records of all data will be maintained, even those judged to be “outliers” or of spurious value. The persons validating the data will have sufficient knowledge of the technical work to identify questionable values.

Analytical data generated in this program will be considered useful if the QC data for spiked and duplicate samples achieve the precision and accuracy goals stated in this work plan and if the sample is analyzed within the maximum holding time. If the precision and accuracy goals established in the QA objectives are not achieved, then these data will be flagged using the qualifiers defined in Table 7-1 and the impact of not meeting the QA objectives will be delineated.

Table 7-1. Definitions of Data Qualifiers Wyckoff/Eagle Harbor Site Bainbridge, Washington

Qualifier	Use
J	Analyte detected below the MDL/RL.
B	Analyte detected at a level greater than 3 times the MDL/RL in the PB. The qualifier is entered for the PB and affected field samples.
ME	Estimated value; significant Matrix Interference.
U	Analyte not detected. "ND" will be reported in the value column.
&	QC value outside the accuracy or precision DQC.

MDL = Method Detection Limit
RL = Reportable Limit
PB = Procedural Blank
QC = Quality Control
DQC = Data Quality Control

7.3. Data Reporting

Project staff will record experimental activities and measurements and will compile analytical data from the analytical laboratories. The analytical data received from each analytical laboratory will be checked by the QAO based on the QA objectives stated in this work plan and will be retained with the project records. These data will be stored in a spreadsheet file for further evaluation and calculations. In addition to test files and QC data, the data report will include the identification of outliers, details regarding the corrective actions taken, and discussion of any necessary deviation from the protocols established in the referenced methods.

7.4. Calculations of Data Quality Indicators

Data quality will be calculated according to precision, accuracy, and completeness, as described below.

7.4.1. Precision. Precision of analytical duplicates will be calculated as the RPD. Precision measurements with three or more replicates will be calculated as the relative standard deviation (RSD). These indicators of precision will be calculated with the following two equations:

$$RPD = \frac{(C_1 - C_2) * 100\%}{(C_1 + C_2)/2} \qquad (7\text{-}1)$$

where RPD = relative percent difference
C1 = larger of two observed values
C2 = smaller of two observed values,

and

$$RSD = \frac{S}{\mu} * 100\% \qquad (7\text{-}2)$$

where RSD = relative standard deviation
S = standard deviation
μ = mean of replicate analyses.

7.4.2. Accuracy. The accuracy of matrix spikes will be determined using the following equation for recovery:

$$\text{Recovery (\%)} = \frac{(\text{Amount in spiked sample}) - (\text{Amount in background sample})^*}{(\text{Spike added})} \times 100\% \qquad (7\text{-}3)$$

*This term is not included in calculating LCS and SIS recoveries.

7.4.3. Completeness. Completeness is defined as follows for all critical measurements:

$$C = 100\% * (V/T) \qquad (7\text{-}4)$$

where C = percent completeness
V = number of measurements judged valid
T = total number of measurements.

8.0. ASSESSMENTS

The following audits will be performed:

- The analytical coordinator from each laboratory will review the validity of all analyses, including laboratory notebooks, instrumentation, calibration records, precision, accuracy, and completeness for compliance with the QA/QC objectives in the work plan.

- The QAO will review the laboratory analysis reports sent by the analytical laboratory coordinator to verify compliance with the QA/QC objectives in the work plan.

9.0. REFERENCES

Battelle. 2000. "Final Level III Quality Assurance Project Plan Natural Attenuation of Persistent Organics in Contaminated Sediments at the Wyckoff/Eagle Harbor Superfund Site."

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APPENDIX A
SOP for RSC

SOP for Immunoassay Techniques

This SOP contains guidelines for using immunoassay techniques for analysis of organic compounds in marine sediment. It does not replace the vendor's instructions included in each immunoassay kit. The operating instructions contain additional information for optimizing instrument performance. Also, see the references listed at the end of this SOP for published reports and product performance evaluations.

Description

Immunoassay (IA) is an analytical technique that uses an antibody molecule as a binding agent in the detection and quantification of substances in a sample. It is useful for the separation, detection, and quantification of both organic and inorganic analytes in a wide variety of environmental and waste matrices. Commercially available immunoassay kits are cost effective, rapid and simple to use with the appropriate training. The kits work well in both laboratory and field settings and allow an operator to analyze a number of samples simultaneously within a short time period. Results are available as soon as the tests are completed and can assist in the on-site management of personnel and equipment and the data management activities of the laboratory. Immunoassay is best used for sites that have a single contaminant, or one type or chemical class of contaminant. It is not recommended for sites with unknown site conditions and contaminants or for those sites that do not have established cleanup criteria.

The most common immunoassay method for environmental analysis, Enzyme Linked Immunosorbent Assay (ELISA), uses antibodies and enzyme conjugates to detect and quantify contaminants of concern (COCs).

Method Summary

Immunoassay products vary in format and chemistry. The characteristics of each product are described in the vendor's package insert. This summary provides a general description of the ELISA method.

