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High Resolution Passive Profiling to Monitor Contaminated Sediments in Support of Remediation Evaluation and Risk Characterization

Andrew Jackson
Danny Reible
Uriel Garza-Rubalcava
Texas Tech University

Paul Hatzinger
Graig Lavorgna
Aptim Federal Services

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6. AUTHOR(S)
Jackson, W. Andrew, Ph.D. (Texas Tech University)
Reible, Danny, Ph.D. (Texas Tech University)
Garza-Rubalcava, Uriel (Texas Tech University)
Hatzinger, Paul, Ph.D. (Aptim Federal Services, LLC.)
Lavorgna, Graig M. (Aptim Federal Services, LLC.)

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911 Boston, Box 41023
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14. ABSTRACT

The overall objective of this project was to demonstrate a sediment High Resolution Passive Profiler (sHRPP) that is capable of evaluating the bioavailable distribution of contaminants (metals and organics) in sediments via passive sampling at cm vertical resolution, while simultaneously evaluating dominant redox processes at the same resolution, key gene/microbial densities, and pore water velocity.

The sHRPP is driven into the sediment and can sample depths as deep as ~80cm. The sHRPP can evaluate at fine-scale: (1) contaminant types and concentrations using either equilibration cell water (e.g. metals, cVOCs, VOCs) or by incorporating SPME fibers for HOCs (e.g. PCBs, PAHs, DDX); (2) the concentrations of biogeochemical species (e.g. DOC, Cl-, NO3-, NO2-, Fe+2,FeT, SO4-2, S-2, CH4, etc.); (3) pore water velocity; (4) the composition of relevant microbial communities via qPCR analysis of Bio-Sep beads. The ability of the sHRPP to improve the measurement of the occurrence, fate, and transport of contaminants in sediment was demonstrated at 4 sites.

The sHRPP was able to measure concentrations of key contaminants at equal or greater sensitivity than comparable traditional technologies. It produced high resolution concentration profiles of geochemical species and measured pore water velocities with depth. It provided increased model resolution and reliability and increased statistical power to evaluate the impact of remedial efforts. The technology required less cost, time, and effort to evaluate sites and produced data not obtainable by other traditional methods.

15. SUBJECT TERMS
sHRPP, sediment, passive sampling, discrete, SPME fibers, equilibration cell, metals, cVOCs, VOCs, HOCs, PCBs, PAHs, DDX, biogeochemical species, pore water velocity, qPCR, Bio-Sep beads, high resolution concentration profiles

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ACRONYMS AND ABBREVIATIONS

µg	microgram(s)
µm	micron
AOC	Area of Concern
APG	Aberdeen Proving Ground
APP	Accident Prevention Plan
APTIM	APTIM Federal Services LLC
As	arsenic
BGS	below ground surface
Br^-	bromide
BSI	below sediment interface
BTEX	benzene, toluene, ethylbenzene, and xylenes
CCSA	Canal Creek Study Area
Cd	cadmium
cis-DCE	cis-1,2-dichloroethene
Cl^-	chloride
cm	centimeter(s)
COC	contaminant of concern
COD	chemical oxygen demand
COPC	chemicals of potential concern
COVID	Coronavirus (COVID-19) pandemic
Cr	chromium
CSIA	compound specific stable isotope analysis
CVOC	chlorinated volatile organic compound
CWMDP	chemical warfare material degradation products
DCB	dichlorobenzene
DDX	DDT (dichlorodiphenyltrichloroethane), DDE (dichlorodiphenyldichloroethylene), and DDD (dichlorodiphenyldichloroethane)
DECO	Dehalobium spp.
DHC	Dehalococcoides spp.
DI	deionized
DL	detection level
DNA	deoxyribonucleic acid
DOC	dissolved organic carbon
DoD	Department of Defense
ECC	Environmental Chemical Corporation
EPA	U.S. Environmental Protection Agency
ESTCP	Environmental Security Technology Certification Program
ET	East Transect

Fe	iron
Fe^{+2}	ferrous iron
FeT	total iron
ft	foot/feet
ft-msl	feet above mean sea level
GAC	granular activated carbon
h	hour
Hg	mercury
HOC	hydrophobic organic compound/contaminant
HPT	hydraulic profiling tool
HRPP	High Resolution Passive Profiler
ICP-MS	inductively coupled plasma mass spectrometry
kg	kilogram(s)
L	liter(s)
LTM	long-term monitoring
m	meter(s)
MCB	Marine Corps Base or monochlorobenzene
mg	milligram(s)
MIP	membrane interface probe
ml	milliliter(s)
Mn	manganese
NaBr	sodium bromide
NAS	Naval Air Station
NAVFAC	Naval Facilities Engineering Command
NO_{2-}	nitrite
NO_{3-}	nitrate
NPDES	National Pollutant Discharge Elimination System
NRC	National Research Council
PAH	polycyclic aromatic hydrocarbon
Pb	lead
PCB	polychlorinated biphenyl
PDMS	polydimethylsiloxane
PE	polyethylene
PED	polyethylene device
POC	point of contact
POM	polyoxymethylene
PQL	practical quantitation level

PRC	performance reference compounds
QC	quality control
qPCR	quantitative polymerase chain reaction
S^{-2}	sulfide
SERDP	Strategic Environmental Research and Development Program
sHRPP	sediment High Resolution Passive Profiler
SO_4^{-2}	sulfate
SOP	standard operating procedure
SPME	solid-phase microextraction
SSHP	site safety and health plan
TCE	trichloroethene
TTU	Texas Tech University
USEPA	U.S. Environmental Protection Agency
USGS	United States Geological Survey
UXO	unexploded ordinance
Va	vanadium or Virginia
wk	week
WT	West Transect
Zn	zinc

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ABSTRACT

INTRODUCTION AND OBJECTIVES

The Department of Defense (DoD) is responsible for the management of hundreds of sites with contaminated sediments. A key factor in appropriate management of contaminants in sediments is an accurate understanding of their distribution and bioavailability; along with appropriate models to predict their fate and transport, as well as associated changes in their bioavailability. In order to meet this need, high resolution data are required, including contaminant distribution and bioavailability, biogeochemical conditions, and microbial activity. The overall objective of this project was to demonstrate a sediment High Resolution Passive Profiler (HRPP) that is capable of evaluating the bioavailable distribution of contaminants (metals and organics) in sediments via passive sampling at cm vertical resolution, while simultaneously evaluating dominant redox processes at the same resolution, key gene/microbial densities, and pore water velocity.

TECHNOLOGY DESCRIPTION

The sHRPP is made of stainless steel or polycarbonate is driven into the sediment and can sample depths as deep as ~80cm. The sHRPP can evaluate at fine-scale (~ 2 cm intervals): (1) contaminant types and concentrations using either equilibration cell water (e.g. metals, cVOCs, VOCs) or by incorporating solid-phase microextraction (SPME) fibers for HOCs (e.g. PCBs, PAHs, DDX); (2) the concentrations of biogeochemical species (e.g. DOC, Cl^-, NO_3^-, NO_2^-, Fe^{+2},FeT, SO_4^{-2}, S^{-2}, CH_4, etc.); (3) pore water velocity; (4) the composition of relevant microbial communities via quantitative polymerase chain reaction (qPCR) analysis of Bio-Sep beads. The ability of the sHRPP to improve the measurement of the occurrence, fate, and transport of contaminants in sediment was demonstrated at 4 sites including: 1) a fresh water tidal marsh (elevated metal concentrations), 2) capped freshwater canal sediments contaminated with PAHs; 3) a freshwater pond contaminated with PCBs; 4) capped river sediments contaminated with DDX.

PERFORMANCE AND COST ASSESSMENT

The sHRPP was able to measure concentrations of key contaminants at equal or greater sensitivity than comparable traditional technologies. It produced high resolution concentration profiles of geochemical species and measured pore water velocities with depth. It provided increased model resolution and reliability and increased statistical power to evaluate the impact of remedial efforts. The technology required less cost, time, and effort to evaluate sites and produced data not obtainable by other traditional methods or combination of methods.

IMPLEMENTATION ISSUES

Currently the sHRPP is not widely available commercially as a turnkey service similar to most passive sampling methods. It is available through Texas Tech University in cooperation with other consultants or a new company called Envirostatus, LLC, which specializes in passive sampling. We developed a SOP and informational voice over power point posted on the ESTCP website that covers the use, applications, and detailed instructions on how to prepare, deploy and sample the sHRPP.

PUBLICATIONS

1. Rubalcava et al., (In Preparation) Long-term monitoring and modeling of PAHs in capped sediments at the Grand Calumet River.

2. Rubalcava et al., (In Preparation) Characterization of transport processes and Zn availability in bank sediments of a tidal creek through high-resolution passive sampling.

3. Jackson et al., (In preparation) The use of high resolution co-located multi parameter profiles to constrain contaminants transport and fate in sediments.

EXECUTIVE SUMMARY

INTRODUCTION

This project was a joint effort between the Department of Civil and Environmental Engineering at Texas Tech University and the Biotechnology Development & Applications Group at Aptim Federal Services LLC (APTIM). During this effort, we demonstrated the application of a cost-effective, commercially deployable sediment High Resolution Passive Profiler (sHRPP) that can be applied to 1) evaluate the performance of remedial/natural attenuation efforts and the corresponding reduction in long-term risk; and 2) access sites and enable improved transport/risk models. The data provided by the sHRPP will increase our understanding of contaminant availability, sediment geochemistry, microbial processing, and sediment pore water contaminant transport as well as the impacts of remedial measures on these processes. The sHRPP is a passive sampler that can be directly inserted into a saturated environment (e.g., marine or freshwater sediments) to simultaneously determine the concentrations of biogeochemical species and pollutants, the composition of microbial communities, microbial activity, and pore water velocity as a function of depth.

The Department of Defense (DoD) is responsible for the management of hundreds of sites with contaminated sediments, with an estimated liability of more than two billion dollars (SERDP/ESTCP, 2012). The primary contaminants and risk drivers in sediments are typically recalcitrant, highly hydrophobic compounds (e.g., polycyclic aromatic hydrocarbons [PAHs] and polychlorinated biphenyls [PCBs]) and/or heavy metals. Due to the large volume and relatively low contaminant concentrations, as well as the risk of contaminant remobilization, removal and ex situ treatment of sediments is often impractical and/or ineffective over the long term (NRC, 2007; Kupryianchyk et al., 2015).

A key factor in appropriate management of contaminants in sediments is an accurate understanding of their distribution and bioavailability; along with appropriate models to predict their fate and transport, as well as associated changes in their bioavailability. Further, in cases where active remediation efforts are utilized, there is a clear need to accurately assess the impact of such efforts on contaminant fate and bioavailability. In order to meet this need, high resolution data are required, including contaminant distribution and bioavailability, biogeochemical conditions, and microbial activity. Older methods to evaluate these parameters mainly relied on sediment cores and/or extraction of pore water for testing (e.g., Chapman et al., 2002; Zoumis et al., 2001). These approaches suffer from numerous issues including an inability to collect cohesive cores, the impacts of sample processing on contaminant availability and geochemical constituents, insufficient pore water generation requiring large integrated depths, and high cost. A number of new passive sampling methods exist. While collectively these techniques are capable of evaluating contaminant profiles and bioavailability, they currently cannot be performed simultaneously in the same profile (a key issue due to the relatively heterogeneous nature of sediments) and do not allow for evaluation of microbial activity, which can be a critical fate process in reducing long-term risk. Moreover, none of the aforementioned methods are capable of evaluating pore water velocities, which can be very important and dynamic in tidal areas, rivers and other environments with contaminated sediments.

In order to effectively assess the risk and/or efficacy of remediation efforts at DoD contaminated sediment sites, it would be technically and economically valuable to employ a technique that can evaluate the dissolved phase hydrophobic organic contaminant (HOC) and/or heavy metal distribution with depth at high resolution (cm scale), while simultaneously measuring geochemistry (e.g. dominant redox processes), pore water velocity, and microbial degradative genes/activity (indigenous or bioaugmented) with depth. The sHRPP demonstrated is a passive sampler based on SERDP project (ER-2419; 2015-2019), that has been modified to allow HOC monitoring, can be directly inserted into the saturated subsurface and possesses all of the aforementioned capabilities.

OBJECTIVES

The overall objective was to demonstrate a modified High Resolution Passive Profiler (HRPP) for sediment (sHRPP) that is capable of evaluating the bioavailable distribution of contaminants (metals and organics) in sediments via passive sampling at cm vertical resolution, while simultaneously evaluating dominant redox processes at the same resolution, key gene/microbial densities, and pore water velocity. This project demonstrated the application of a cost-effective, commercially deployable sampler that can be applied to: 1) assess contaminant distribution, fate, and availability, 2) evaluate the performance of remedial efforts or natural attenuation and corresponding reductions in long term risk, and 3) increase our understanding of contaminant fate and the overall impact of typical and novel remediation measures on sediment geochemistry, microbial processing, and sediment pore water transport. Moreover, all parameters can be analyzed by commercial laboratories, overcoming a long-standing barrier to passive sampling.

TECHNOLOGY DESCRIPTION

The sHRPP is based on a groundwater direct drive passive sampler (HRPP), developed, refined, and field validated during SERDP project ER-2419 (Schneider etal., 2019, 2020, Rubalcava et al., 2022). The sHRPP incorporates the use of SPME fibers that enable the measurement of HOCs. The sHRPP is made of stainless steel or polycarbonate is driven into the sediment and can sample depths as deep as ~80cm (Figure ES-1). The sHRPP can evaluate at fine-scale (~ 2 cm intervals): (1) contaminant types and concentrations using either equilibration cell water (e.g. metals, cVOCs, VOCs) or by incorporating solid-phase microextraction (SPME) fibers for HOCs (e.g. PCBs, PAHs, DDX); (2) the concentrations of biogeochemical species (e.g. DOC, Cl^-, NO_3^-, NO_2^-, Fe^{+2},FeT, SO_4^{-2}, S^{-2}, CH_4, etc.); (3) pore water velocity; (4) the composition of relevant microbial communities via quantitative polymerase chain reaction (qPCR) analysis of Bio-Sep beads; and (5) biotic and/or abiotic degradative activity via compound specific stable isotope analysis (CSIA) of contaminants in solution or adsorbed to Bio-Sep beads (Figure ES-1). Dissolved porewater constituents are measured by allowing a reservoir of water to equilibrate with porewater across a micro-porous (0.2 to 0.45µm) membrane (nylon, polysulfonone, or stainless) selected for the intended application. For HOCs with very low water solubilities polymeric passive samplers (SPME) are used to accumulate compounds and include performance reference compounds to correct for equilibrium. Velocity is measured by using the loss of a conservative tracer and a developed relationship between the mass transfer coefficient and pore velocity.

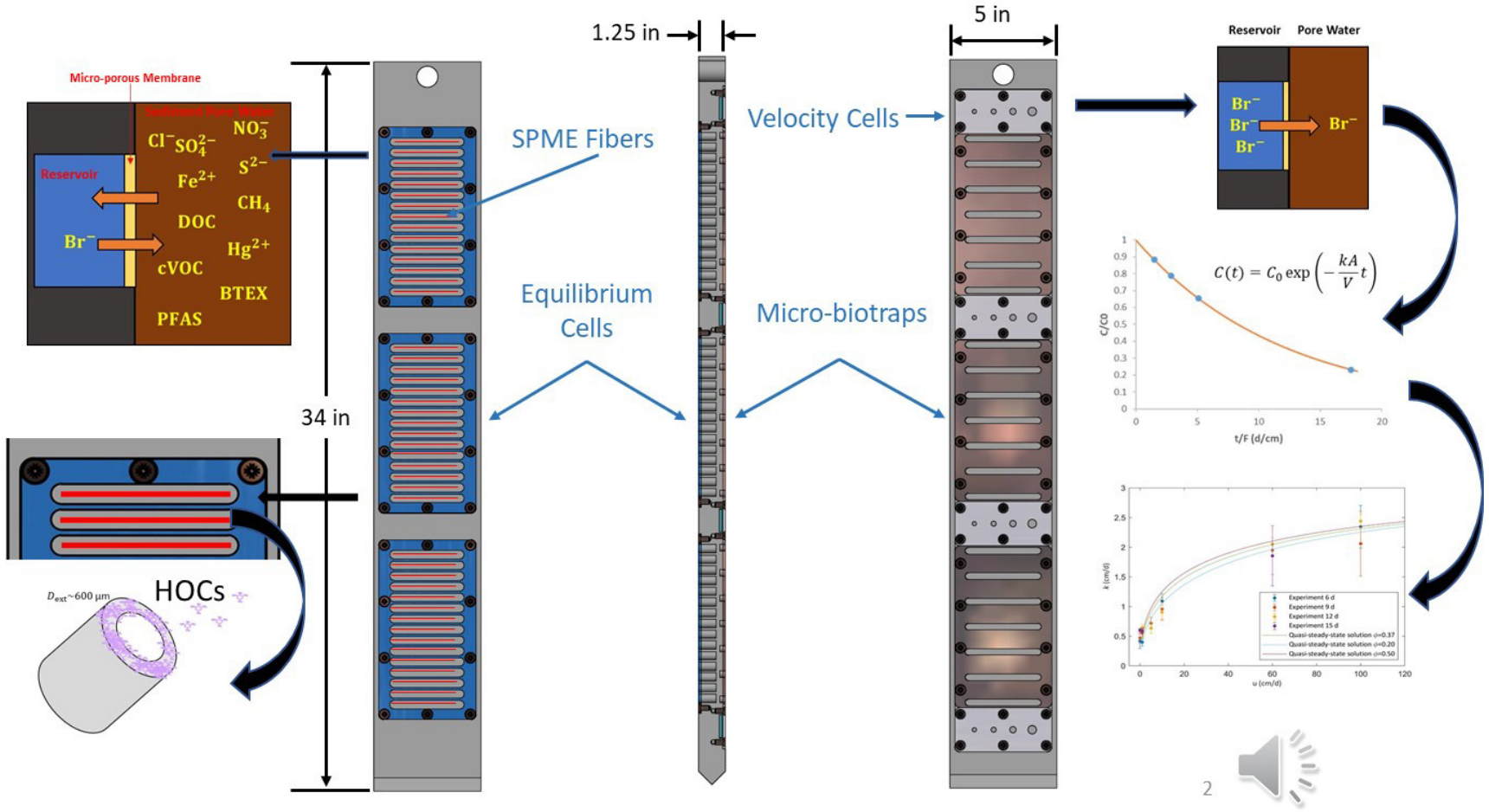


Figure ES-1. Schematic of sHRPP Including Each Side and Profile View (Center Figures).

Illustration of the application of equilibrium porewater diffusion for dissolved constituents (Top left) and HOC sampling using SPME fibers (Bottom left). Velocity estimation using Br- to measure the mass transfer of Br and relate to pore velocity (Right figures).

PERFORMANCE ASSESSMENT

The ability of the sHRPP to improve the measurement of the occurrence, fate, and transport of contaminants in sediment was demonstrated at 4 sites including: 1) a fresh water tidal marsh with elevated metal concentrations (Canal Creek), 2) capped freshwater canal sediments contaminated with PAHs (Grand Calumet); 3) a freshwater pond contaminated with PCBs with areas that were native, capped with Sedimite, and capped with a bioaugmented Sedimite containing PCB degrading organisms (Abraham's Creek, Quantico; 4) river sediments contaminated with DDX and capped with sand (The Embayment, Quantico). Detailed results are available for each site in the full report. Here we summarize and the major findings in relation to the performance objectives by synthesizing the results from all sites.