An enzyme is chemically linked to a COC molecule to create a labeled COC reagent known as a conjugate. The conjugate is mixed with an extract of the native sample, which contains the COC. A portion of the mixture is applied to a surface to which an antibody specific for the COC is attached. The native COC and the COC-enzyme conjugate compete for a limited number of antibody sites. After a period of time, the solution is washed away. What remains is either COC-antibody complexes or enzyme-COC-antibody complexes attached to the test surface. The proportion of the two complexes is determined by the amount of native COC in the original sample. The enzyme present on the test surface is used to catalyze a color change reaction in a solution added to the test surface. The amount of color development is inversely proportional to the concentration of the COC. In other words, a sample with intense color development will have a low concentration of the COC. A sample with little color development will have a high COC concentration.

Kit Information

Environmental IA kits are engineered to detect a single target compound, or one or more structurally similar target compounds within a chemical class, depending upon

- the compounds present in the chemical class,
- the molecular size of the target compound(s), and
- the specificity of the engineered antibody.

The effectiveness of each IA kit for sample analysis will depend upon:

- the various product mixtures present in the sample,
- the kit's sensitivity to the target compound and structurally similar compounds, and
- the presence of interferences in the sample.

Most vendors have designed their environmental IA kits for use in both field and laboratory settings. All of the available field kits can be used by a fixed or field laboratory as a screening tool prior to sample preparation and/or instrumental analysis.

Field kits are differentiated from laboratory-based kits by the number of samples analyzed per batch. The sequence of standard, blank, samples, and QC samples – followed by the standard and blank set again – constitutes a batch sequence in both settings. Only the number of samples between the standard and blank sets changes. Field kits recommend performing fewer samples (4-6) between standard and blank sets, whereas laboratories will set up banks made up of several batches or sequences of up to ten samples each (possibly 40 samples at one time).

Each IA kit is designed to function within a particular detection and/or calibration range, depending on whether the kit produces quantitative, semi-quantitative, or qualitative data. The kit detection limits must be lower than the project Action Levels.

IA kits are usually more sensitive than is needed for most environmental studies, which generally requires dilution of the sample extracts to bring the COC concentrations into the kit's detection/calibration range. Vendors' instruction guides usually detail step-by-step procedures for performing their specific assays on soil (sediment) matrices. Several vendors have simplified this process by developing a formula to calculate the required dilution factor. Others have ready-to-use dilution kits available to simplify IA use.

Interferences and Possible Problems

The following factors can affect the results of IA analyses, which must be performed in a very consistent manner to ensure the production of usable data. IA methods are also affected by kit storage and operating circumstances, field conditions, and sample matrix characteristics.

- **Vendor's Instructions**
  The vendor of each immunoassay kit includes specific procedures, which are engineered and validated for that particular product. Do not use one vendor's procedures with another vendor's kit.

- **Storage Conditions**
  Most IA kits require storage at 2-8°C. Bring the kit to ambient temperature just before use.

- **Shelf Life**
  The antibody, enzyme conjugate, and color reagents are biological media and have a limited shelf life. The vendor must identify the maximum length of time the reagents will produce usable results. Many vendors put an expiration date on each kit. Do not use a kit past its expiration date.

- **Operating Temperature Range**
  The operating temperature range of an IA kit is one of the most important criteria for generating precise and accurate data. Operate the kit within the vendor's recommended temperature range. Do not use the kit at temperatures that will inhibit or increase the recommended processing times. If there are large temperature fluctuations in the field, make sure that all field samples, standards, blanks, and QC samples are analyzed at the same relative temperature conditions. Inaccurate results can occur if samples are analyzed during the day under normal temperatures (60-80° F) and then later in the day as temperatures drop (40°F). The data generated at 60° F will not be comparable to the data generated at 40° F using the calibration curves and QC samples analyzed at 60° F. Also, temperatures below –40° or –50° F will cause false negatives by interfering with the reaction times for incubation and color development. In very cold climates, operate the IA kit in a heated enclosure or field trailer.

- **Operational Consistency**
  Analyze all samples, standards, blanks, and quality control samples under the same operating conditions. The sequence and timing of reagent additions, sample additions, and washing procedures is critical to the proper use of each IA kit. Reagent additions between samples, etc., must be performed rapidly, precisely, and consistently once the immunochemical reaction has started so that each sample will incubate with the same reagent volume for the same time period. Because the timing of these assays is so critical, most vendors of field kits recommend small batch sizes. Any deviation from the vendor's prescribed procedure can affect the results within and between batches. Also, user training is critical to consistently accurate and precise IA results. Immunoassays require proficiency in sampling, weighing, pipetting, sample dilution, and colorimetric measurement. Each vendor offers product-specific training. Personnel should attend the vendor's training course and practice with the kit before going out in the field.

- **Sediment Characteristics**
  The physical characteristics of some types of sediment, mainly the particle size and the organic content, can affect the adsorption and retention of organic compounds, especially chlorinated organics. Sediments containing increasing amounts of silt, clay, and organic content are much more difficult to quantitatively extract. Sediment pH and cation exchange capacity can also affect extraction. Some organic compounds may be in the salt form and, therefore, will have poor extraction efficiencies. Highly colored sediments, or sediments that cause highly colored solutions upon extraction, may interfere with the color development stage of the assay. Sediment samples with >30% moisture may require further water removal

techniques, such as decanting, filtration, air drying, or oven drying. Note that some PAH compounds are volatile and may evaporate if the sample is heated. Immunoassay may not be the best technique to use on samples with more than 70% moisture.

- **Extraction Solvent**
  Most IA kits use methanol as the extraction solvent for sediments and solids because it is completely soluble in water, does not break down the antibody or enzyme conjugate, and does not inhibit reactions between the antibody and the COC. However, methanol may not efficiently extract COCs from sediments and solids that contain large quantities of water (>30%). Water dilutes the methanol and limits its solubilizing properties, especially for higher molecular weight organic compounds. In situations where the COC is less soluble in methanol, enhance the extraction step by heating gently, shaking for a longer period of time, or by using sonication.

- **False Results**
  The engineering of the antibody/COC along with the enzyme conjugate controls the selectivity of the IA kit to particular target compounds and nontarget compounds. Nontarget compounds that are structurally similar to the COC may bind with the antibody present, producing false positive results. These "cross reactive" nontarget analytes compete for the finite number of antibody binding sites, which affects color development. In addition, interferences caused by the testing of incompatible matrices may increase the number of false positive or false negative results. Immunoassay products contain sample-processing technology that has been developed and validated for use with specified matrices. Each product designates the intended sample matrices.

Kit Standardization and Quality Control (QC)

Most vendors design their kits for use in one of the following modes:

- Quantitative – produces results from a specified lower detection limit to a linear upper limit
- Semiquantitative –produces results either (1) above or below a specified detection limit (Action Level or Go/No Go test) or (2) between an upper and lower range
- Qualitative – detects the presence or absence of a specific COC

Most environmental IA kits are used in the quantitative or semi-quantitative mode. For the data from these analyses to be considered usable, quality control procedures must be performed at the correct frequency. The QC must also meet the criteria specified in the pre-approved Quality Assurance Project Plan. In addition, IA results for a representative number of samples (10% minimum) must be confirmed through the use of split samples. Split samples are collected throughout the entire sampling and analysis episode. They are prepared and analyzed using conventional full protocol analytical methods performed in a fixed laboratory or a field laboratory (mobile or transportable) setting. The split sample results obtained using both analytical methods must not deviate from the criteria specified in the Quality Assurance Project Plan.

To develop the QC requirements for a project, the analyst should consult the vendor's kit instructions, which contain recommended QC requirements. Key QC elements for IA analyses

include process calibration, the analysis of continuing calibration checks, blanks, duplicates, and performance evaluation samples. Documentation that all QC elements were performed and met project requirements is essential. The documentation must include the kit lot number, the kit expiration date, and the temperature at which the tests were performed.

Samples can be analyzed once the project QC criteria have been met. If QC objectives were not met, the analyst must implement and document the appropriate corrective actions. Samples run after the last in-control QC sample must be prepared and/or analyzed again.

- **Calibration**
  Calibration using standards of known concentrations is performed to determine the sensitivity and detection/calibration range for the IA kit.

  – Semiquantitative kits in the Action Level test mode use one calibrator – a standard that contains the target compound at the detection limit.
  – Semiquantitative kits in the detection range mode use two calibrators to define a detection range (i.e., a 1 ppm standard and a 10 ppm standard).
  – Quantitative kits are calibrated using multiple calibrators to create a calibration curve. Usually, one calibrator is a zero point.

  When using semiquantitative and quantitative kits, continuing calibration checks are necessary to evaluate the calibration stability and accuracy for each batch. At the beginning of each batch of samples multiple standard initial calibrations are performed. In the field setting, bracket every 4 to 6 samples with a continuing calibration standard. The vendor's kit instructions usually define how many samples can be successfully analyzed between standards. If samples are from different areas of the site, or temperature or weather conditions change, perform full calibrations before and after each batch.

  The absorbance of the continuing calibration standard should not vary more than 20% from the absorbance of that standard in the initial calibration. If the continuing calibration standard is not within 20%, perform a full calibration, and retest all samples run prior to the non-compliant standard.

- ***Blanks***
  Blanks represent the highest absorbance of color and indicate the absence of the COC. Blanks are analyzed to evaluate the presence of contaminants originating from sampling and analysis activities. Equipment blanks assess the effectiveness of equipment decontamination procedures performed in the field. Reagent blanks, which are included with every batch or a chosen sequence of samples, evaluate the purity and reactivity of reagents used in the IA kits. They also help the analyst determine the kit's response when no target contaminants are present. Blanks should not show contamination above the kit's detection limit.

If contamination is found in the reagents or the equipment rinsates, the analyst must determine the cause and eliminate the contamination. Do not analyze samples until the blanks meet the vendor's recommended acceptance criteria.

- ***Duplicates***
  Field duplicates measure the precision of the IA test as well as the sample homogeneity. Analyze duplicates at a frequency of 1 per 10 samples, or 1 per batch of samples prepared, whichever is greater. Perform duplicates at a greater frequency when samples are less homogeneous.

- ***Performance Evaluation (PE) Samples***
  Performance evaluation (PE) samples are analyzed to evaluate qualitative and quantitative accuracy for each IA kit batch. PE samples should contain the target compound at or near the project Action Level and should be tested under the same conditions as the calibrations, blanks, and field samples.

Depending on the batch size of the individual analysis episode, run a PE sample at least once in 20 samples or once per day, whichever is greater. If multiple sets or batches are analyzed under the same conditions during one day, one PE sample per day is recommended. Analyze the PE sample more frequently if there are changes in field conditions (temperature and relative humidity) during the sampling episode. Poor PE sample results may indicate incomplete sample extraction, operation of the IA kit outside its required operating temperature range, or inconsistent timing of reagent additions and performance of batch processes.