Performance Objective 1. Ability to Measure Concentrations of Key Contaminants at Equal Sensitivity and With Lower Error Estimates with Depth

One of the primary objectives of this demonstration was to demonstrate that the sHRPP can measure concentrations of key contaminants [PCBs, DDX, PAHs, metals] with depth in sediments with the same or better levels of detection and with greater confidence than traditional methods (either in- situ passive sampling or core processing). Here we define confidence in terms of both absolute depth, depth resolution, as well as contaminant sediment concentrations. This objective was evaluated by deploying multiple sHRPP for ~ 4 weeks at 3 field sites contaminated with PAHs. PCBs, or DDX. At each site at least one alternate method of measuring HOCs with depth was utilized as a basis of comparison.

For HOCs this objective was considered to be mostly met. Detection limits for HOCs (PCBs, PAHs, DDx) are a function of the length of fiber extracted and final volume of solvent. At all HOC sites we were able to measure HOC concentrations at ~ 2cm depth resolution and with ~ 2-4 cm resolution of absolute depths in relation to the sediment water interface. Detection limits were generally similar to traditional vertical deployed insitu SPME sampling but lower than PE or exsitu SPME sampling. However ex-situ SPME analysis does not represent field conditions (e.g., benthic exchange) and PE samplers have slow equilibration rates and have difficulty to penetrate to deeper depths or through consolidated sediment. The sHRPP provide greater fiber mass per depth (~5-7 cm every ~2cm) due to horizontal rather than vertical integration and therefor had lower detection limits than traditional vertical SPME sampling in relation to specific depths (See Figures 5.31-5.33). Traditional vertical SPME must average 5-7cm of depth to produce the same detection limit. sHRPP therefore have increased spatial resolution providing ~ 3X the fiber length over any sampled depth compared to vertical SPME. Ex-situ resolution using cores is also lower due to the need for sufficient material (see Figures 5.62-5.64). sHRPP also sample a longer sampling length per sample depth compared to vertical placement providing a more spatially integrated concentration (5-7cm sampled each ~2cm) compared to vertical placement (2cm sampled per 2cm of depth). This reduces error due to spatial variation in sediment and decreases the uncertainty in concentration (See Figures 5.39, 5.40, 5.78-5.92). In addition, vertical SPME or PE sheet placement and ex-situ SPME using cores produces more uncertainty in sampled depth, as the only way to determine depth of vertical SPME or PE sheet placement is by measuring the depth of water to the sediment interface. This can be difficult in sediments with deep overlying water (e.g., Grand Calumet and Abrahams Creek) and soft bottomed sediment. Incomplete core retrieval and compression also impact ex-situ depth assignment (see Figures 5.62-5.64; 5.69-5.92).

The sHRPP depth of deployment was verified by evaluating the concentration of conservative species (e.g., Cl-) with depth which can clearly show the sediment/water interface (See Figures 5.6, 5.2, 5.26, 5.55, 5.66).

For metals this objective was also considered partially met as detection limits were theoretically similar to processing cores based on maximum porewater available from cores sectioned at the same resolution. However, due to issues with oxidation of processed core material (Figure 5.18) no metal analysis was performed on core extracts and so no data is available for comparison. The sHRPP resolution was greater than achieved with cores (Figure 5.17 and 5.18) with less depth assignment uncertainty and without changes caused by compression, porewater extrusion, or oxidation, due to core acquisition, shipping and processing. Metal concentrations measured by the sHRPP are a function of the instrument detection limit and any dilution factor required to produce sufficient volume for analysis. The sHRPP provided a total of 10ml of volume every 2cm for metal analysis based on reserving 4ml for analysis of major anions (Cl^-, Br^-, NO_3^-, NO_2^-, SO_4^{-2}), sulfide, and iron concentrations. Metal analysis (ICP) requires ~10ml and HgT analysis requires 20ml for maximum sensitivity. In this study we diluted the sample for metal analysis by 2.5X (4ml in 10ml) and for HgT 4X (5ml in 20ml). This increased our quantification limit by the same factors. In comparison, traditionally cores would be acquired and shipped to a lab. In a glove bag or anaerobic chamber to prevent redox changes, the cores would be sectioned, followed by centrifugation, and filtration. In this study we acquired 10cm diameter cores. The amount of porewater produced is a function of the length of core homogenized, porosity and sediment type (silt, clay, plant material). In theory the 2cm core section could provide more porewater than the sHRPP but in practice the volume is only slightly greater or similar (as in this study). This is due to the loss of material while filling the centrifuge bottles, some material having little free water content (plant roots), and limits on sediment compaction. However, even assuming the cores can provide equivalent or greater water per depth, it is almost impossible to process a core at 2cm intervals without freezing the core. Extensive plant roots and the soft nature of the sediment limit the spatial resolution. Secondly, processing the cores anaerobically to prevent oxidation while homogenizing the sections is also problematic. In this study, although we used a glove bag and continuous nitrogen purge, significant sulfides were oxidized to sulfate (Figure 5.18) potentially releasing metals and altering concentrations of geochemical species. Finally, significant core compaction and incomplete recovery occurs during sampling, this reduces the depth resolution, depth confidence, and can allow porewater to be extruded altering the depth dependence of measured parameters. Finally, it should be noted that unless cores are frozen in the field, the shipping of cores can allow for mixing and will alter the redox conditions of the upper core.

Performance Objective 2. Measure Key Geochemical Parameters

The second primary objective was to effectively measure changes in geochemical parameters [NO_3^-, NO_2^-, Cl^-, Fe^{+2}, SO_4^{2-}, DOC] and conservative species (e.g., Cl^-) at a scale equal to the scale in change of depth due to redox changes or transport of conservative species.

This objective was met. We measured changes in NO_3^-, SO_4^{2-}, sulfide, and Fe^{+2} with depth at both Canal Creek, Abrahams Creek, and the Embayment (e.g., Figures 5.6, 5.7, 5.9, 5.11, 5.13,5.15, 5.27, 5.68). In many cases redox transitions between major electron acceptors were observed to occur over a scale of centimeters often within a few centimeters of the surface water interface. These depth profiles can also be complex due to vertical and horizontal flow as well as tidal fluctuations.

We also show that Cl- profiles can be used to establish the sediment interface depth more precisely (all sites) (See Figures 5.6, 5.2, 5.26, 5.55, 5.66). These Cl- profiles also allow both qualitative (all sites, see sections 5.5.6.1, 5.4.6.3.1, 5.3.6.1, 5.2.6.3) and quantitative (Canal Creek and Grand Calumet) evaluation of transport (see below). This includes in some cases the ability to constrain transport increasing the confidence of HOC transport modeling (Figure 5.99). The only other method by which to obtain sufficiently detailed depth profiles would theoretically be core acquisition and processing. However as detailed above, core acquisition and processing introduce numerous uncertainties and is unlikely to produce sufficient resolution. Our data clearly show substantial changes in profiles of both conservative and non-conservative species in processed core material (Figure 5.17). It should also be noted that the biotic zone near the sediment water interface is the most important zone for contaminant exposure. This zone is also typically the most variable with respect to transport and redox changes, many of which occur in the top 5cm. Maintaining insitu porewater concentrations in these depths during acquisition, shipping, and storage is very problematic if not unrealistic.

Performance Objective 3. Measure Pore Water Velocity

Porewater velocity was measured at each site using the deployed sHRPP. Following retrieval, the equilibrated pore water from the specialized velocity cells in the sHRPP was analyzed for the remaining concentration of a conservative tracer (Br-). The depletion of Br- was used to determine pore water velocity. Pore velocity was measured at all sites at a resolution greater than 0.5m (5.6, 5.7, 5.9, 5.11, 5.13, 5.15, 5.27, 5.44, 5.52, 5.55, 5.67). Pore velocity can be measured down to a lower resolution of ~2 cm/d. Estimates of pore velocity by other methods were only available at Grand Calumet, where historical estimates based on seepage meters ranged from 1-5 cm/d as a seepage flux while estimates based on sHRPP were 2-12 cm/d as true pore velocity which based on typical sediment porosities are essentially the same range of velocities. At Canal Creek and the Embayment, it appears that there is a significant horizontal component. We are unaware of any other system than can be direct driven into sediments to measure horizontal flow. It should be noted that while the sHRPP cannot differentiate between horizontal and vertical fluxes, it can capture the magnitude of either. In the near surface, the samplers also respond to bioturbation and tidal pumping although the measured velocity in these cases does not reflect a simple mono-directional flux but rather an overall mixing effect.

Performance Objective 4. Measure Microbial Community Structure and Key Degradative Organisms/ Genes

The fourth primary objective was to measure microbial community structure and key degradative organisms/genes using micro-Bio-Traps. At Abraham's Creek, we utilized the sHRPP to measure the occurrence of bacteria capable of PCB reductive dehalogenation [*Dehalococcoides spp.* (DHC) and *Dehalobium spp.* (DECO)]. One test plot at this site had previously been bioaugmented by addition of Sedimite as well as bioaugmented with a culture capable of reductive dechlorination. We measured concentrations of two species of bacteria capable of PCB reductive dehalogenation (DHC and DECO) throughout the profile (Figure 5.28). Due to budget constraints, we only analyzed selected depths. However, Biosep beads were available in all micro-biotrap cells (resolution ~ 3cm) which could have been analyzed. No comparison to core data is possible as due to issues with the Coronavirus pandemic (COVID) the cores samples were unable to be analyzed directly. It should be noted that while in this effort only two species were evaluated, the sHRPP is capable of evaluating any species for which commercial methods exist.

In past efforts we have used the same biotraps in sHRPP to measure the abundance of a wide variety of organisms and genes in coastal sediments.

Performance Objective 5. Quantify Differences in Site Evaluation (Existing Data vs New sHRPP Data)

This performance objective was evaluated using the data obtained for two sites (Grand Calumet and Canal Creek). Predicted attenuation and transport of contaminants were compared using data based on 1) existing data and/or data produced from traditional methods (e.g., from soil cores, traditional 1D SPME) or 2) data from the sHRPP. For sites that have both unaltered and remediated areas, we also compared the transport and fate of contaminants of concern (COC) using each data set (e.g., traditional vs sHRPP). Emphasis was on evaluating model resolution and reliability. Conservative profiles produced a transport model that predicted accumulation of dissolved species due to evapotranspiration, bank drainage, and tidal fluctuation (5.5.7.2). This model when qualitatively coupled with geochemistry and metal concentrations suggest metals are concentrated from surface water and sequestered due to reduced conditions. A dynamic zone near the surface exists with dynamic fluctuations in metal concentrations, due to tidal and seasonal changes. We are unaware of any other sampling methods that could produce the required data to perform this evaluation. At Grand Calumet, transport of HOCs were modeled using CapSim (5.5.71). The effort combined the velocity estimates, and Cl^- depth profiles to determine the magnitude of benthic exchange and then verified the conservative transport model which was applied to PAHs transport. Without the sHRPP data it is difficult to constrain transport parameters and thus predictions of long-term PAH transport have large uncertainties. Treatment efficacy was evaluated at Abraham's Creek (see section 6.7) where we show that sHRPP produced more statistical power for comparing treatments. Cost and effort are explicitly addressed in Performance Objective 7.

Performance Objective 6. Measure Quantitative Parameters Required to Evaluate Remediated and Unremediated Sediments

Quantitative data from remediated and unremediated areas of some demonstration locations were compared based on the technologies deployed at each site (e.g., activated carbon). Multiple sHRPPs were deployed in control and treated areas and we also used traditional evaluation methods as appropriate for the site (e.g., vertical 1D SPME, etc.). Using the data produced by each method we evaluated the efficacy of the treatment. Our intention was to both highlight the ability to evaluate remedial efforts and compare the power of each data set. Our main focus was not specifically to determine whether there is or is not a difference based upon the remedial approach (i.e., this was not a remediation technology evaluation) but rather whether the sHRPP can better measure such differences versus traditional sampling. As such, we compared qualitative measures such as resolution (sHRPP vs traditional) and quantitative measures, such as contaminant concentrations confidence intervals. We used appropriate statistical analyses (e.g., ANOVA) as a measure of past treatment effect(s) on measured sediment parameters where appropriate but our focus was on comparing the confidence of any given comparison using data produced by the sHRPP compared to traditional methods.

This objective was met. We evaluated this objective by comparing the PCB concentration distribution produced by the sHRPP and T-Bar sampler in the upper 15cm of each plot in each treatment (Control, Sedimite, and Sedimite +Bioaugmentation) of the Abraham's Creek site (Section 5.3.1) (Figure 5.4). The sHRPP HOC concentration data passed the normalcy test and using a one-way ANOVA, there was a statistical difference between treatments ($p=0.002$).

The control treatment was statistically lower in concentration compared to both the sedimite (p=0.004) and sedimite+ bioaugmentation (p=0.011) treatments but there was no difference between plots with sedimite (p=0.782). The T-bar data from the sedimite+ bioaugmentation plot had a much larger range of values on the high end and the normalcy test failed. However, based on the T-Bar data set, using a Kruskall-Wallis one-way analysis of variance by ranks, there was no difference in means (p=0.068) between treatments. In order to better compare the statistical power of each data set (sHRPP and T-bar), only the data sets that passed the normalcy test for both samplers were evaluated. The control and sedimite treatment were compared using a t-test. Both the sHRPP and T-bar data for those two treatments pass the normalcy test. Using the sHRPP data, the concentrations of PCBs in the control plot were higher (p=0.001) than in the sedimite plot, while using the T-bar data set there was no statistical difference (p=0.803). It should be noted both T-bar and sHRPP use the same SPME technique. However, the sHRPP produces more samples per depth and more spatial integration per depth, reducing spatial variation. Given these results, we show that the sHRPP produces concentration distributions with more statistical power to discern differences.

Performance Objective 7. Ease of sHRPP Deployment and Sampling

This performance objective is qualitative; therefore, a quantifiable data set was replaced with feedback from the field technician(s) on usability of technology and time required to deploy, retrieve, and sample sHRPPs in the field trials.

This objective was met. The cost of site evaluation using the sHRPP and traditional methods was compared assuming the same spatial resolution was required (Table 6.1). It should be noted that for all parameters this resolution cannot be achieved by traditional methods and for some parameters traditional sampling is unable to measure the parameters (e.g., unstable constituents such as sulfide or reduced iron). For the analysis, we assumed 12 sample locations and that there would be 3 field technicians on site for both methods and that divers would be required to install seepage meters as part of traditional sampling. Finally, assuming that both methods had similar resolution, we did not include the cost of the sample analysis as it would be the same for both methods. Also not included in the analysis, are the costs of the sHRPP. Including cost in the comparison is difficult as they can only currently be acquired through Texas Tech University, but the design is publicly available, and any contractor could purchase or manufacture their own leading to a range of equipment costs based on the number of total deployments. For a general comparison, the sHRPP cost ~ 2500 to manufacture. The samplers can be reused indefinitely, and the current rental cost is ~ 800$/sampler. The cost comparison was made solely on person time which is the major cost of site sampling excluding analytical costs. For this analysis total labor cost for traditional methods is estimated at ~$32,000 and for the sHRPP $20,400.

COST ASSESSMENT

The cost of using the sHRPP for site assessment is difficult to quantify as it very dependent on the specific site, contaminants, and goals of the assessment. Some generalities can be made in comparison to traditional site assessment techniques. In general, no traditional techniques alone or in combination can provide the resolution or suite of parameters produced by the sHRPP. While this level of resolution and range of parameters may not be required at all sites, there are numerous advantages as outline in the report for using co-located high resolution profiles that incorporate

diverse parameters capable of describing not only contaminant distribution but also the geochemical status of the sediment and transport parameters. Performance objective 7 and Table 6.2, illustrate a comparison of the labor requirements and costs for a given scenario for both traditional methods and using the sHRPP assuming that the traditional methods could produce the same resolution. Analysis costs would be the same for either method being only a function of the number of samples generated. Most other costs would be comparable including travel costs as they are based on number of personnel and required deployments which are both similar for each method. There is a cost to either manufacture, buy, or contract for the use of the sHRPP. The sHRPP are reusable and so this cost is dependent on the number of deployments over which the cost is distributed. As an estimate in the sHRPP used in this study cost ~ 3,000 per sHRPP to manufacture including materials.

IMPLEMENTATION ISSUES

Currently the sHRPP is not available commercially as a turnkey service similar to most passive sampling methods such as SPME, PE or DGT. It is available through Texas Tech University in cooperation with other consultants or a new company called Envirostatus, LLC specializing in passive sampling. However, we have developed a standard operating procedure (SOP) and informational voice over power point which is posted on the ESTCP website that covers the use, applications, and detailed instructions on how to prepare, deploy and sample the sHRPP. This presentation includes imbedded videos that demonstrate these activities.

1.0 INTRODUCTION

1.1 BACKGROUND

This project is a joint effort between the Department of Civil and Environmental Engineering at Texas Tech University and the Biotechnology Development & Applications Group at Aptim Federal Services LLC (APTIM). During this effort, we demonstrated the application of a cost-effective, commercially deployable High Resolution Passive Profiler (HRPP) that can be applied to 1) evaluate the performance of remedial/natural attenuation efforts and the corresponding reduction in long-term risk; and 2) access sites and enable improved transport/risk models. The data provided by the HRPP will increase our understanding of contaminant availability, sediment geochemistry, microbial processing, and sediment pore water contaminant transport as well as the impacts of remedial measures on these processes. The HRPP is a passive sampler that can be directly inserted into a saturated environment (e.g., aquifer, marine or freshwater sediments) to simultaneously determine the concentrations of biogeochemical species and pollutants, the composition of microbial communities, microbial activity, and pore water velocity as a function of depth.

The Department of Defense (DoD) is responsible for the management of hundreds of sites with contaminated sediments, with an estimated liability of more than two billion dollars (SERDP/ESTCP, 2012). The primary contaminants and risk drivers in sediments are typically recalcitrant, highly hydrophobic compounds (e.g., polycyclic aromatic hydrocarbons [PAHs] and polychlorinated biphenyls [PCBs]) and/or heavy metals. Due to the large volume and relatively low contaminant concentrations, as well as the risk of contaminant remobilization, removal and ex situ treatment of sediments is often impractical and/or ineffective over the long term (NRC, 2007; Kupryianchyk et al., 2015). Rather, in cases where sediments pose an unacceptable risk, in-situ remediation strategies are often preferred. Mitigation strategies can include traditional methods such as “cap-in-place” to limit the transport of pollutants to overlying water, or more active in-situ treatment or capping strategies including (1) addition of granular activated carbon (GAC) based adsorbents to sequester contaminants and reduce their bioavailability, (2) bioaugmentation with or without GAC or clays to sequester compounds, and/or (3) biostimulation using PCB surrogates, electron donors or electron acceptors depending on the specific chemicals of concern (e.g., Bedard et al., 1998; Zimmerman et al., 2005; Cho et al., 2009; Payne et al., 2011; Sowers and May, 2013; Sowers et al., 2015; Kupryianchyk et al., 2015).