Equipment and Reagents

Immunoassay methods include sample processing and immunoassay components. The immunochemical reagents and sample processing components are specific to each manufacturer. The following table lists examples of the equipment and reagents that are typically supplied by the vendor for IA analysis and sample preparation, depending on the particular kit used. The table also indicates other items necessary for analysis that may not be supplied by the vendor.

Examples of Equipment and Reagents for IA Analysis

Supplied with Immunoassay Component	Supplied with Sample Processing Component	Other Items Not Necessarily Supplied by Kits

• Antibody-coated test tubes or antibody-coupled paramagnetic particles • Standards • Controls • Enzyme conjugate • Color solution • Washing solution • Stopping solution	• Sediment collection device • Filter units/caps • Extract collection vials • Chain-of-custody container labels • Portable Styrofoam tube holder • Extraction solution • Extract diluent • 25 µL precision pipette with tips • Weigh boats • Wooden spatulas • 20 cc syringe with coupler	• Digital balance • Precision pipettes and tips • Combos-syringes • Positive displacement pipette • Vortex mixer • Test tube racks • Methanol • Distilled water • Wash bottle • Test tube rack • Magnetic separation rack • Timer • Permanent marking pen • Lab coat, gloves, and goggles • Photometer

Sample Preparation

Testing solid waste by immunoassay requires the production of a particulate-free leachate, using a solvent that allows the reproducible extraction and recovery of the target analytes. This solvent must also be compatible with the antibody/enzyme conjugate of the immunoassay system used. Effective extraction is accomplished using buffers, detergents, and solvents, together or in combination. Filtration of particulate matter may be integrated into the immunoassay test or completed as a separate step within the protocol.

In general, IA sample preparation for sediment includes the following steps:

- Sample measurement by weight
- Introduction of the extractant
- Extraction of the sample
- Filtration of the extract
- Pipetting sample extract into the IA container

Procedural Notes

The recognition characteristics, sensitivity, detection ranges(s), effective operating temperature, interferences, and cross-reactivity of the immunoassay will depend on the product being used. Methods available from different manufacturers for the same compound and application may have significantly different performance characteristics.

The analysis procedure, which includes pipetting, incubation, and color development, usually takes 25 – 45 minutes per sample batch (or per sample if only one sample is being analyzed). The exact analysis time depends on the specific requirements of each vendor's kit and the COCs being analyzed. The timing sequences for each vendor's kit control the number of samples that

can be accurately and precisely analyzed in a single batch. Approximately 35 to 200 samples/person/day can be processed using IA kits, depending on the COC tested, the extent of sample preparation, and the experience of the analyst. To ensure accurate results, the analyst must

- use the test products before the specified expiration date,
- use reagents only with the test products for which they are designated, and
- use the test products within their specified storage temperature and operating temperature limits.

Analysis Procedure

The vendor supplies the specific procedure for each immunoassay test product in the package insert. Follow the manufacturer's instructions for the test product being used. Critical factors in immunoassay include the timing of each step and the order in which the samples and reagents are added. Refer to the manufacturer's instructions for the specific timing of each step and the correct sequence for adding samples and reagents.

General steps are listed below for assays using antibody-coated test tubes.

1. Collect and prepare the sample.
2. Prepare standards and controls as directed.
3. Add the sample, blank, standards, and controls to appropriately labeled antibody-coated test tubes.
4. Add the enzyme conjugate to the test tubes.
5. Mix as directed.
6. Incubate. Refer to the package insert for the correct incubation time and temperature.
7. Add the wash solution to the test tubes. Follow the washing procedure in the package insert.
8. Add color reagent to the test tubes.
9. Incubate as directed.
10. Add the stopping solution.
11. Measure the optical density of the test tube contents using a photometer at the appropriate setting. The tubes must be read within a specified time period after the addition of the stopping solution.

The following general steps are for assays that use paramagnetic particles with specific antibodies attached.

1. Collect and prepare the sample.
2. Prepare standards and controls as directed.
3. Pipette the sample, standards, and controls into test tubes.
4. Add the enzyme conjugate.
5. Add the antibody.
6. Mix as directed. Avoid foaming.
7. Incubate. Refer to the package insert for the correct incubation time and temperature.
8. Separate in a magnetic rack for the length of time indicated by the manufacturer.

9. Decant and gently blot.
10. Remove tubes from the magnetic rack.
11. Add the washing solution and mix.
12. Separate in a magnetic rack for the specified time.
13. Decant and gently blot
14. Repeat steps 10-13.
15. Remove the tubes from the magnetic rack.
16. Add the color solution to the test tubes.
17. Incubate as directed by the manufacturer.
18. Add the stopping solution.
19. Place the test tubes in a photometer and read absorbance using a photometer at the appropriate setting. The tubes must be read within a specified time period after the addition of the stopping solution.

Instrument Vendors and Models

Several IA instruments are available commercially. See Section 2.2.3 of the main document for a description of specific instruments identified below.

Instrument Vendor	Instrument Model
Strategic Diagnostics	RaPID Assay System
Strategic Diagnostics	EnviroGard PCB Test Kit
Strategic Diagnostics	D TECH PCB Test Kit
Hach	PCB in Soil, Pocket Colorimeter
EnviroLogix	PCB Soil Tube Assay

References

U.S. Environmental Protection Agency. 1996. Region 1, EPA-New England, Immunoassay Guidelines for Planning Environmental Projects, October. www.epa.gov/region01/measure/ia/ia_guide.pdf

U.S. Environmental Protection Agency. 1996. Method 4000, Immunoassay, December. www.epa.gov/sw-846/4000.pdf

U.S. Environmental Protection Agency. 1998. Environmental Technology Verification Report, Immunoassay Kit, Strategic Diagnostics, Inc., RaPID Assay System for PCB Analysis. EPA/600/R-98/111, August.

U.S. Environmental Protection Agency. 1998. Environmental Technology Verification Report, Immunoassay Kit, EnviroLogix, Inc., PCB in Soil Tube Assay, EPA/600/R-98/173, December.

U.S. Environmental Protection Agency. 1998. Environmental Technology Verification Report, Immunoassay Kit, Hach Company, PCB Immunoassay Kit, EPA/600/R-98/110, August.

U.S. Environmental Protection Agency. 1998. Environmental Technology Verification Report, Immunoassay Kit, Strategic Diagnostics, Inc., EnviroGard PCB Test Kit, EPA/600/R-98/113, August.

U.S. Environmental Protection Agency. 1998. Environmental Technology Verification Report, Immunoassay Kit, Strategic Diagnostics, Inc., D TECH PCB Test Kit, EPA/600/R-98/112, August.

APPENDIX B

USEPA Region 10 Dive Plan for June 2006 Conductivity Survey

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION 10
1200 Sixth Avenue
Seattle, Washington 98101

DIVE PLAN

Date of Request: May 16, 2006
Dates of Dive: May 31, June 1-2, 2006

From: Rob Pedersen, UDO, Divemaster **Approval**
To: Keven McDermott, OEA
William Riley, Director, OEA

Project: EagleHarbor-ORD Cincinnati Research Project Approximately N47 12.500 W123.01.565

Scientific Objectives: ORD study to evaluate recontamination of sediment caps (one site is Eagle Harbor, Bainbridge Island). In May, 2005, divers assisted the ORD scientists in collecting conductivity surveys on the cap.
This time measurements will refine the area of groundwater upwelling through the cap to guide future locations of monitoring wells. [During the first week of June, sediment core will be obtained for this study - without the use of divers.]

Scientific Observations/Data collection: Clusters of shore-side and subtidal piezometers will be installed within one year of groundwater sampling. The goal is to determine possible contaminate transport up into and through the clean sediment cap. An evaluation will also be made of sediment cap effectiveness and cap augmentation (to reduce/prevent contaminate transport back into/through the cap). In May, divers will conduct conductivity measurements to identify the best locations for groundwater movement into the cap.

There is also a biological component of this study involving bioassays and genotoxicity work. The objective of these other techniques are to use biological endpoints to determine if there are locations in the cap where PAHs are at higher concentrations than in other locations. The hypothesis (Jim Lazorchak/Marc Mills) is that where we find high levels of genotoxicity or changes in gene expression in organisms dwelling in the surface sediments, these are areas where PAHs are most likely coming up through the cap and/or correspond to an upwelling area. (See attached .pdf for a project overview.) (See also, DP2005-05-23-24-25 Eagle H ORD.doc.)

For the dive work - much of what was done last May was at the edge or entirely off the capped area. Now, the researchers are proposing a more limited grid with an increased resolution once we find areas of high upwelling. Much of the upwelling areas identified and mapped last time were off the cap or on its edge. This is not useful data for the overall project. So, the grid spacing will be increased and focused on only three transects. Once an area of upwelling is found, we will refine the grid and also move laterally or radially off the transect line to obtain a better map of those upwelling zones. We are also working under the assumption that the zones of upwelling are going to be larger this year due to the low rainfall totals last year at this time compared to this year.

This time we will be going after very specific geo-referenced points on the cap (to be sure we are safely within the capped areas and also using the information we collected last time). Transects will be located from last year's GPS data. Any new sampling locations will be logged on the Monitor's GPS. Alternatively, the Wooldridge will float over the diver's location (given sufficient depth for safe clearance and visibility of the diver) or at a diver-deployed float and obtain the GPS coordinates with the Garmin

276c. The diver will be on tether to the two-point-anchored Monitor. Conductivity readings (location, depth) will be coordinated via hard-wired communications.

Pollution Sources: Potential exposure to “recontaminates” in the sediment cap and marine sewage.

Decontamination Required: Divers will utilize AGAs, and Viking drysuits as a matter of course for diving on tether equipment with pony bottles. Divers will receive a freshwater bottle-spray on the boat. Post-dive FW washing, soaking, and decon of dive gear.
Potential Hazards: Boat traffic.

Maximum Expected Water Depth: **30** fsw

Maximum Expected Water Current: < 1 knot

Diving Platform: EPA's Monitor

Dive Site Location: Eagle Harbor

Figure 1A. Eagle Harbor at Bainbridge Island.