A key factor in appropriate management of contaminants in sediments is an accurate understanding of their distribution and bioavailability; along with appropriate models to predict their fate and transport, as well as associated changes in their bioavailability. Further, in cases where active remediation efforts are utilized, there is a clear need to accurately assess the impact of such efforts on contaminant fate and bioavailability. In order to meet this need, high resolution data are required, including contaminant distribution and bioavailability, biogeochemical conditions, and microbial activity. Older methods to evaluate these parameters mainly relied on sediment cores and/or extraction of pore water for testing (e.g., Chapman et al., 2002; Zoumis et al., 2001). These approaches suffer from numerous issues including an inability to collect cohesive cores, the impacts of sample processing on contaminant availability and geochemical constituents, insufficient pore water generation requiring large integrated depths, and high cost. A number of new passive sampling methods exist to characterize the bioavailability and distribution of hydrophobic pollutants in sediments (e.g., review by Lydy et al., 2014 and references therein).

These samplers, which typically utilize polydimethylsiloxane (PDMS), polyoxymethylene (POM), and/or polyethylene (PE) to adsorb the hydrophobic contaminants, typically have high resolution, reasonable deployment times (1-4 weeks), few artifacts, and reduced costs compared to coring. Geochemical conditions can be evaluated separately using diffusion-based samplers (Jackson et al., 2005). While collectively these techniques are capable of evaluating contaminant profiles and bioavailability, they currently cannot be performed simultaneously in the same profile (a key issue due to the relatively heterogeneous nature of sediments) and do not allow for evaluation of microbial activity, which can be a critical fate process in reducing long-term risk. Moreover, none of the aforementioned methods are capable of evaluating pore water velocities, which can be very important and dynamic in tidal areas, rivers and other environments with contaminated sediments.

In order to effectively assess the risk and/or efficacy of remediation efforts at DoD contaminated sediment sites, it would be technically and economically valuable to employ a technique that can evaluate the dissolved phase hydrophobic organic contaminant (HOC) and/or heavy metal distribution with depth at high resolution (cm scale), while simultaneously measuring geochemistry (e.g. dominant redox processes), pore water velocity, and microbial degradative genes/activity (indigenous or bioaugmented) with depth. The sediment High Resolution Passive Profiler (sHRPP) demonstrated is a passive sampler based on SERDP project (ER-2419; 2015-2019), that has been modified to allow HOC monitoring, can be directly inserted into the saturated subsurface and possesses all of the aforementioned capabilities of the HRPP.

1.2 OBJECTIVE OF THE DEMONSTRATION

The overall objective was to demonstrate a modified HRPP for sediment (sHRPP) that is capable of evaluating the bioavailable distribution of contaminants (metals and organics) in sediments via passive sampling at cm vertical resolution, while simultaneously evaluating dominant redox processes at the same resolution, key gene/microbial densities, and pore water velocity. This project demonstrated the application of a cost-effective, commercially deployable sampler that can be applied to: 1) assess contaminant distribution, fate, and availability, 2) evaluate the performance of remedial efforts or natural attenuation and corresponding reductions in long term risk, and 3) increase our understanding of contaminant fate and the overall impact of typical and novel remediation measures on sediment geochemistry, microbial processing, and sediment pore water transport. Moreover, all parameters can be analyzed by commercial laboratories, overcoming a long-standing barrier to passive sampling.

1.3 REGULATORY DRIVERS

This next generation monitoring tool addresses multiple critical and high priority needs documented in the 2012 SERDP/ESTCP Workshop including needs for improved “special and temporal interrogation of site sediments” and the need to “develop and demonstrate a multi-purpose passive sampling device capable of collecting data on several contaminants of interest” (SERDP/ESTCP, 2012).

2.0 TECHNOLOGY

2.1 TECHNOLOGY DESCRIPTION

Over the past two decades, passive samplers have been employed for contaminated site evaluations, including the detection of discharges of chlorinated volatile organic compound (CVOC) contaminated groundwater to surface water at various locations (Vroblesky et al., 1996; Vroblesky and Hyde, 1997); assessment of the fate of CVOCs in wetland sediments (Vroblesky et al., 1991; Lorah et al., 1997; Lorah and Olsen, 1999); and evaluation of perchlorate fate in stream sediments (Tan et al. 2005). More recently, specialized passive samplers have been developed by our group to evaluate deeper sediments and shallow groundwater including characterizing contaminant [chlorinated benzenes, benzene, toluene, ethylbenzene and xylene (BTEX), PAHs, and mercury (Hg)] distribution in deep (~4 m) lake sediments (Kiehl-Simpson et al., 2007), as well as the impact of phytoremediation on chlorinated solvent fate in shallow (~4 m) groundwater (Jackson et al., 2005).

Single-parameter passive samplers utilizing solid phase microextraction (SPME) have also been widely used to assess contaminated sediments and to evaluate remedy performance. Dr. Danny Reible, one of the Co-Principal Investigators on this project, has employed PDMS fibers as a passive sampler specifically for these applications at over 25 sites including Hunter's Point Naval Shipyard, California (PCBs); Portland Harbor, Oregon (PCBs, PAHs); San Jacinto River, Texas (Dioxins); Anacostia River, DC (PAHs); Puget Sound, Washington (PAHs); and Chattanooga Creek, TN (PAHs). Methods of analysis and interpretation have been documented in Ghosh et al., 2014; Thomas et al., 2014 and Lampert et al., 2015, among others. Although conventional chemical analyses can be used for the polymer sorbent, a limitation of the use of the technique has been a commercially available deployment tool that can provide consistency in the samples provided to a laboratory. The sHRPP will overcome that limitation.

2.2 TECHNOLOGY DEVELOPMENT

The HRPP (Figure 2.1) can be directly inserted into the saturated subsurface even at depths in excess of 10 meters (m). The sampler can evaluate: 1) the concentrations of biogeochemical species (e.g., dissolved organic carbon (DOC), chemical oxygen demand (COD), nitrate (NO_3^-), nitrite (NO_2^-), ferrous iron (Fe^{+2}), total iron (FeT), sulfate (SO_4^{-2}), etc.); 2) the composition of microbial communities in different sediment layers; 3) microbial activity using compound specific isotope analysis (CSIA); and 4) the velocity of pore water (Schnieder at al., 2019, 2020; Rubalcava et al., 2022). The HRPP uses equilibrium diffusional sampling to evaluate dissolved biogeochemical and metal species in the pore water. The microbial community is evaluated using a micro-scale Bio-Trap (Microbial Insights) consisting of Bio-Sep beads placed within a modified chamber separated from the sediments using a mesh. In some instances, contaminants adsorbed on the Bio-Sep beads can also be evaluated via CSIA to assess their transformation potential in sediments. Pore water velocity is estimated using the loss of a conservative tracer and a developed relationship between the mass transfer co-efficient and velocity. The HRPP can be used to evaluate a wide range of contaminants including metals, anions, CVOCs, HOCs, and explosives, among others.

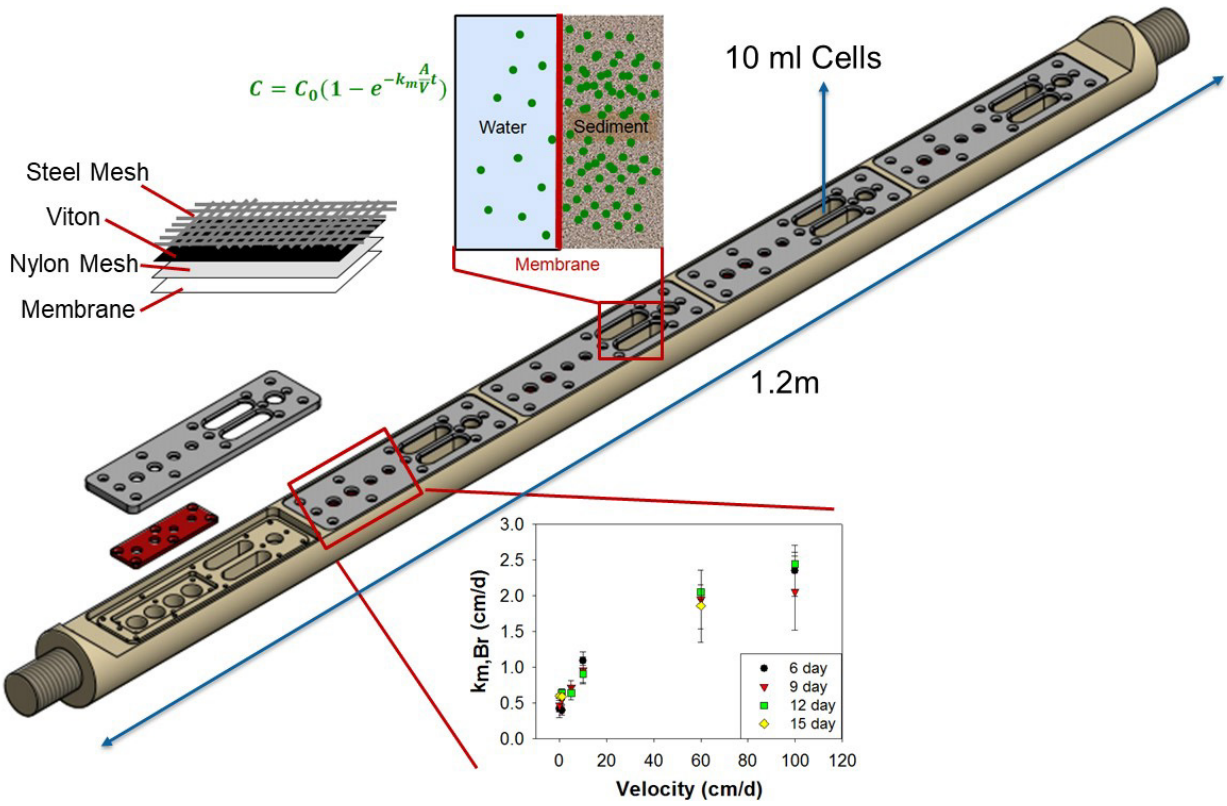


Figure 2.1. HRPP Schematic

HRPP schematic for deep subsurface saturated sediments demonstrating the sampler's ability to evaluate multiple types of information at high resolution. The samplers can be stacked to provide continuous coverage over a 4-30 ft range.

The HRPP is a significant advance over simpler passive samplers due to its capacity to measure contaminant, hydrogeological, geochemical, and microbial parameters concurrently with fine-scale delineation and using a single sampling device. The initial prototype of the HRPP was developed with SERDP funding (Project ER-2419) specifically for use in groundwater aquifers.

The potential utility of this approach is typified by the data collected at Fort Dix NJ, where two prototype HRPPs were installed for 3 weeks (wk) using a standard Geoprobe at depths of 18 to 22 and 21 to 26 ft below ground surface (bgs). The site consists of a trichloroethene (TCE)-contaminated aquifer bioaugmented with a dehalogenating consortium containing *Dehalococcoides* spp. (DHC), and fed buffer and lactate to increase groundwater pH and to provide a carbon source for the dechlorinating organisms, respectively. After retrieval, the HRPP units demonstrated varying concentration profiles of CVOCs, geochemical indicators, microbial population composition, and microbial activity (see Figures 2.2 and 2.3).

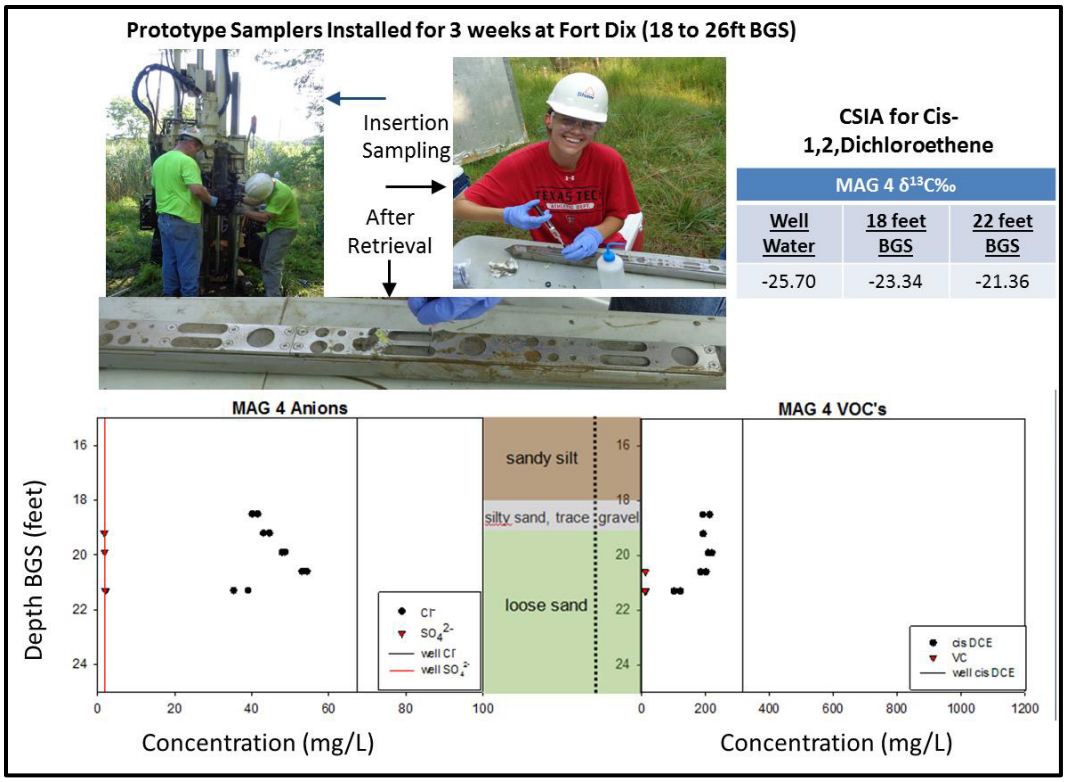


Figure 2.2. Results Summary: HRPP Deployment at Fort Dix, NJ.

Photographs of HRPP insertion at Fort Dix and distribution of Cl^-, SO_4^{-2}, CVOCs, and CSIA of cis-DCE with depth compared to water produced from well within 5 ft of sampler location.

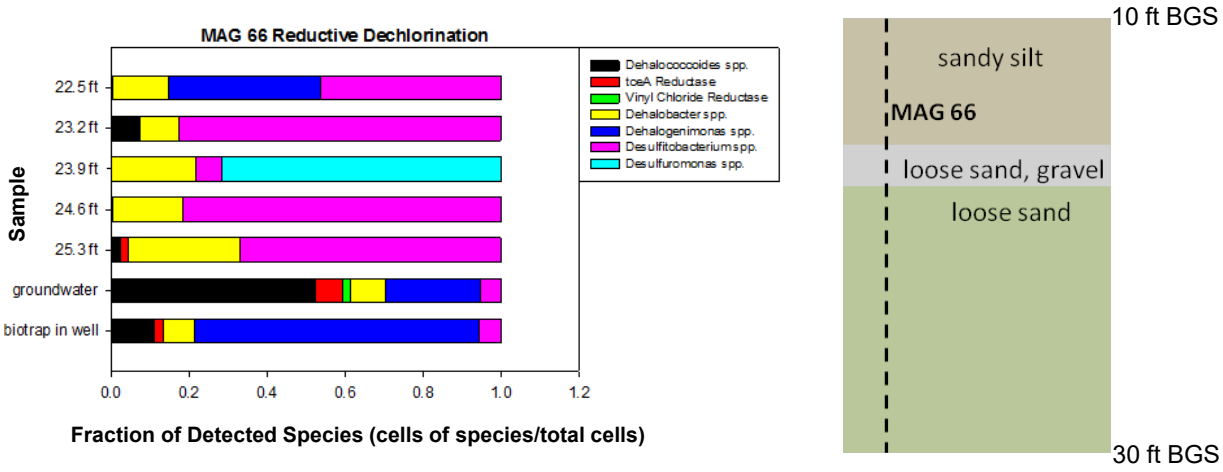


Figure 2.3. Microbiology Profile with Depth at Fort Dix, NJ.

Profile of important microorganisms/genes involved in anaerobic degradation of CVOCs with aquifer depth at the Fort Dix site. Samples were collected from HRPP cells and results are compared to samples from groundwater or Bio-Traps placed within a local groundwater well.

Each HRPP produced duplicate data sets at 20 cm intervals over a 1.2 m sampling depth. Varying concentration profiles of cis-1,2-dichloroethene (*cis*-DCE) were observed even over the 1.2 m interval (Figure 2.2), which were distinct from concentrations in local monitoring wells due to preferential flow through a thin highly permeable zone. As expected, no nitrate and only minimal sulfate was present throughout the depth interval due to the strongly reducing conditions produced by ongoing substrate injections to stimulate reductive dechlorination. Microbial analysis using the QuantArray procedure (quantitative polymerase chain reaction (qPCR) analysis to detect a broad array of organisms/genes involved in both anaerobic and aerobic CVOC degradation; Microbial Insights, Knoxville, TN) of HRPP-embedded micro Bio-Traps, demonstrated a diverse population of known dechlorinators. The abundance and diversity of organisms varied between well samples and depth dependent HRPP samples (Figure 2.3). Interestingly, DHC were observed to compose nearly 50% of the dehalogenating organisms in the groundwater samples, but were not present in 3/5 HRPP cells that were directly in contact with the aquifer sediment layers, and were present as only a small percentage of the bacteria detected in the other two HRPP cells (emplaced at different aquifer depths; Figure 2.3). This may indicate that DHC in this aquifer were primarily planktonic and/or formed biofilms only in more conductive zones. In contrast, *Desulfitobacterium* was dominant in 4/5 aquifer zones sampled by the HRPP, accounting for more than 40% of the community, and *Desulfuromonas* was dominant in one aquifer zone, suggesting also that these dechlorinating organisms and not DHC were dominant in the aquifer sediment layers in contact with the HRPP sampler. The microbial community detected using a standard in-well Bio-Trap also differed appreciably from each of the HRPP samples. The data indicate that the composition of microbial communities in the aquifer sediment layers differs significantly from that in the bulk groundwater and/or the most conductive aquifer sediments (from which that water is largely derived). This information may be critical to understanding and predicting degradation kinetics in complex environments, including aquifers and sediments. Finally, even with the relatively low concentrations of chlorinated solvents, we demonstrated that the HRPP was capable of collecting enough contaminant mass to successfully conduct CSIA, a technique that is increasingly used to distinguish destructive contaminant loss (e.g., via biological or abiotic degradation) from non-destructive processes (e.g., dilution) (e.g., Hatzinger et al., 2013) (see Figure 2.2).

In an additional field trial conducted at former Naval Air Station (NAS) Alameda, California, the HRPP proved effective in the fine-scale evaluation of contaminant concentrations, geochemical indicators, microbial community composition, CSIA of CVOCs, and hydraulic flux. Effectiveness of the HRPP at Alameda was not only based on comparisons with groundwater data from monitoring wells, but also from membrane interface probe (MIP), hydraulic profiling tool (HPT), soil core, and passive flux meter investigations (Figure 2.4). Similar to our observations at Fort Dix, the HRPPs at Alameda produced higher resolution data profiles than standard monitoring wells.