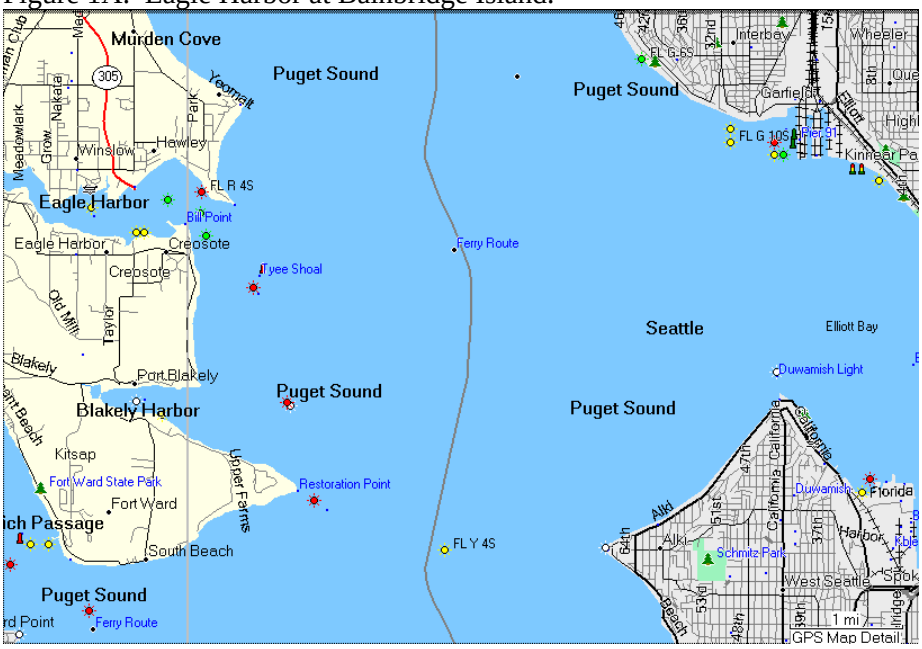
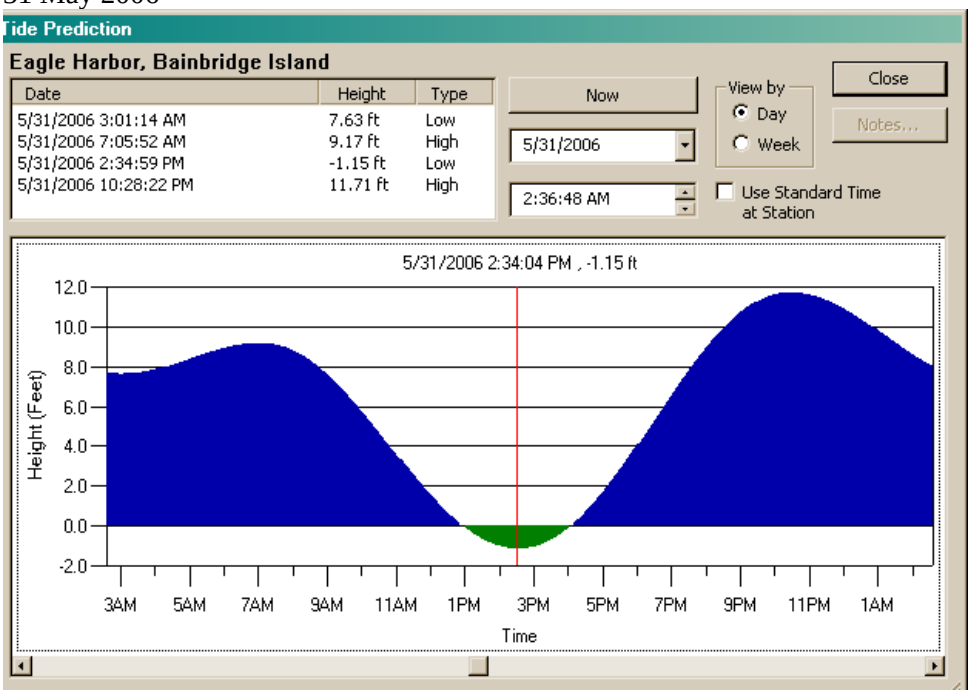


Figure 1B Eagle Harbor study area. Graphics indicate future sampling locations – show general area to be surveyed during this dive operation.