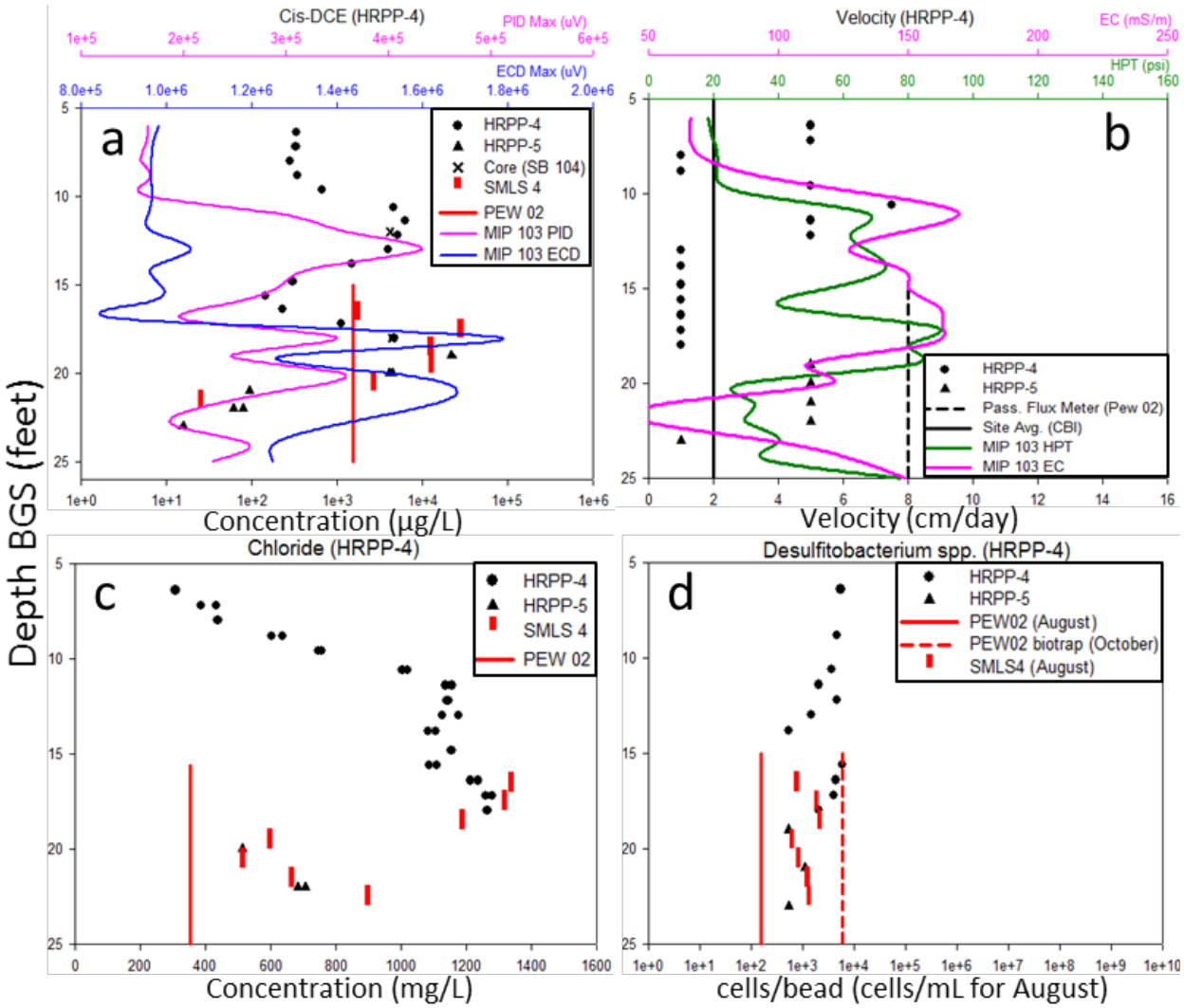


Figure 2.4. Results Summary: HRPP Deployment in Alameda, CA.

Sample of data collected from HRPP-4 and 5 including a) cis-DCE concentrations compared to MIP, soil core, and well water; b) velocity estimates; c) chloride concentrations compared to well water; d) and desulfitobacterium concentrations compared to well water and bio-traps in wells.

In a different effort, we demonstrated the ability to combine high resolution profiles of HOCs and geochemical indicators to study cap performance (Figure 2.5). Two separate samplers were placed side by side in the Anacostia River to evaluate the performance of two different capping materials (sand and Aquablock). The profiles clearly show the variations in phenanthrene as a representative HOC and a pore water tracer (Cl^-) due to variable sorption and transport. The data also provide a nice example of the importance of capping impacts on redox processes as well as the impact of the capping material (e.g., SO_4^{2-} in Aquablock). Under the sand cap, the SO_4^{2-} was completely consumed within a few cm of the sediment surface while the profile under the Aquablock shows a large SO_4^{2-} peak produced by the capping material.

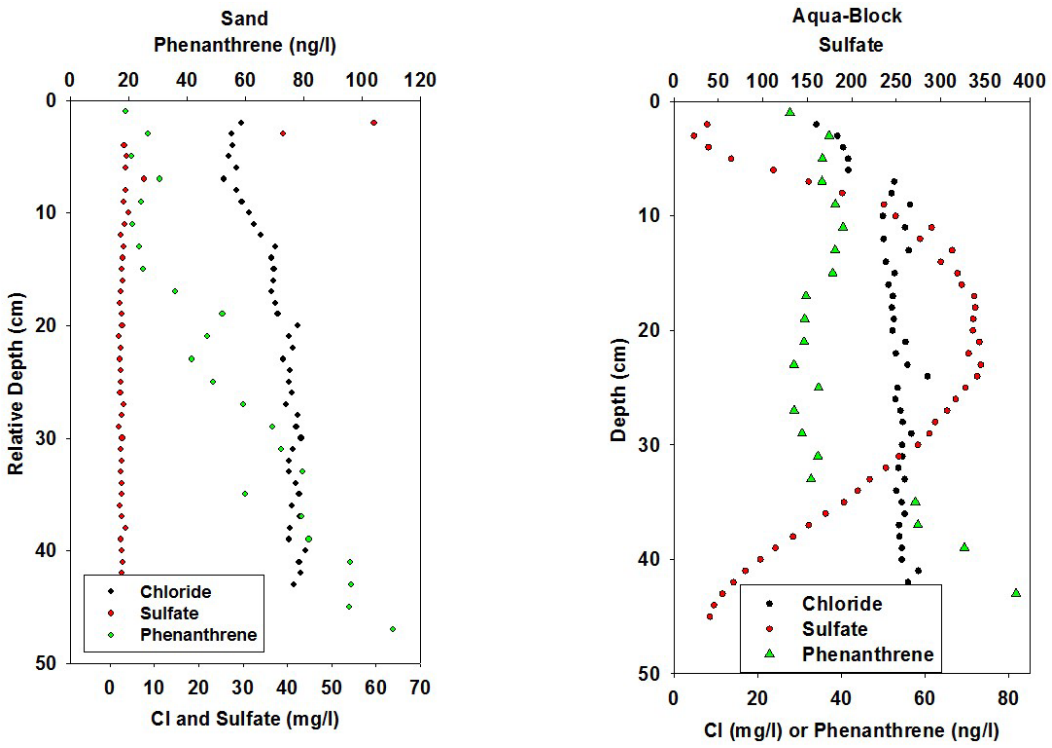


Figure 2.5. Evaluation of Cap Performance (Aqua-Block and Sand) in the Anacostia River

Using combined data from diffusion based samplers including SPME sampling for phenanthrene and pore water equilibration for the geochemical species Cl^-, SO_4^{2-}.

The sHRPP is based on a groundwater direct drive passive sampler (HRPP), developed, refined, and field validated during SERDP project ER-2419 (Schneider etal., 2019, 2020, Rubalcava et al., 2022). The sHRPP incorporates the use of SPME fibers that enable the measurement of HOCs. The sHRPP is made of stainless steel or polycarbonate is driven into the sediment and can sample depths as deep as ~80cm (Figure 2.6). The sHRPP can evaluate at fine-scale (~ 2 cm intervals): (1) contaminant types and concentrations using either equilibration cell water (e.g. metals, cVOCs, VOCs) or by incorporating SPME fibers for HOCs (e.g. PCBs, PAHs, DDX); (2) the concentrations of biogeochemical species (e.g. DOC, Cl^-, NO_3^-, NO_2^-, Fe^{+2},Fe_T, SO_4^{-2}, S^{-2}, CH_4, etc.); (3) pore water velocity; (4) the composition of relevant microbial communities via qPCR analysis of Bio-Sep beads; and (5) biotic and/or abiotic degradative activity via CSIA of contaminants in solution or adsorbed to Bio-Sep beads (Figure 2.6). Dissolved porewater constituents are measured by allowing a reservoir of water to equilibrate with porewater across a micro-porous (0.2 to 0.45µm) membrane (nylon, polysulfonone, or stainless) selected for the intended application. For HOCs with very low water solubilities polymeric passive samplers (SPME) are used to accumulate compounds and include passive reference compounds to correct for equilibrium. Velocity is measured by using the loss of a conservative tracer and a developed relationship between the mass transfer coefficient and pore velocity.

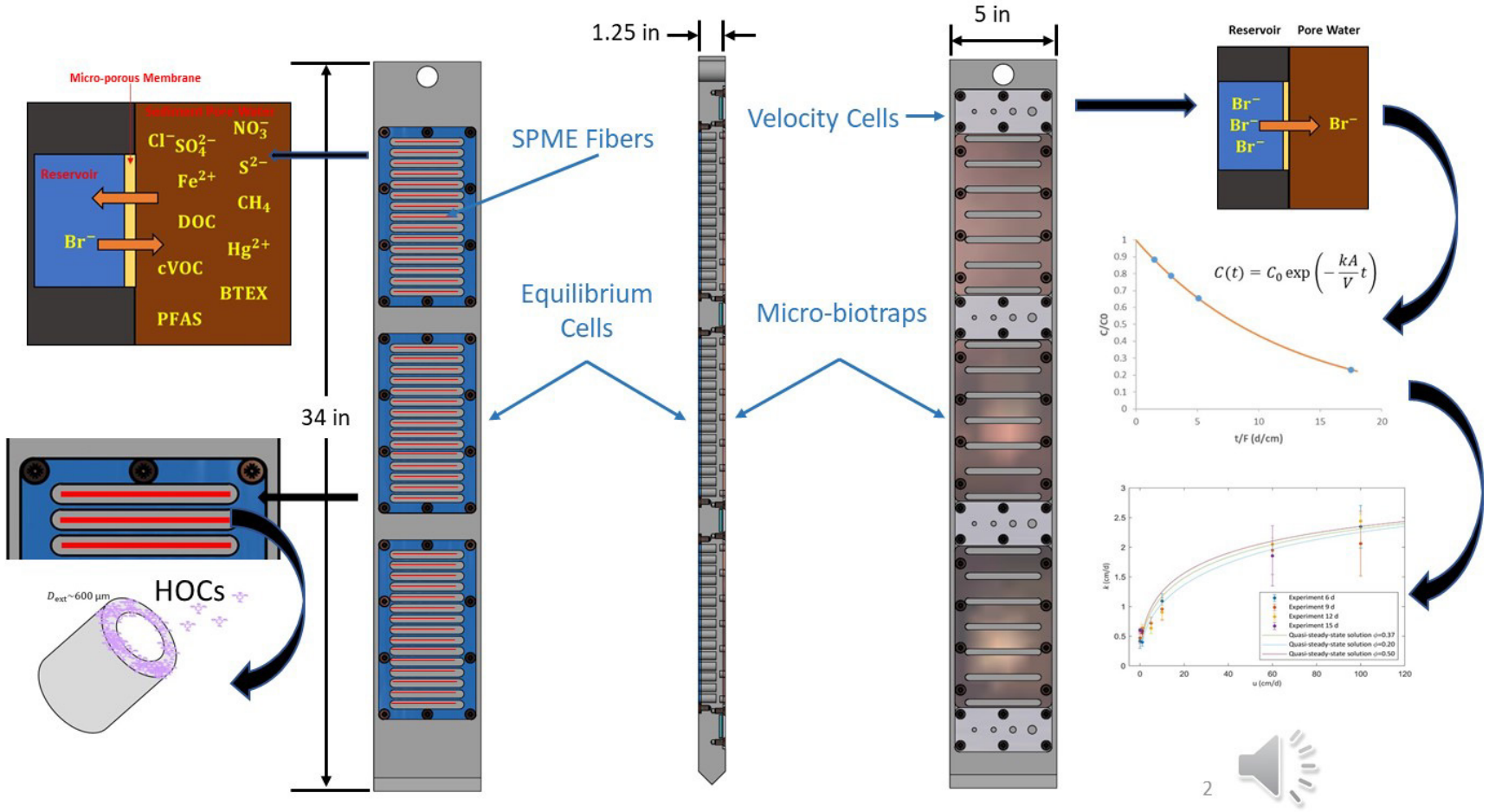


Figure 2.6. Diagram of a Model sHRPP.

Schematic of sHRPP including each side and profile view (center figures). Illustration of the application of equilibrium porewater diffusion for dissolved constituents (Top left) and HOC sampling using SPME fibers (Bottom left). Velocity estimation using Br- to measure the mass transfer of Br and relate to pore velocity (Right figures).

2.3 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

The sHRPP for contaminated sediment characterization is innovative and advantageous in its ability to produce high resolution data sets that combine contaminant concentrations, geochemical conditions, microbial community composition (which is seldom performed in sediments), and transport in a single co-located profile. Individual methods exist for each of these components, but currently they cannot be simultaneously evaluated in a single profile. Further, the efficacy of remediation efforts, whether based on microbial transformation and/or sorption, is difficult to evaluate. Another advantage of the sHRPP is that it can evaluate changes in contaminant bioavailability, transformation, and impact of remediation efforts on biogeochemistry and transport. The combined data will lead to more accurate models of contaminant bioavailability, transformation, and overall fate and transport; as well as better estimates of the long-term reductions in contaminant bioavailability by producing higher fidelity sediment characterization.

3.0 PERFORMANCE OBJECTIVES

The project performance objectives consisted of demonstrating that the sampler could obtain samples capable of being measured for various contaminant and geochemical parameters with sufficient sensitivity and at a resolution high enough to decrease uncertainty in measured parameters compared to traditional methods and thereby improve site assessment, increase confidence in efficacy of applied remediation technologies (active or passive), and decrease uncertainly in modeling efforts of long term fate and transport. As discussed in Section 4.0, there were three primary DoD demonstration sites chosen, along with a separate EPA site (Grand Calumet). Not all parameters were measured at every site. Rather, we used this combination of sites to demonstrate all of the potential capabilities of the sHRPP, as each site has unique attributes and/or contaminants. Performance objectives are summarized in Table 3.1, and details are provided in Sections 3.1 through 3.7. The individual objectives of each site deployment are specified in Table 3.1, but not every site was used to evaluate every objective. Site specific performance objectives are discussed in Section 5.0.

3.1 MEASURE CONCENTRATIONS OF KEY CONTAMINANTS AT EQUAL SENSITIVITY AND WITH LOWER ERROR ESTIMATES WITH DEPTH

One of the primary objectives of this demonstration was to demonstrate that the sHRPP can measure concentrations of key contaminants [PCBs, DDX, PAHs, metals] with depth in sediments with the same or better levels of detection and with greater confidence than traditional methods (either *in- situ* passive sampling or core processing).

3.1.1 Data Requirements

This performance objective was evaluated through the 4-wk deployment of multiple sHRPPs at the field sites. Following retrieval, the sHRPP SPME PDMS fibers were analyzed for dissolved HOCs (PCBs, PAHs or DDX) according to EPA 8270 (PAHs), EPA 8081A (DDX), and EPA 1668c (PCBs). Remaining concentrations of PRCs were analyzed in the SPME fibers by the appropriate methods above, depending on which analyte was of interest. For sites with PCBs, DDX, or PAHs, we also measured concentrations in pore water using traditional vertical *in-situ* SPME sampling and/or ex-situ SPME sampling and at Grand Cal we also compared to PE sheet samplers at shallow depths. At sites where heavy metals are present, a portion of the equilibrated pore water in the sHRPP cells was attempted to be analyzed for heavy metals (Hg, Fe, Pb, As, Zn).

3.1.2 Success Criteria

This objective was considered to be met if the concentrations of organic hydrophobic contaminants (PAHs, PCBs, DDX), measured in pore water:

1. were acquired by the sHRPP at the desired resolution (~2 cm) and were detected with comparable or improved sensitivity compared to current industry-standard (e.g., *in-situ* vertical SPME sampling) passive sampling methods.
2. had statistically smaller confidence intervals (smaller uncertainty) than concentrations provided by standard vertical samplers.

Table 3.1. Performance Objectives

Performance Objective	Data Requirements	Success Criteria
Quantitative Performance Objectives		
Measure concentrations of key contaminants [PCBs, PAHs, metals] in sediments using HRPPs that decrease uncertainty in depth dependent measurements of COCs and modeled predicted concentrations at a detection limit and resolution that provides statistically lower error estimates of concentration with depth.	SPME - EPA 1668c (PCBs) (Abraham's Creek) SPME-EPA 8270 (DDX) (Quantico Embayment) Aqueous ICP-MS (metals) (Canal Creek) SPME - EPA 8270 (PAHs) (Grand Calumet)	Quantification of key contaminants with depth with sensitivity (e.g., DL) comparable to traditional methods (in-situ vertical SPME for HOCs and core processing for metals). Quantification of COCs at a resolution that produces statistically lower error estimates with respect to sediment depth.
Measure changes in geochemical conditions and conservative species at a scale equal to the scale in change of depth due to redox changes or conservative transport.	Anions - EPA 300 (all sites) DOC (EPA 5310) (Abraham's Creek and Quantico Embayment)	Quantification of key geochemical parameters with depth at a scale that equals the distance redox changes occur and conservative transport processes occur and with sufficient sensitivity to measure redox transitions and transport processes.
Measure pore water velocity in sediments using HRPPs	Br- - EPA 300 (all sites)	Quantification of pore velocity with depth
Measure microbial community structure and key degradative organisms/genes	qPCR analysis of Bio-Sep beads in HRPP cells for key organisms/genes (contaminant dependent) (Abraham's Creek)	Quantification of key organisms/genes with depth at comparable resolution to cores.
Measure quantitative parameters required to evaluate remediated and non-remediated sediments.	Quantitative data from above parameters (Abraham's Creek)	Demonstrate that measured concentrations (e.g., COCs, bioaugmented bacteria, and presence of lower chlorinated PCB congeners) based on sHRPP data have lower error estimates and lead to higher statistical power (significance) than data produced by standard sampling measurements. (Abrahams Creek).
Qualitative Performance Objectives		
Quantify differences in site evaluation based on traditional existing data and cores/traditional passive sampling from this study and new high resolution integrated data	Compare attenuation and transport of contaminants at sites for both unaltered and remediated areas where present using existing data and data from sHRPP above (Abraham's Creek, Quantico Embayment, Grand Calumet)	Quantify differences in site interpretation, model predictions, resolution, confidence interval, and cost of data collection
Ease of HRPP deployment and sampling	Feedback from field technician on usability of technology and time required (all sites)	Deployment time is comparable or less than traditional measures (site dependent). Technical skill required to utilize samplers is comparable to that required for traditional methods.

For metals, the objective was met if the concentrations in the equilibrated pore water of the sHRPP cells:

1. had the desired resolution (~2 cm) and were detected with comparable or improved sensitivity compared to current industry-standard pore processing methods.
2. had measured and predicted (spatial) concentrations at depths of concern that have statistically smaller confidence intervals (smaller uncertainty) than concentrations provided by core processing.

3.2 MEASURE KEY GEOCHEMICAL PARAMETERS

The second primary objective was to effectively measure changes in geochemical parameters [NO_3^-, NO_2^-, Cl^-, Fe^{+2}, SO_4^{2-}, DOC] and conservative species (e.g., Cl^-) at a scale equal to the scale in change of depth due to redox changes or transport of conservative species.