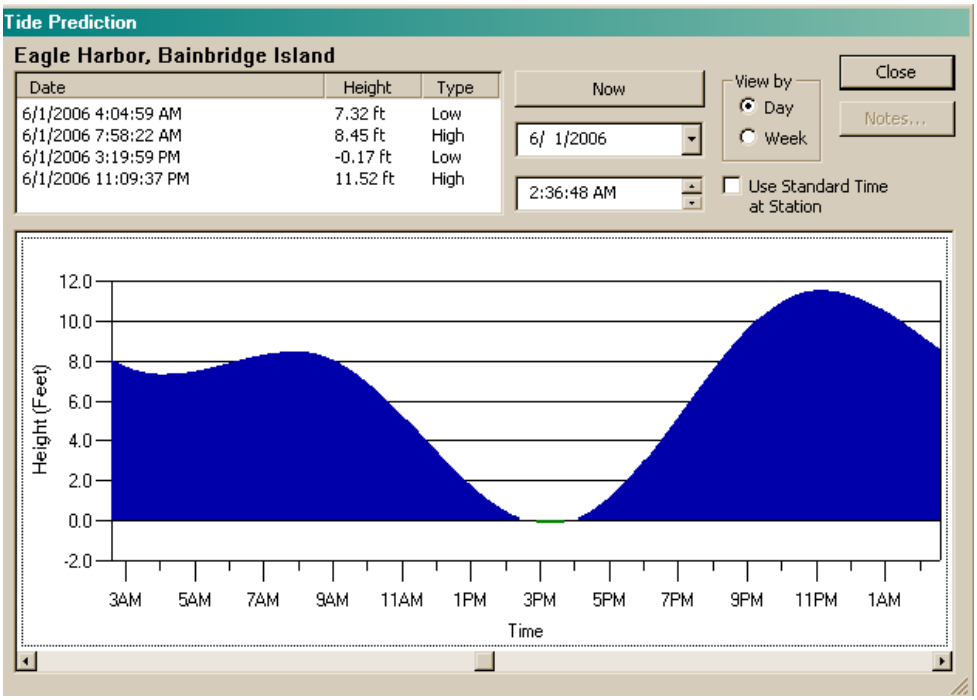

TG
P
P
P
P
UW

Tides:

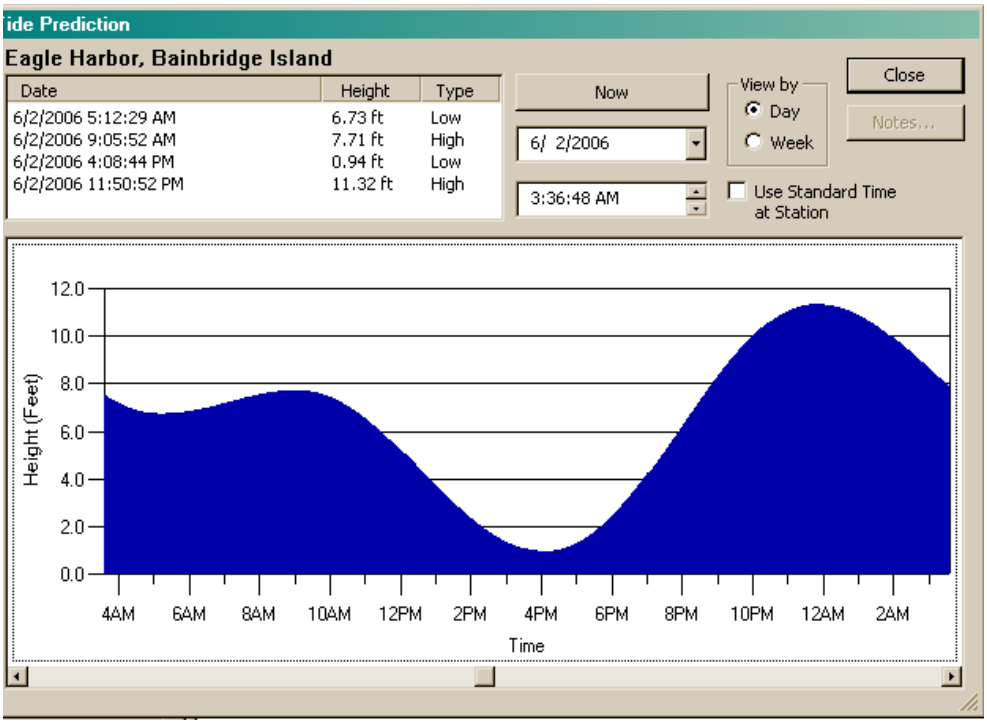
31 May 2006



1 June 2006



2 June 2006



Currents:

Eagle Harbor, Bainbridge Island, Washington

31 May 2006 - 1 June 2006

47.6200° N, 122.5150° W

```
2006-05-31  00:45 PDT   Moonset
2006-05-31  03:01 PDT   7.63 feet  Low Tide
2006-05-31  05:16 PDT   Sunrise
2006-05-31  07:07 PDT   9.18 feet  High Tide
2006-05-31  09:09 PDT   Moonrise
2006-05-31  14:35 PDT  -1.15 feet  Low Tide
2006-05-31  20:59 PDT   Sunset
2006-05-31  22:26 PDT  11.71 feet  High Tide
2006-06-01  01:12 PDT   Moonset
2006-06-01  04:04 PDT   7.32 feet  Low Tide
2006-06-01  05:16 PDT   Sunrise
2006-06-01  07:59 PDT   8.46 feet  High Tide
2006-06-01  10:20 PDT   Moonrise
2006-06-01  15:20 PDT  -0.17 feet  Low Tide
```

```
2006-06-01  20:59 PDT   Sunset
2006-06-01  23:10 PDT  11.53 feet  High Tide
```

1 June 2006 - 2 June 2006

```
47.6200° N, 122.5150° W

2006-06-01  01:11 PDT   Moonset
2006-06-01  04:04 PDT   7.32 feet  Low Tide
2006-06-01  05:16 PDT   Sunrise
2006-06-01  07:59 PDT   8.46 feet  High Tide
2006-06-01  10:20 PDT   Moonrise
2006-06-01  15:20 PDT  -0.17 feet  Low Tide
2006-06-01  20:59 PDT   Sunset
2006-06-01  23:10 PDT  11.53 feet  High Tide
2006-06-02  01:31 PDT   Moonset
2006-06-02  05:13 PDT   6.73 feet  Low Tide
2006-06-02  05:15 PDT   Sunrise
2006-06-02  09:06 PDT   7.72 feet  High Tide
2006-06-02  11:30 PDT   Moonrise
2006-06-02  16:07 PDT   0.94 feet  Low Tide
2006-06-02  21:00 PDT   Sunset
2006-06-02  23:50 PDT  11.33 feet  High Tide
```