3.2.1 Data Requirements

In addition to the previous objective, this performance objective was evaluated through the same 4-wk deployment of multiple sHRPPs at the field sites. Following retrieval, a portion of the equilibrated pore water in the sHRPP cells was analyzed for concentrations of key geochemical indicators (e.g., NO_3^-, NO_2^-, Cl^-, SO_4^{2-}). Depending on the site, we also analyzed Fe^{+2} and S^{-2} on site and DOC. Diffusion equilibrium sampling is the accepted method for monitoring of geochemical species with depth and so we did not compare concentrations with alternate methods (e.g., core processing), as it is well established that cores cannot produce reliable and spatially relevant distributions of geochemical indicators.

3.2.2 Success Criteria

Quantification of key geochemical parameters with depth at a scale less than the distance redox indicators change and conservative transport processes occur and with sufficient sensitivity to measure redox transitions and transport processes. It should be noted that the sHRPP uses the "traditional" passive sampling method for geochemical indicators and comparisons were made on the sensitivity from past applications and to the processes being evaluated. For instance, does the sHRPP produce data that can be used to evaluate SO_4^{2-} reduction with a resolution that is less than the distance over which the reduction occurs? Major processes we evaluated include transport of Cl^-, SO_4^{2-} reduction (measuring both SO_4^{2-} and S^{2-}) and Fe reduction.

3.3 MEASURE PORE WATER VELOCITY

The third primary objective was to measure pore water velocity in sediments using HRPPs.

3.3.1 Data Requirements

In addition to previous objectives, this performance objective was evaluated through the 4-wk deployment of multiple sHRPPs at the field sites. Following retrieval, the equilibrated pore water from the specialized velocity cells in the sHRPP was analyzed for the remaining concentration of a conservative tracer (Br^-). The depletion of Br^- was used to determine pore water velocity.

3.3.2 Success Criteria

The performance objective was considered to be met if the pore water velocity measured with the sHRPP was at the desired resolution (~0.5 m) and with comparable or improved sensitivity compared to current industry-standard sampling methods. It should be noted that at some sites (e.g., lower Canal Creek) no field deployable alternative devices were available and so, although we measured velocity at all sites, only some sites were able to provide alternative measurement techniques for comparison. This approach represents a significant advance over current technologies.

3.4 MEASURE MICROBIAL COMMUNITY STRUCTURE AND KEY DEGRADATIVE ORGANISMS/GENES

The fourth primary objective was to measure microbial community structure and key degradative organisms/genes using micro-Bio-Traps.

3.4.1 Data Requirements

This performance objective was evaluated through the 4-wk deployment of multiple sHRPPs at Abraham's Creek. Following retrieval, the Bio-Sep beads were collected from the micro-Bio-Traps and shipped on ice to Microbial Insights (Knoxville, TN) for QuantArray analysis. We also quantified bacteria known to dechlorinate PCBs.

3.4.2 Success Criteria

The performance objective was considered to be met if microbial population densities were acquired at the desired resolution (~3 cm) and were detected above background values. There are currently no corresponding standard methods for comparison, thus this approach represents a significant advance in this area.

3.5 QUANTIFY DIFFERENCES IN SITE EVALUATION (EXISITING DATA VS NEW SHRPP DATA)

The fifth primary objective was to quantify differences in site evaluation based on existing data from traditional sampling methods and new, high-resolution, integrated data from the sHRPPs.

3.5.1 Data Requirements

This performance objective was evaluated using the data obtained for two sites (Grand Cal and Canal Creek). Predicted attenuation and transport of contaminants were compared using data based on 1) existing data and/or data produced from traditional methods (e.g., from soil cores, traditional 1D SPME) or 2) data from the sHRPP. For sites that have both unaltered and remediated areas, we also compared the transport and fate of COC using each data set (e.g., traditional vs sHRPP). Emphasis was on evaluating model resolution and reliability.

3.5.2 Success Criteria

The performance objective was considered to be partially met by both quantitative and qualitative measures. Quantitative measures include demonstrating that modeled concentrations with time and depth have lower error terms using data collected by sHRPP than by traditional methods. Qualitative measures were met if differences in site interpretation and cost of data collection for traditional sampling methods compared to the sHRPP are quantified.

3.6 MEASURE QUANTITATIVE PARAMETERS REQUIRED TO EVALUATE REMEDIATED AND UNREMEDIATED SEDIMENTS

3.6.1 Data Requirements

Quantitative data of from Abraham's Creek were compared based on the technologies deployed at each site (e.g., activated carbon). Multiple sHRPPs were deployed in control and treated areas and we also used traditional evaluation methods as appropriate for the site (e.g., vertical 1D SPME). Using the data produced by each method we evaluated the efficacy of the treatment. Our intention was to both highlight the ability to evaluate remedial efforts but also to compare the power of each data set. Our main focus was not specifically to determine whether there is or is not a difference based upon the remedial approach (i.e., this was not a remediation technology evaluation) but rather whether the sHRPP can better measure such differences versus traditional sampling. As such, we compared qualitative measures such as resolution (sHRPP vs traditional) and quantitative measures, such as contaminant concentrations confidence intervals. We used appropriate statistical analyses (e.g., ANOVA) as a measure of past treatment effect(s) on measured sediment parameters where appropriate but our focus was on comparing the confidence of any given comparison using data produced by the sHRPP compared to traditional methods.

3.6.2 Success Criteria

Documentation of the increase in the precision of the measurement of concentration with depth for each sampling method.

3.7 EASE OF sHRPP DEPLOYMENT AND SAMPLING

The final performance objective was to determine the ease of sHRPP deployment and sampling.

3.7.1 Data Requirements

This performance objective is qualitative; therefore, a quantifiable data set was replaced with feedback from the field technician(s) on usability of technology and time required to deploy, retrieve, and sample sHRPPs in the field trials.

3.7.2 Success Criteria

The success criteria are partially qualitative, but the performance objective was considered to be met if time and cost efficiency of the sHRPPs are comparable to or less than industry-standard sampling methods. The improved resolution of sHRPP data relative to traditional sampling methods was considered when evaluating time and cost efficiency.

4.0 SITE DESCRIPTION

Due to the robust nature of the sHRPP technology, a wide variety of sediment sites could be accommodated. Site selection, as discussed in detail in the ESTCP-approved Site Selection Memorandum (Texas Tech and APTIM, 2018), included an initial review of available data provided by current and former ESTCP researchers, DoD and EPA contacts, and others. The Canal Creek site at Aberdeen Proving Ground (APG) in Maryland, both the Abraham's Creek site (Site 102) and the Quantico Embayment (Site 99) at Marine Corps Base (MCB) Quantico in Virginia, and the Great Lakes Grand Calumet River AOC in Indiana were determined to be the most appropriate locations for demonstrating the sHRPP tool. These sites have many characteristics that made them ideal for this demonstration, including site accessibility, the presence of appropriate contaminants of concern in shallow sediments, a reasonable depth and thickness of the target interval, significant historical contaminant concentration data, and application of various trial remediation technologies in portions of the site.

The Canal Creek site at APG contains a number of different contaminant categories of interest that fulfill the goals of this project; though only the metals-impacted sediments were selected for this demonstration. The Abrahams Creek site at MCB Quantico contains PCBs in sediments (with areas of remediation that include activated carbon or bioaugmented activated carbon addition), while DDX is found in sediments under the sand cap at the Quantico Embayment. The Grand Calumet River AOC contains sand capped PAH-impacted sediments. A brief description of each site location and history, along with a summary of the geology/hydrogeology and nature and extent of contaminants of interest (those pertaining to this demonstration) for each of the demonstration sites, is included in the following subsections (Sections 4.1 through 4.4).

4.1 CANAL CREEK (APG) SITE SUMMARY

4.1.1 Site Location and History

APG is an approximately 72,000-acre US Army-controlled military installation, located in portions of the southeastern Baltimore County and southern Hartford County, MD. It is comprised of two main areas: (1) the Aberdeen Area to the north, and (2) the Edgewood Area (formerly known as the Edgewood Arsenal) to the south. These areas are separated by the Bush River. Excluding wetlands within the open water areas, the wetlands at APG total about 13,600 acres or about 35 percent of the land surface area. Non-tidal wetlands total over 6,000 acres with approximately 1,770 acres of emergent wetlands, 4,350 acres of forested wetlands and 134 acres of scrub/shrub wetlands (Ruiz et al., 2016). The Canal Creek Marsh and Landfill site is located within the Canal Creek Study Area (CCSA), which is a 1,600-acre study area in the northern region of the Edgewood Area. Canal Creek is located on the Edgewood peninsula, which is situated between the Gunpowder River to the west and the Bush River to the east (see Figure 4.1).

The site has been identified as an Army Environmental Database-Restoration site due to historical discharges and disposal practices. Historically, the CCSA has been used for chemical warfare research and development activities since 1917, including laboratory research, field testing, and pilot- and full-scale chemical materials manufacturing (EA, 2008).

Other activities within the CCSA included operation of machine and maintenance shops and garages, metal parts fabrication, degreasing, and metal plating. Prior to the late 1960s and early 1970s, almost all municipal and industrial wastewater generated by CCSA facilities was discharged into Canal Creek and its associated marsh through chemical sewer outfalls (EA, 2008). Chemicals produced in the plants near the West Branch of Canal Creek include chlorine, CN, clothing-impregnating material, arsenicals, nerve agents, mustard, and organic solvents. Solid waste was generally disposed along the edges of the East Branch marshes and consisted largely of concrete and steel construction debris, discarded process equipment, and miscellaneous items (ADERP, 2017). Portions of the Canal Creek marsh were used for landfilling of sanitary wastes and production waste disposal (EA 2008). Chemicals of potential concern (COPCs) included chemical warfare material degradation products (CWMDPs), PCBs, metals (e.g., mercury, arsenic, lead), explosives, solvents, and petroleum products and lubricants (Ruiz et al., 2016). The demonstration site previously worked as part of ER-200825 is located along the West Branch of Canal Creek, north of Hanlon Road (see Figure 4.2).

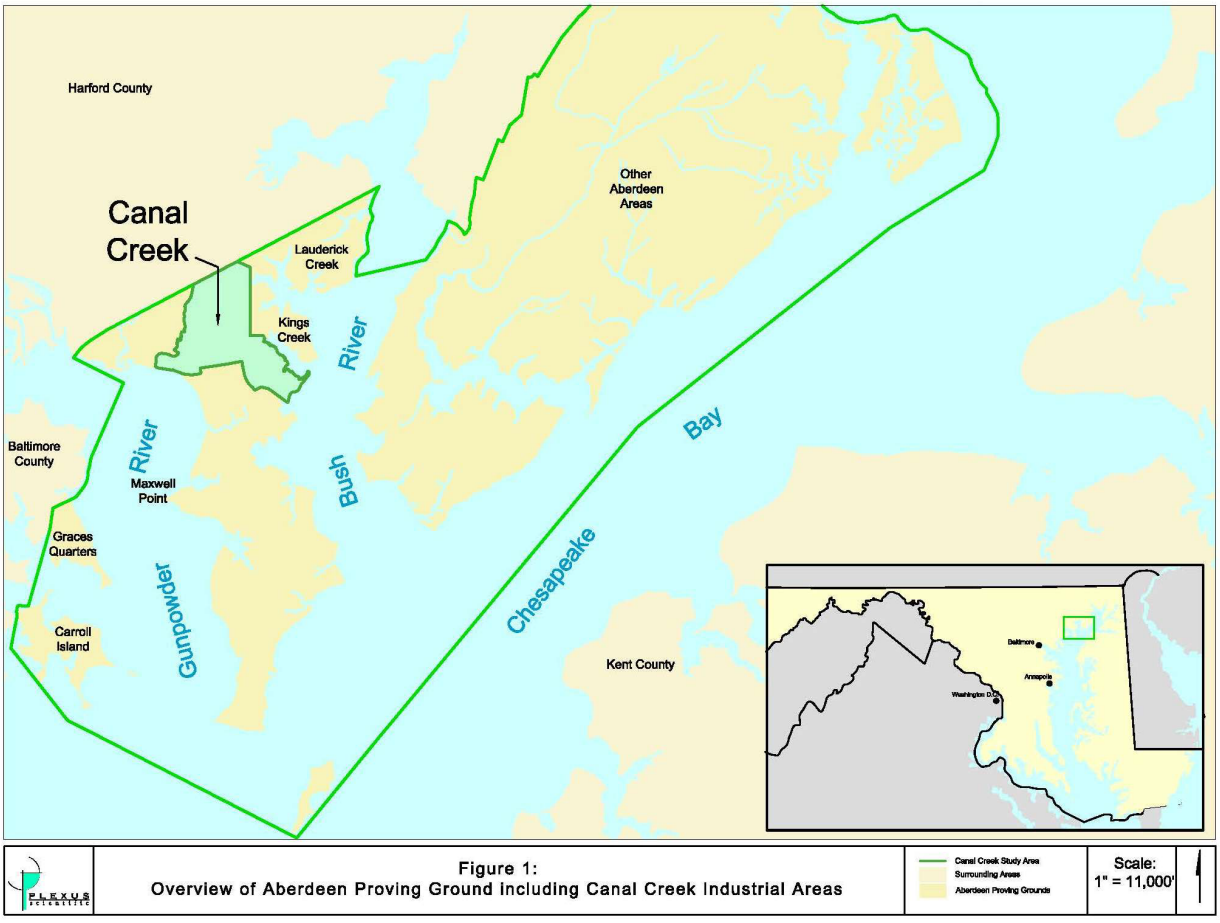


Figure 4.1. Canal Creek Study Area Site Location Map

(U.S. Army, 2008)

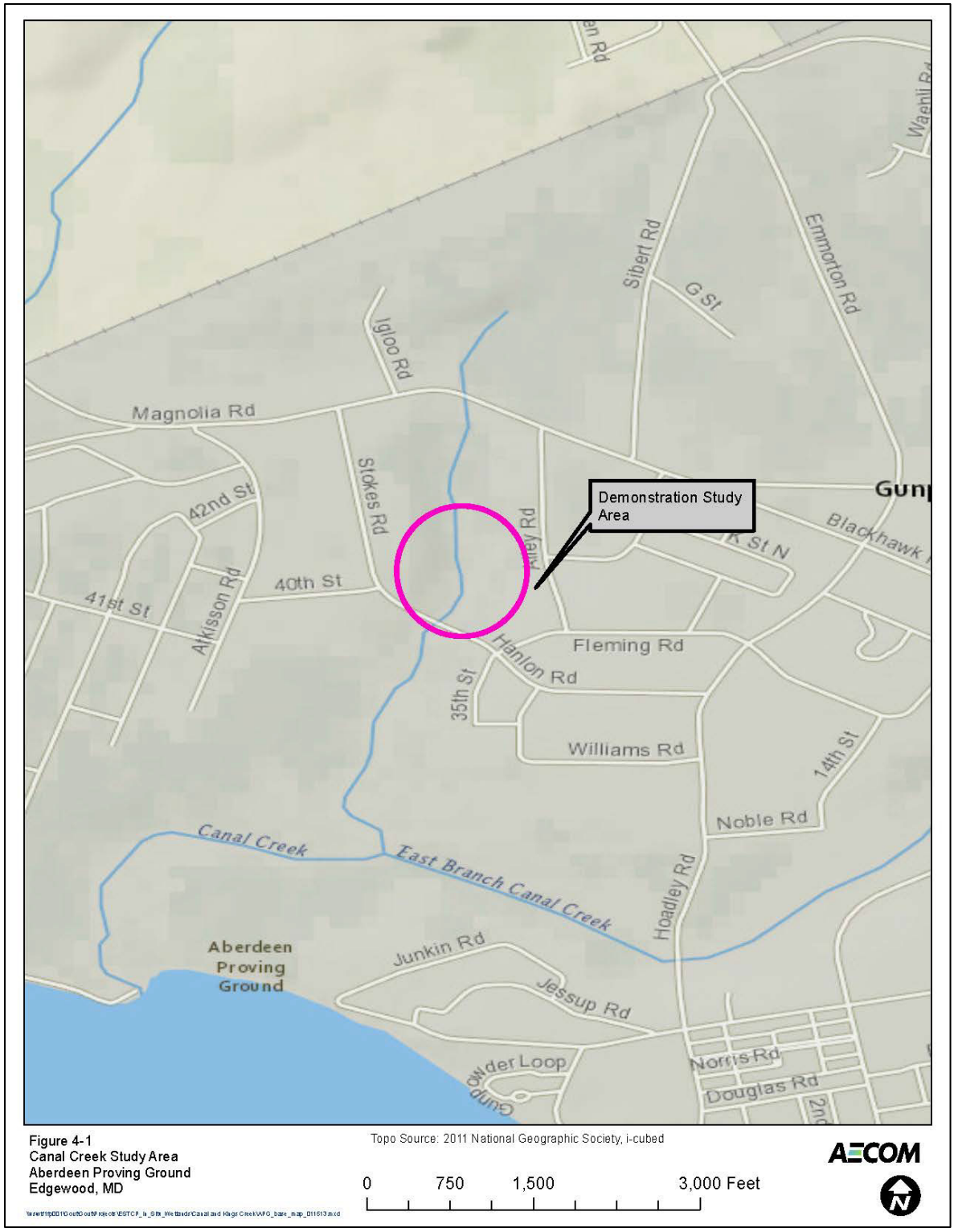


Figure 4.2. Demonstration Site Location Map

(Ruiz et al., 2016)

Canal Creek no longer receives wastewater and is posted by the US Army as an area deemed not accessible for recreational and commercial use, due to the presence of ordnance. No use of the creek is allowed unless approved by APG personnel and under the escort of an unexploded ordinance (UXO) support team that clears areas with regard to ordnance (Menzie et al., 2016).

4.1.2 Site Geology/Hydrogeology

The East and West Branches of Canal Creek, which is a non-tidal to tidal oligohaline to freshwater creek along its approximate 2-mile length, flow southward to the Gunpowder River, draining an area of over 3,000 acres. The creek is bordered by tidal marsh emergent vegetation with small areas of scrub-shrub and forested wetland, and receives some input from contaminated groundwater seeps, with the salinity of the creek ranging from freshwater to approximately 5 parts per trillion (ppt) (EA, 2008). The headwaters are drainages and small streams fed by overland runoff and seeps. The general land cover surrounding the creek includes gently rolling grassy areas, wooded areas with low shrubs, wetlands, and buildings and pavement areas. Elevations range from approximately 40 ft above mean sea level (ft-msl) at several locations near the northern Edgewood Area boundary, to about 10 ft-msl near the West Branch of Canal Creek (U.S. Army, 2008).

The CCSA is located within the Atlantic Coastal Plan Physiographic Province, with predominantly fine-grained unconsolidated sediments, consisting of clay, silt, sand, and gravel deposited by streams, river, and seas, which form a wedge-shaped body that dips southeastward. Alluvial deposits occur adjacent to and within drainage ways and topographic lows (U.S. Army, 2008).

The West Branch of Canal Creek originates as non-tidal freshwater, becoming a tidal creek downstream of Magnolia Road. It is bordered by 45 acres of tidal marsh emergent vegetation with small areas of shrub and forested wetlands. The marsh forms several infrequently flooded side arms. The West Branch has been the site of extensive historic discharge of wastes and also receives inputs from contaminated groundwater via seeps (Ruiz et al., 2016).

4.1.3 Contaminant Distribution

Canal Creek was sampled extensively by EA Engineering as part of the performance of a baseline ecological risk assessment (EA, 2008). PCBs, DDX, mercury and other metals were identified as the primary contaminants of concern at the CCSA. The areas of elevated mercury and other metals to the south of Hanlon Road (near seeps 3-2E and 3-3E, see Figure 4.3) will be the focus of the current demonstration.

During their enhanced bioremediation pilot test in a tidal wetland seep, the U.S. Geological Survey (USGS), in cooperation with the U.S. Army Garrison, APG, studied the design and performance of a reactive mat for enhanced bioremediation of chlorinated solvents at the groundwater/surface water interface. As reported in Majcher et al. (2009) sediment sampling was conducted at Seep Area 3-4 as part of their performance monitoring program between October 2004 and September 2005. Native sediments in the test plot, located to the south of Hanlon Road along the west branch of canal creek (see Figure 4.3), were sampled for metals. Table 4.1 summarizes the maximum concentrations of select metals. Noteworthy, are mercury concentrations up to 4.7 mg/kg, arsenic concentrations up to 39.3 mg/kg, and lead up to 247 mg/kg (Majcher et al., 2009).

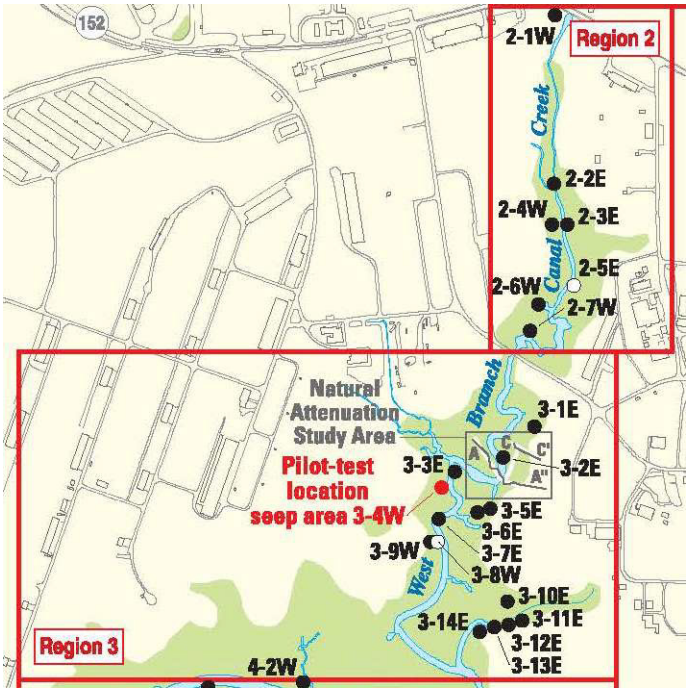


Figure 4.3. Enhanced Bioremediation Pilot Test Location Map: Seep Area 3-4W

(Majcher et al., 2009)

Table 4.1. Select Total Metals Concentrations

(Majcher et al., 2009)

Metals	Max Conc. (mg/kg)
Arsenic	39
Barium	408
Cadmium	4
Chromium	94
Cobalt	59
Copper	153
Iron	36900
Lead	205
Manganese	304
Mercury	5
Nickel	72
Zinc	1050

More recent (2016/2017) sediment sampling conducted by Environmental Chemical Corporation (ECC) at the CCSA as part of a remedial investigation indicate that elevated concentrations of metals (arsenic, chromium, mercury and lead, among others) exist within and adjacent to the natural attenuation study area south of Hanlon Road (see Figure 4.3).

Appendix B includes concentration maps of relevant metals and contains historic sediment metals concentrations and those measured by ECC during their recent work (ECC, 2018). As shown on these maps, relatively high concentrations of metals in sediment have been detected near seep locations 3-2, 3-3, and 3-4; this area was selected as the ideal location to deploy the sHRPPs for monitoring of metals-impacted sediments.

4.2 ABRAHAM'S CREEK (QUANTICO) SITE SUMMARY

4.2.1 Site Location and History

MCB Quantico is located near Triangle, Virginia, and covers over 55,000 acres in the counties of Prince William, Stafford, and Fauquier. The base, used primarily for training purposes, is home to the Marine Corps' Combat Development Command, The Marine Corps Officer Candidates School, and the Marine Corps Research Center.

Abraham's Creek is located in the southeastern portion of Chopawamsic Creek near the confluence with the Potomac River (Figure 4.4) and is an active training area. The site was originally included within Site 100 Chopawamsic Creek, designated as Area 4. Battelle performed the Quantico Watershed Study (QWS) Chopawamsic Creek Investigation in June/July 2005, which determined that the area of contamination in Abraham's Creek was much larger than previously suspected. Though the Final Proposed Plan (Tetra Tech NUS, 2010) for Site 100 recommended no further action for Area No. 4, it excluded Abraham's Creek, which was subsequently separated into its own site and identified as Site 102, due to the potential need for remedial action.

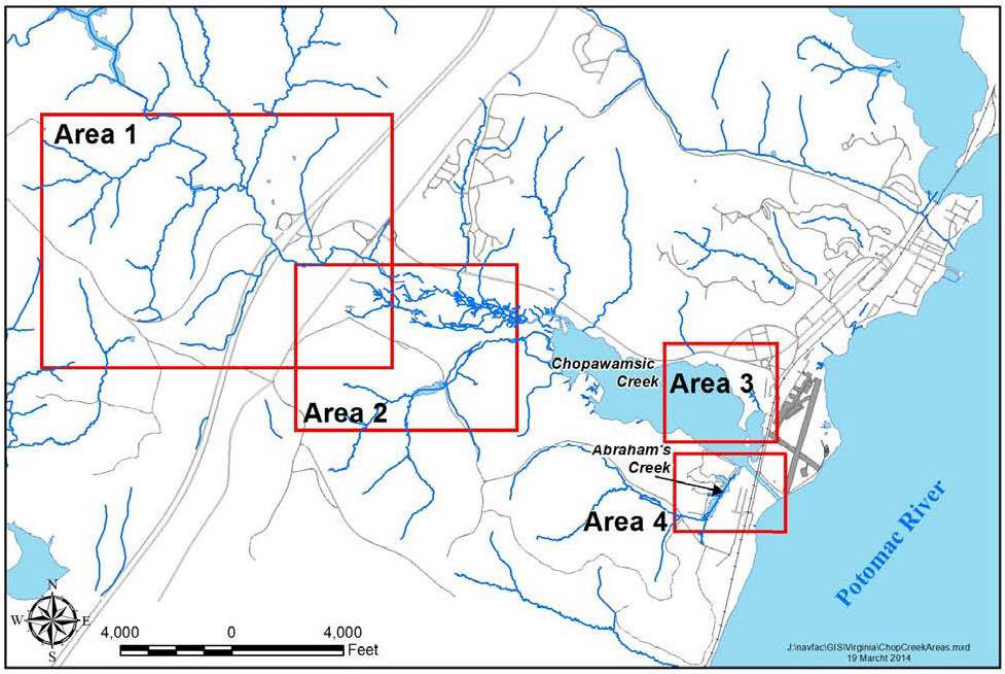


Figure 4.4. Site Location Map

(Battelle et al., 2014)

4.2.2 Site Geology/Hydrogeology

Abraham's Creek is an approximately 17-acre watershed that consists of three pond/wetland areas, as shown in Figure 4.5, and is partially influenced by tidal fluctuations in the northern (downstream) section of the creek (Area 1). However, a land bridge and beaver dam restrict tidal influence in the upstream regions of the creek, designated as Areas 2 and 3. Water flooding upstream Area 3 flows through culverts beneath the land bridge and discharges downstream through Areas 2 and 1, eventually making its way into Chopawamsic Creek.

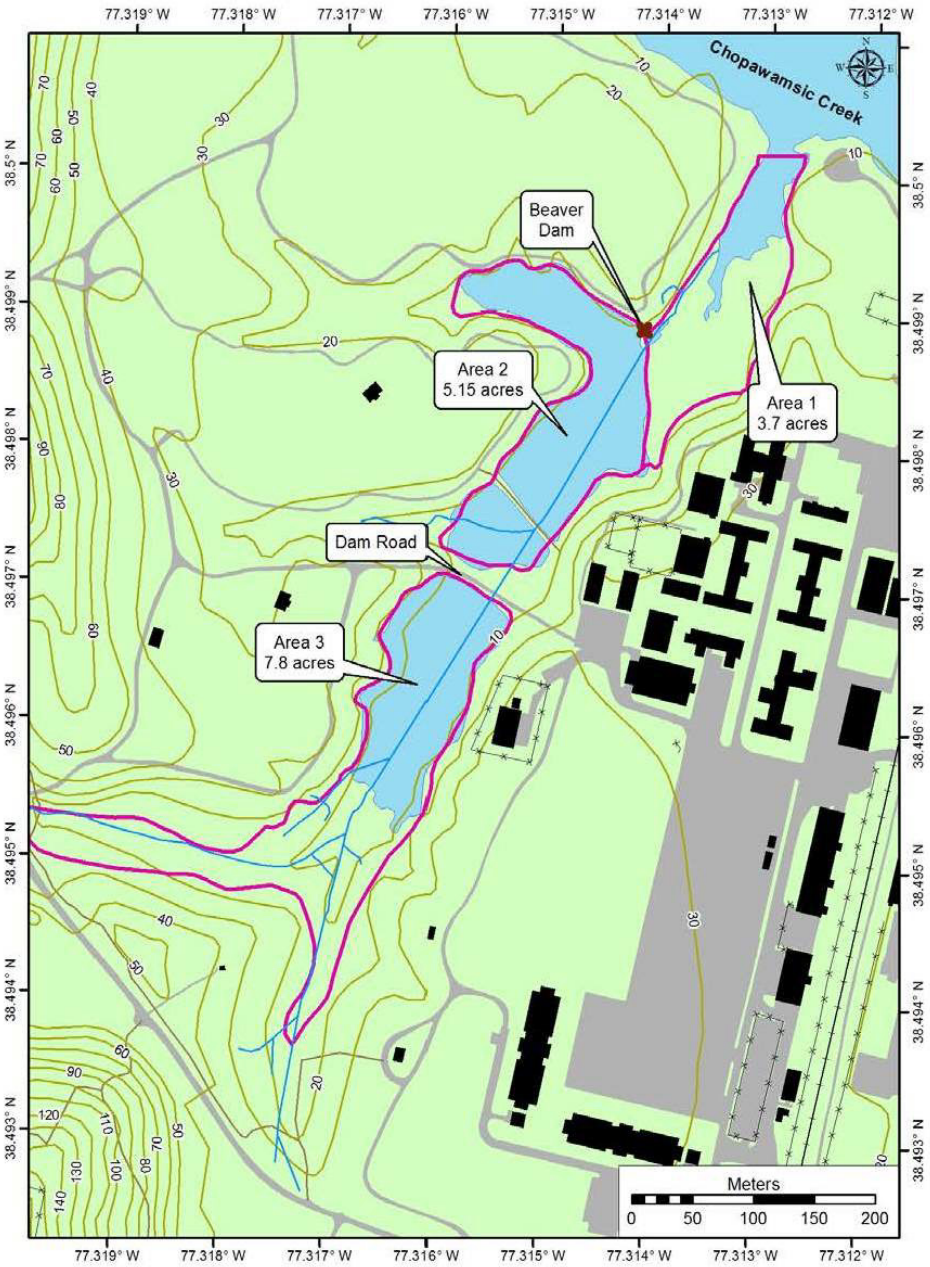


Figure 4.5. Site 102 Subarea Location Map

(Battelle et al., 2014)

Small streams flow into the main body of water in Area 3 (see Figure 4.6), which has relatively shallow water depths, ranging from approximately 0.5 ft in the upload streams to 4 ft in the northernmost area located at Dam Road. The northernmost portion of Area 3 is the proposed location for this sHRPP demonstration (gray box presented on Figure 4.6). The northern section consists of open water surrounded by steep walls and forest along much of the western shoreline. The eastern side is adjacent to a cleared training area and parade grounds that is separated by trees and vegetation. Much of the stream bank is surrounded by steep banks with trees and vegetation up to the shoreline (Sowers et al. 2017).

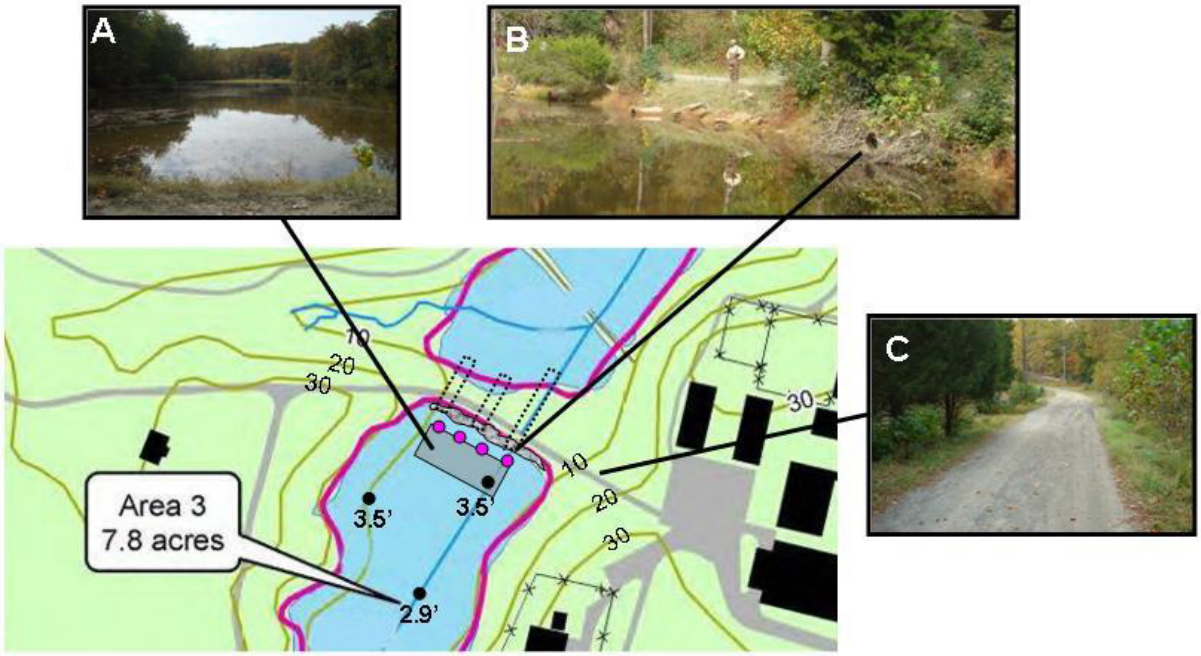


Figure 4.6. Abraham's Creek Area 3 Map

Gray shaded box represents the proposed location for the sHRPP demonstration.

Photo A: view from the access road; Photo B: shoreline adjacent to access road with three corrugated steel culverts connecting Areas 2 and 3; Photo C: the access road (Dam Road)

(Sowers et al., 2017)

Sediment samples collected by Battelle from Abraham's Creek during the QWS Chopawamsic Creek Investigation in June/July 2005 showed a varying material composition depending on the location within each of the three pond areas. Generally, this area was composed of sandy clay, while the wetland areas contained more organic material (in the shallow core intervals) and the upstream tributaries were dominated by more sandy material (Battelle et al., 2005; Battelle et al., 2008).

Area 3 ranges from open water near the access road (Dam Road), to marshy areas and then an upland environment upstream, which consists of small creeks or tributaries. The upstream portions of Area 3 are bordered by very steep sloping terrain. Battelle's sediment sample locations are presented on Figure 4.7. Sample locations AC-10, -11, and -12 consisted of very soft clay with silt in the top 6 inches and then clay and sand layers at depth. Sample AC-12 had a layer of gravel (2.5-3 cm in diameter) at a depth of 4.5 ft. Samples AC-13 and AC-14 were located in the marshy areas and were composed of clayey sand with a top layer (1 ft) of soft organic clay with some roots.

AC-15, -16, and -17 in the upstream portions of Abraham's Creek were generally composed of medium to coarse sand (Battelle et al., 2008).

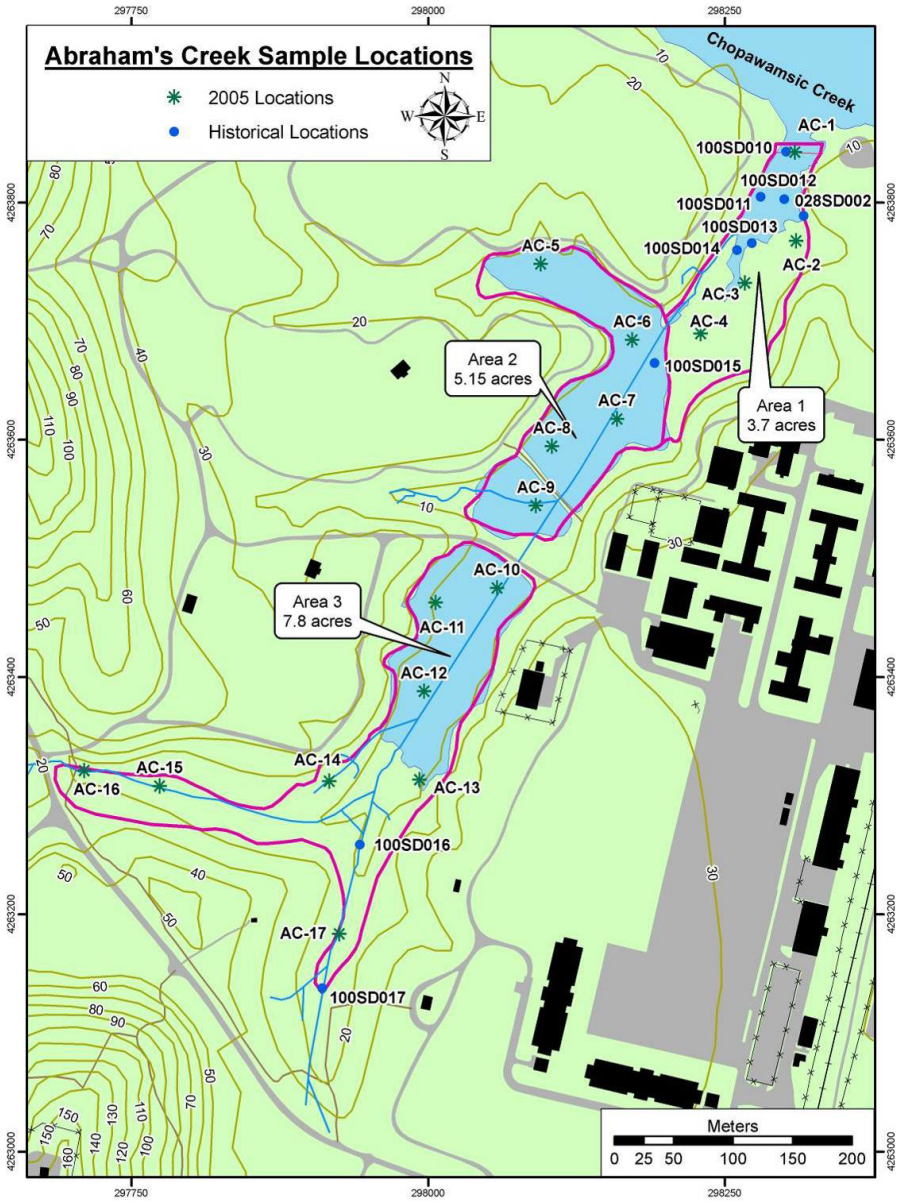


Figure 4.7. Abraham's Creek Sediment Sample Locations – June/July 2005

(Battelle et al., 2008)

4.2.3 Contaminant Distribution

Through all investigation activities, no known onshore point sources to Abraham's Creek were discovered. Evidence that sediments within the creek contained elevated levels of some pesticides and PCBs were reported by Tetra Tech (Tetra Tech NUS, 2007). Potential wide-spread application of DDT to the surrounding area is suspected as the historical source to Abraham's Creek, although the disposal of DDT into the creek cannot be dismissed as a potential historical release. (Battelle et al., 2008).