2 June 2006 - 3 June 2006

```
47.6200° N, 122.5150° W

2006-06-02  01:31 PDT   Moonset
2006-06-02  05:13 PDT   6.73 feet  Low Tide
2006-06-02  05:15 PDT   Sunrise
2006-06-02  09:06 PDT   7.72 feet  High Tide
2006-06-02  11:30 PDT   Moonrise
2006-06-02  16:07 PDT   0.94 feet  Low Tide
2006-06-02  21:00 PDT   Sunset
2006-06-02  23:50 PDT  11.33 feet  High Tide
2006-06-03  01:48 PDT   Moonset
2006-06-03  05:15 PDT   Sunrise
2006-06-03  06:20 PDT   5.85 feet  Low Tide
2006-06-03  10:30 PDT   7.13 feet  High Tide
2006-06-03  12:37 PDT   Moonrise
2006-06-03  16:06 PDT   First Quarter
2006-06-03  16:58 PDT   2.15 feet  Low Tide
2006-06-03  21:01 PDT   Sunset
```

Divemaster: RPedersen 5/31, 6/2
SSheldrake 6/1

Divers: 5/31 JG, RR, RP (bkup LM)
6/1 SS, LM, BD (bkup RR)
6/2 RR, KM, RP (bkup SS)

Cox'n: CB 5/31, 6/2; DT 6/1 (Almar/dive boat).

Wooldridge: DT 5/31, 6/2; BC 6/1.

Tender: divers.

Security Issues/Traffic Lanes - Notify USCG of dive plan/operations: __X (, RP)Yes___No ___N/A
Advanced notification of USCG for dives near sensitive areas (e.g., port facilities, bridges) or in high traffic lanes/ areas. Call 24hr. CG Sector Seattle 206-217-6001 (call at start and stop of dive ops.); e-mail dive plan to d13-gruseattleswo@uscg.mil
CG Notice to Mariners 206-220-7280 ____Yes _X_ No
Notice to Mariners (NTM): N/A

Monitor VHF CHANNELS 13 (BRIDGE TO BRIDGE) & 14 (USCG WORKING CHANNEL);
-Vessel must display (at least) the alpha dive flag when divers are in the water; and

Contact Information: OEA cell phone:	206-369-7500
Rob Pedersen's personal cell:	206-920-0758
Doc Thompson cell/Curt Black cell	
Marc Mills:	513-205-7220

Proposed Schedule:

Load Van: 1330 on 5/30	
Day's schedule	
Depart EPA office:	**0725**
Bainbridge ferry:	**0755**
Depart boat launch:	**0900**
Return ferry:	**14:55, 15:50 preferred latest, 16:35**

Source of EMERGENCY TRANSPORTATION:

Nearest MEDICAL Facility: Virginia Mason Hospital - 206-583-6433 (Chamber phone is 206-583-6543)
Address: admission is through the Emergency Room on Spring Street at the corner of Terry and Spring streets
Nearest HYPERBARIC Facility: Virginia Mason, (See note 2 below) - 206-583-6543
Address: Terry and Spring Street, Seattle (admission is through the Emergency Room on Spring Street)

Egress: from city park boat ramp. (Recommend return to Seattle due to travel time comparisons.)

Pacific Surgery Ctr
20669 Bond Rd NE, Poulsbo, WA (10.35 miles away)
360-779-6527

Start out 0.2 miles

going EAST
on WINSLOW WAY E
toward MADRONE LN N.

Turn LEFT onto WA-305/WA-305 NE. — 12.6 miles

Turn LEFT onto BOND RD NE. — 0.1 miles

End at **Pacific Surgery Ctr**
20669 Bond Rd Ne, Poulsbo, WA 98370

Total Est. Time: 26 minutes **Total Est. Distance:** 13.01 miles
Notes:

(1) Emergency helicopter transport in Puget Sound is available through the U.S. Coast Guard (Channel 16 or telephone 220-7001 *or *CG* in Seattle).

(2) Primary Hyperbaric Chamber is located at the Virginia Mason Hospital (admission is through the Emergency Room on Spring Street at the corner of Terry and Spring streets; E.R. phone 583-6433, Chamber phone, 583-6543). Alternative Hyperbaric Chambers are the U.S. Naval Torpedo Station (Keyport, (206) 396-2522/2563 or after hours (206) 396-2551/2553). Although chambers are on site at NOAA, victims of barotrauma will be transported to Virginia Mason.

(3) Diver's Alert Network: For diving emergencies use 1-919-684-8111, for non-emergency diving questions during normal working hours use 1-919-684-2948.

Pre/Post Dive Taskings and Schedule

Drop-off tanks needing VIP+, fill others – divers as available;
Dive plan / report – RP;
Coord. Remaining equip. return to Manchester – BD
GPS follow-up for report/mapping – SS
Transect line soak/hang dry/stow untangled in bucket – JG
AGA clean/reassemble – RR/KM