Since the base has been an active training site since 1917 a possible source of PCB contamination was the addition of a PCB Aroclor to volatile insecticides to increase treatment effectiveness. Contaminants associated with other base activities could have migrated to Chopawamsic and/or Abraham's Creek via deposition, surface water runoff, and groundwater discharge from nearby operations. (Sowers et al., 2017)

Sowers et al., as a part of their site characterization activities for ESTCP Project ER-201215, were provided split samples by Battelle in June 2012 during the remedial investigation, for Total PCB determination via congener analysis. These sediment sample locations are provided on Figure 4.8, while the measured Total PCB concentrations are summarized on Table 4.2. Sample location 15 (in the northernmost region of Area 3) contained the highest Total PCB concentration (6.9 mg/kg), and that area (as identified on Figure 4.8) was selected by their project team as the appropriate location for their demonstration.

Table 4.2. Total PCB Concentrations – June 2012

(Sowers et al., 2017)

Sediment Sample ID	Total PCBs (mg/kg)
1	0.6
2	2.9
3	0.6
4	2.2
5	0.8
6	1.5
7	1.5
8	1.4
9	0.6
10	0.4
11	1.0
12	2.2
13	1.3
14	1.1
15	6.9

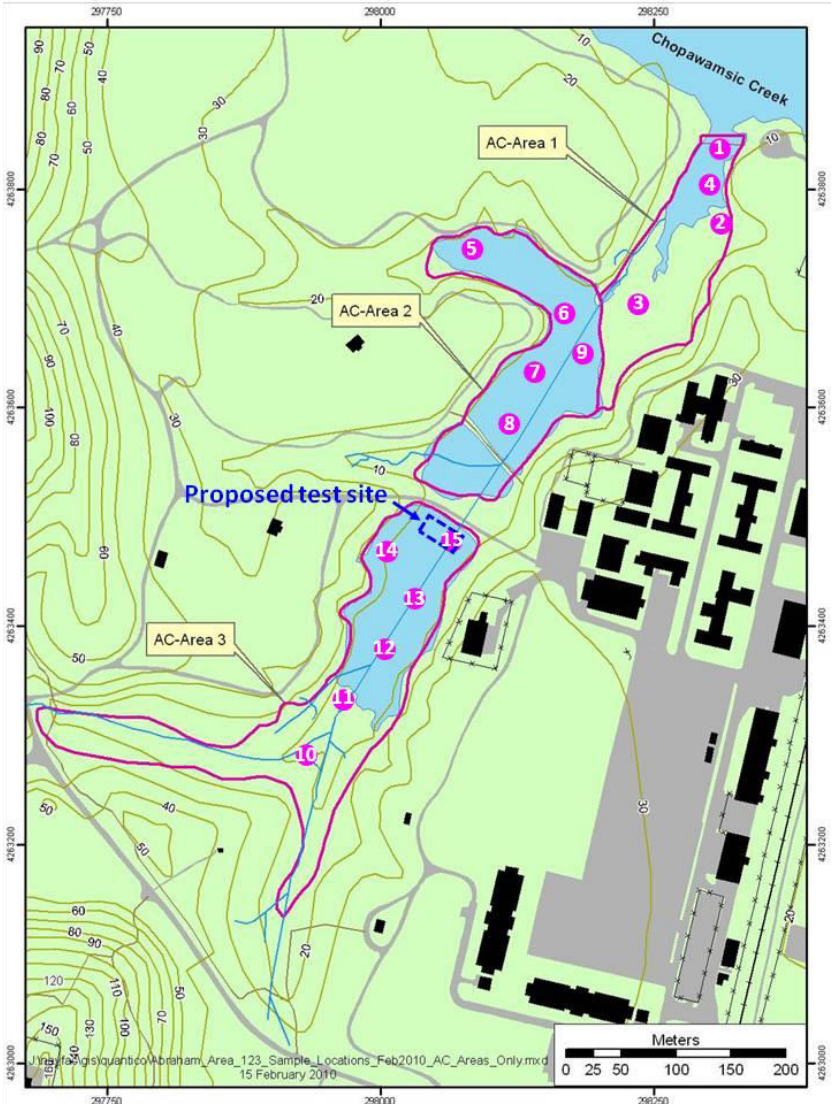


Figure 4.8. Abraham's Creek Sediment Sample Locations – June 2012

(Sowers et al., 2017)

As a final assessment of PCB concentrations across this area for their Site Selection Memorandum, Sowers et al. collected four sediment cores in October 2012 at the locations shown on Figure 4.9 to determine the homogeneity of PCB distribution. Sediment samples were collected in 3 to 3.5 feet of water using a petite Ponar sampler. Assessment of all samples indicated that PCB concentrations were sufficiently high (5.1 mg/kg) and homogeneous (±1 mg/kg) across the length of the plot site, and the area was selected as the demonstration site for ESTCP ER-201215 (Sowers et al., 2017). This area was selected for testing during the sHRPP demonstration.

Figure 4.9. Abraham's Creek Sediment Sample Locations – October 2012

(Sowers et al., 2017)

4.3 QUANTICO EMBAYMENT SITE SUMMARY

4.3.1 Site Location and History

Also a part of MCB Quantico, Quantico Embayment (Site 99) is a semi-circular inlet of the Potomac River to the northeast of Abraham's Creek, on the opposite side of Turner Airfield (see Figure 4.10), approximately 190 acres in area. Approximately 500 ft from the shoreline in the southeastern portion of the bay, is a 12-acre private island called Chopawamsic Island. To the northeast of the island is a broad shelf 3 to 5 ft in depth. West of the island is a historical river channel approximately 16 to 20 ft deep. Both of these features can be seen on the aerial photo presented as Figure 4.11. In general, water depths in the bay range from tidal level along the shoreline to 5 to 6 ft where the bay meets the Potomac River (SPAWAR, 2017).

The Potomac River is not used for domestic or agricultural uses within the vicinity of MCB Quantico and is not expected to be a future source of drinking water because potable water at the Base is provided by two surface reservoirs (Breckenridge Reservoir and Lunga Reservoir). The Potomac River is used for both recreational and commercial fishing near the base.

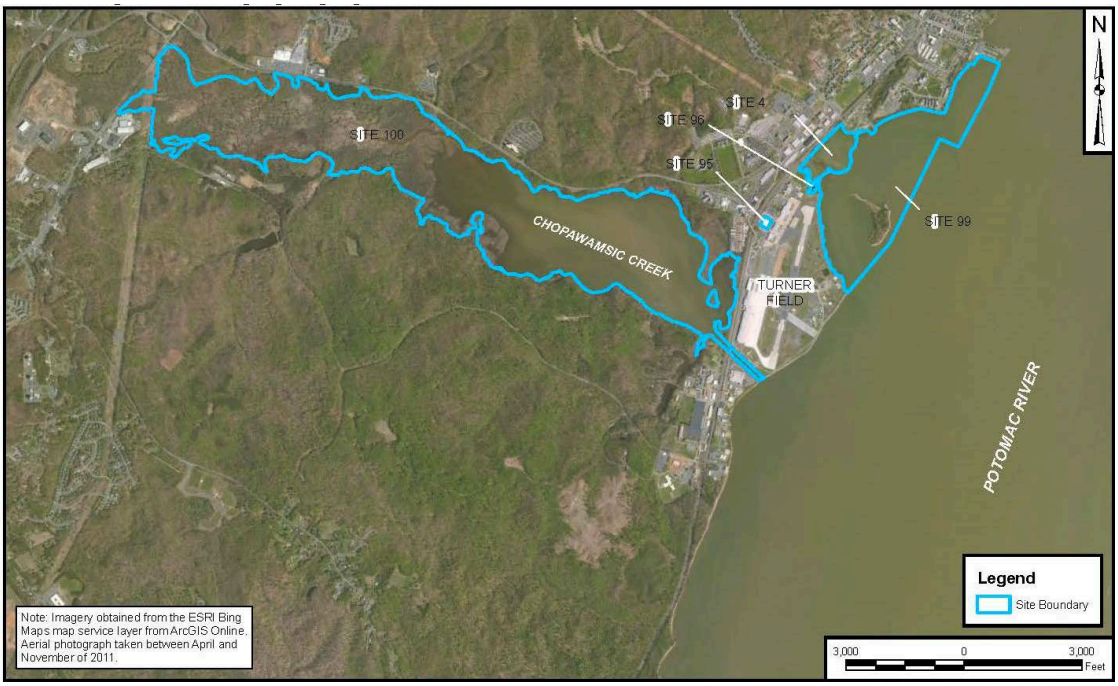


Figure 4.10. Site 99 Location Map

(NAVFAC, 2013)

Figure 4.11. Quantico Embayment Aerial View

(SPAWAR, 2017)

4.3.2 Site Geology/Hydrogeology

The Quantico Embayment is defined as a predominantly freshwater system, with an approximate 1 to 2.5 ft tidal range. Surface water salinity at this site ranges from between 0.5 part per thousand (ppt) in the spring to 3 ppt in the fall, with the higher salinity occurring during lower river flow conditions in the late summer and early fall. Sediment is typically fine-grained, with greater than 55% silt and clay (Battelle and Neptune 2004). More abundant coarse-grained sediment is located along the shoreline and adjacent to outfalls, while finer-grained sediment (greater than 80% silt and clay) is located in outer areas of the embayment (Battelle et al., 2007). Others have assumed, based on the grain size distribution and evidence of low flow velocities within the embayment, the embayment is depositional in nature (SPAWAR, 2017).

4.3.3 Contaminant Distribution

Quantico Embayment Site 99 is surrounded by several possible historic sources of contamination (see Figure 4.12), including Site 4 (Old Landfill), Site 32 (Pesticide Control Building); the Mainside Sewerage Treatment Plant; and an active airfield (Turner Airfield). Various activities have been completed to eliminate or control the on-shore sources, though historical releases have contributed to sediment contamination. The primary contaminants that resulted in a response action at Site 99 (and Site 96) are PCBs and pesticides (specifically DDX).

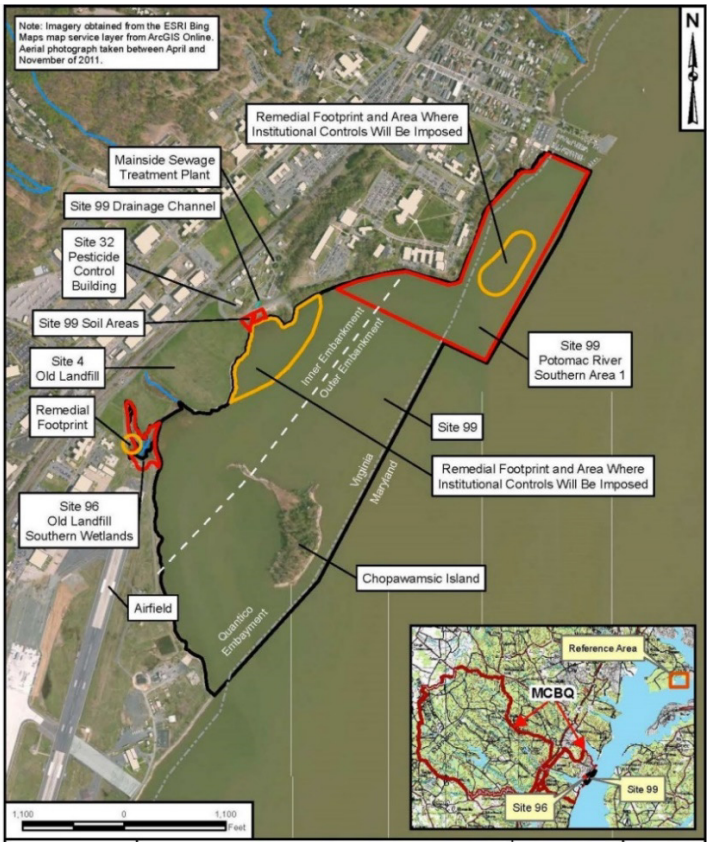


Figure 4.12. Historic Site 99 Contaminant Sources

(NAVFAC, 2013)

Several historical and current storm water outfalls had or have discharge points draining to the Quantico Embayment. Prior to the separation of the storm and sanitary sewer systems at MCB Quantico, these outfalls may have been a source of chemical constituents to the embayment from various operations (e.g., maintenance facilities, floor drains, and wash racks). Six outfalls are currently regulated under National Pollutant Discharge Elimination System (NPDES) permits and drain directly into the Southern Wetlands and/or Quantico Embayment. Two of these outfalls discharge non-contact cooling water and steam condensate, and one discharges steam condensate only (SPAWAR, 2017). NPDES permitted outfalls within MCB Quantico are not expected to be a significant current source of potential contamination; non-NPDES permitted outfalls are also not expected to be continuing sources of potential contamination as they only drain storm runoff from buildings and parking lots (Battelle, 2009). Chemical introduction to Quantico Embayment from Potomac River sources are considered minimal (Battelle and Neptune, 2004).

Although COCs at this site included PAHs, metals, chlorinated pesticides, and PCBs in both surface (0 to 10 cm) and subsurface sediment, the presence and concentration of DDX compounds have driven the requirement for a site remedy (SPAWAR, 2017). DDX compounds, consisting of DDT and its degradation products DDD and DDE, have generally been measured at the highest concentrations in the northern region of the inner portion of the Quantico Embayment adjacent to the northern edge of the Site 4 Old Landfill and adjacent to the potential runoff stream from the Former Pesticide Control Building (see Figure 4.13). Sediment sampling suggests that DDX concentrations both increase with depth in the sediment and are generally highest in the near-shore area, hence the placement of a thin layer cap (see green shaded area on Figure 4.14) in the summer of 2014. This area of the thin layer cap and the DDX-impacted sediments below was selected for testing during the sHRPP demonstration.

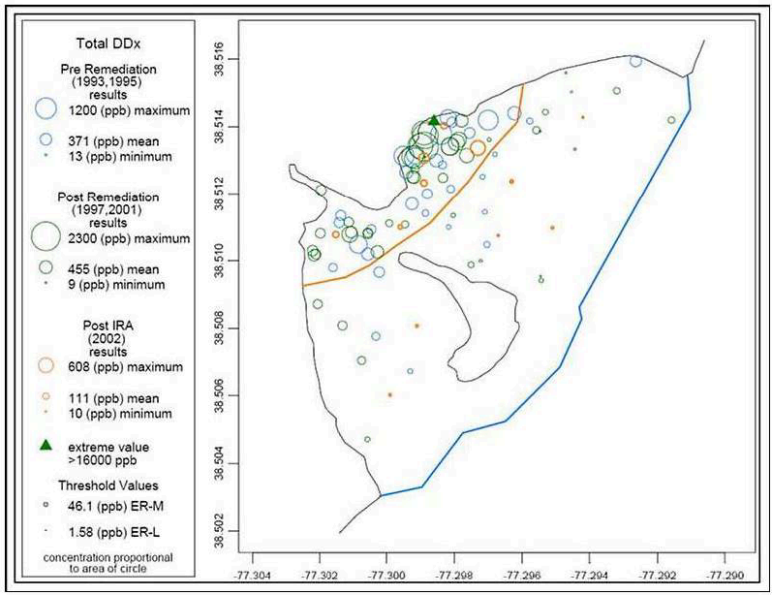


Figure 4.13. DDX Concentrations in Quantico Embayment Sediment

(NAVFAC, 2013)

The orange line represents the boundary between the inner and outer Quantico Embayment. The blue line represents the boundary between the outer Quantico Embayment and the Potomac River (Battelle and Neptune 2004).

Figure 4.14. Quantico Embayment Aerial View

(SPAWAR, 2017)

4.4 GREAT LAKES GRAND CALUMET RIVER AOC SITE SUMMARY

4.4.1 Site Location and History

The Grand Calumet River originates in the east end of Gary, Indiana, and flows 13 miles through the heavily industrialized cities of Gary, East Chicago and Hammond (see Figure 4.15). The Grand Calumet River AOC includes five zones (Figure 4.16):

- Zone A: West Branch including Roxana Marsh
- Zone B: East Branch
- Zone C: Hohman Avenue to the Illinois/Indiana state line
- Zone D: Cline Avenue to the US Steel dredging project (completed in 2007)
- Zone E: Remaining Grand Calumet River segments within East Chicago, Indiana

The focus area for this demonstration was Zone A near the Roxana Marsh (see Figure 4.16). Dredging operations in this area of the West Branch were completed in December 2011. Approximately 235,000 cubic yards of impacted sediment were removed from the river and adjacent wetlands between Columbia Avenue in Hammond, Indiana and Indianapolis Boulevard in East Chicago, Indiana. A cap now covers 345,000 cubic yards of contaminated sediment in the dredged area and consists of 6 inches of organoclay covered by 12 inches of sand. Restoration of the site took place in spring 2012 and included planting native seeds and plants in the 25-acre Roxana Marsh.

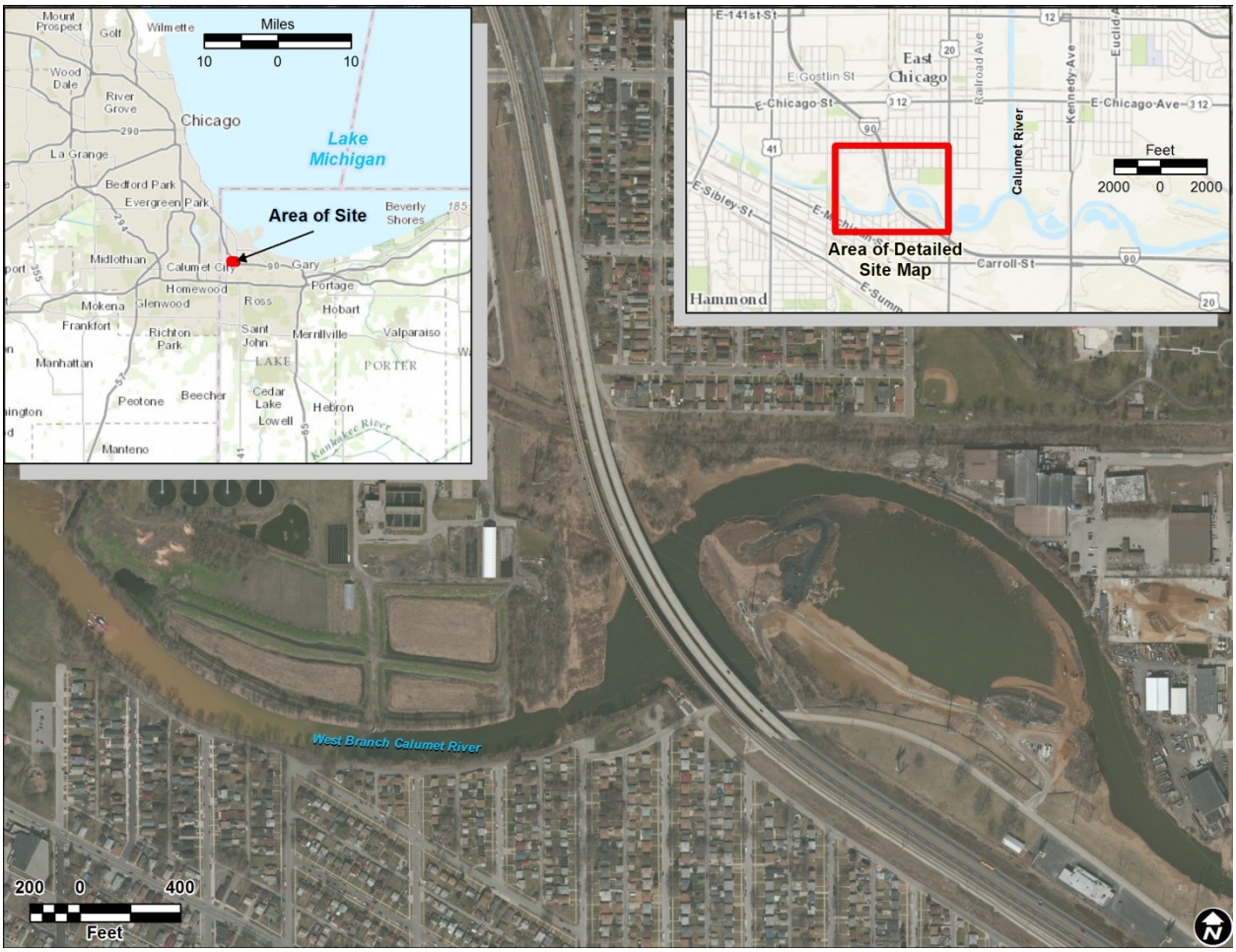


Figure 4.15. West Branch of the Grand Calumet River

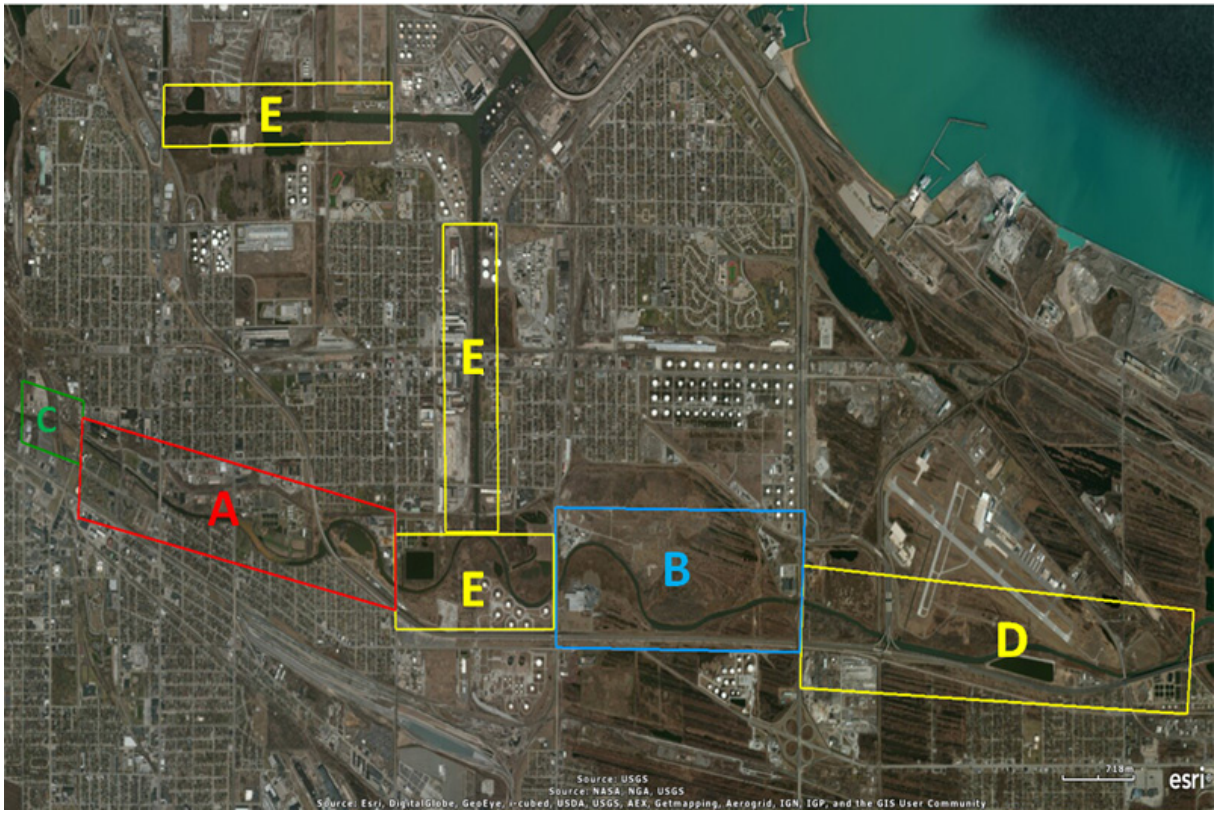


Figure 4.16. Grand Calumet River AOC Zones

4.4.2 Site Geology/Hydrogeology

The Grand Calumet River AOC Zone A is located completely within the Calumet Lacustrine Plain section of the Northern Moraine and Lake Region physiographic province. This area is an abandoned glacial and postglacial lake bottom. The land surface is made up of parallel sand ridges with intervening swales. These remnants of ancient shorelines mark a steady decrease in the size of Lake Michigan. These small dune ridges, with intervening swampy swales, diminish in size from east to west. The surficial geology is mostly glacial and lacustrine sand, silt, and clay deposits of Wisconsinan and Recent age. Large areas with artificial fill and substantially modified land are present along the Lake Michigan shoreline and surrounding Lake George. Wetlands are present in a variety of geomorphic settings. Interdunal wetlands occupy the swales between the numerous parallel beach ridges. Other wetlands are associated with the meanders of the Grand Calumet River and the Little Calumet River, and with lakes and ponds within the AOC (Cohen et al., 2002).

Surface drainage is to the Grand Calumet River, the Indiana Harbor Canal, and Lake Michigan in the north and to the Little Calumet River in the south. The drainage divide separating these areas of surface-water discharge approximately coincides with the Tolleston Beach Ridge, an arcuate upland in the southern part of the area.

The Grand Calumet River consists of the two east-west oriented branches that meet at the southern end of the Indiana Harbor Canal. The east branch of the Grand Calumet River headwaters in the Marquette Park Lagoons and flows westward about 10 miles to its confluence with the Indiana Harbor Canal.

The west branch is about 6 miles long with a surface-water flow divide approximately 1 mile west of its confluence with the Indiana Harbor Canal. Water in the west branch typically flows westward from this divide approximately 5 miles to its confluence with the Little Calumet River in Illinois, and eastward from this divide to its confluence with the Indiana Harbor Canal. Over 90 percent of the flow in the east and west branches of the Grand Calumet River is effluent discharge from industries and municipal wastewater-treatment plants. The position of the flow divide on the west branch of the Grand Calumet River is variable and affected by numerous factors including water levels in Lake Michigan, the amount of effluent flow into the east and west branches and the Indiana Harbor Canal, and the wind speed and direction (Cohen et al., 2002).

The area is underlain by approximately 40 to 225 ft of unconsolidated glacial, eolian, lacustrine, and paludal sediments of Pleistocene and Holocene age that were deposited on a bedrock surface modified by pre-Pleistocene erosion. These sediments form a surficial aquifer and an underlying confining unit that overlie a carbonate bedrock aquifer (Cohen et al., 2002).

4.4.3 Contaminant Distribution

The largest extent of impact to the AOC comes from legacy pollutants found in the sediments at the bottom of the Grand Calumet River and Indiana Harbor and Ship Canal. Contaminants include PCBs, PAHs and heavy metals such as mercury, cadmium, chromium and lead. High fecal coliform bacteria levels, biochemical oxygen demand, suspended solids, and oil and grease are also an issue.

As mentioned above, sediment dredging and placement of a cap were complete by 2012 in the Zone A area of the AOC. A study was performed by USEPA in 2013 to understand cap performance (USEPA, 2015). The cap performance monitoring program included push core sampling for particle size analyses and physical core characterization of cap layers, pore-water monitoring using in-situ monitoring approaches (including SPME pore-water sampling, surface water and sediment sampling, and horizontal transect samplers within and below cap), gas ebullition sampling and analysis, groundwater advection temperature monitoring, sediment PAH surface deposition (comparison to below cap), and sediment deposition evaluation tracer study.

The results for two areas within Zone A (West and East transect locations, see Figure 4.16) are relevant to this demonstration, and are briefly discussed below.

Upwelling data through the cap at the two transects are presented on Figure 4.17, which shows that upwelling at the West Transect is approximately 1 cm/day, while it is more than twice that (2-4 cm/day) at the East Transect. One question that we strive to answer using the sHRPP in this demonstration is whether the upwelling is slow enough to allow significant biodegradation before release into the overlying surface water.

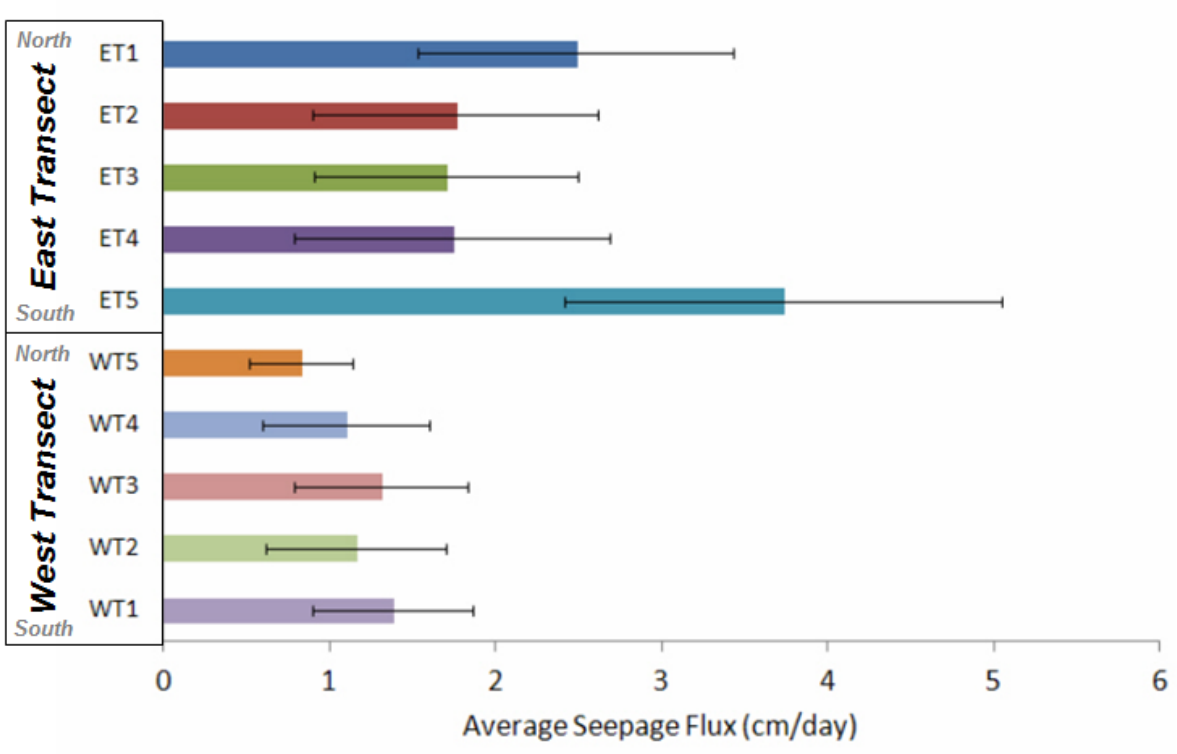


Figure 4.17. Upwelling through the Cap at East and West Transects

(USEPA, 2015)

Significant PAH concentrations are present in sediment below the cap. At the West Transect, long-term monitoring location 10 (LTM-10) contained approximately 10,000 mg/kg of PAH-34 and 1,000 mg/kg of PAH-16. At the East Transect, LTM-4 contained approximately 7,000 mg/kg of PAH-34 and 1,000 mg/kg of PAH-16. Due to these elevated PAH concentrations and the significant amount of data recorded to date in the adjacent area, these two transect locations were utilized during the sHRPP demonstration.

5.0 TEST DESIGN

5.1 SHRPP DESIGN AND PARAMETERS MEASURED

The sHRPPs were designed at Texas Tech and milled from stainless steel or polycarbonate at commercial fabricators. The sHRPP design is presented in Figure 5.1. Similar to the groundwater HRPP, the sHRPP consists of different cells designed to measure soluble geochemical species, contaminant concentrations, microbial community, and pore water velocity as described below.

5.1.1 Geochemical Species

On one face of the sHRPP, there are 20 ml cells (10 cm x 1 cm x 2 cm) every 3 cm on center along the length of the sampler (Figure 5.1). Prior to sampler deployment, these cells were filled with de-aerated Milli-Q water and covered by a 0.2-µm nylon membrane and a 10-µm nylon mesh (for protection), which was held in place with a cover. Dissolved species (e.g., NO_3^-, NO_2^-, Cl^-, Mn, Fe, SO_4^{2-}, DOC, Hg, etc.) diffused through the pores and equilibrated with the water in the cells. Based on extensive testing (SERDP ER-2419), as well as previous work (Kiehl-Simpson et al., 2007), the maximum time to 90% equilibration for the sHRPP is ~2 weeks and can be calculated using equation 1 and the known specific surface (V/A) area of the cells.

$$C_t = C_o\,(1-exp(-k_m * t * A/V)) \qquad \text{Eq. 1}$$

where C_t is the concentration of any measured species at time t in the sampler, C_o is the average concentration in the pore water, K_m is the mass transfer velocity, and A/V (the specific surface area of the sampler). The mass transfer coefficient K_m is a function of the diffusion coefficient of the species equilibrating, porosity of the sediment, and pore water velocity. Once the K_m for a species is determined (e.g., Br^- as an equilibrium reporter compound), equilibration time of other species can be evaluated by scaling the mass transfer coefficient to the ratio of the free water diffusion coefficients of the known species and unknown species. In cases where there is pore water movement (vertical or other) either due to one or bi-directional movement (e.g., tidal flux), the equilibration time will be shorter due to the impact of pore water velocity on the effective mass transfer coefficient (K_m), which conveniently also provides a means of estimating average pore water velocity as discussed below. Analysis of the water in the sHRPP cells produces concentration profiles at detection limits lower than alternative pore water sampling methods (e.g., coring) and at higher resolution and without possible coring related artifacts (compression of soft sediment layers, incomplete cores, alteration of geochemistry during core processing).

5.1.2 Contaminant Concentrations

Dissolved HOCs (e.g., PCBs, PAHs, DDX) were measured using SPME PDMS fibers. PDMS was employed here due to its convenient geometry, spatial resolution and relatively fast kinetics (Lu et al., 2011, Thomas et al., 2014; Lampert et al. 2015). Less hydrophobic organic compounds (monochlorobenzene [MCB], dichlorobenzene [DCB], BTEX, CVOCs, etc.) and heavy metals (e.g., Hg, methyl-Hg, Pb, Cd, etc.) can be measured directly from the equilibrated pore water described above. Thin SPME fibers coated with PDMS (10-100 µm) were employed as a passive organic sampler.

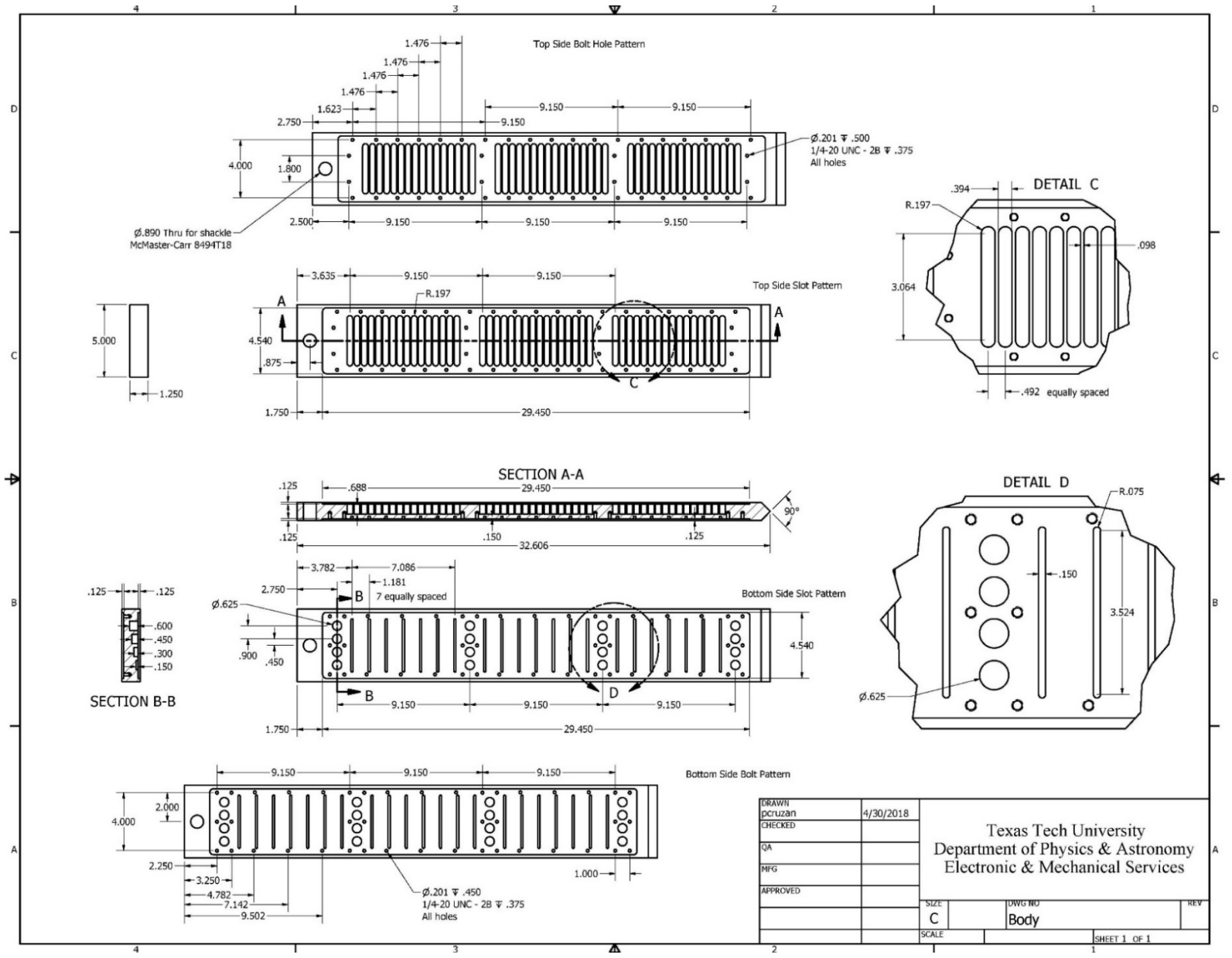


Figure 5.1. sHRPP As-Built Design

The PDMS will absorb hydrophobic compounds accumulating much higher concentrations than the pore water concentrations with which they are in contact. Kinetics of absorption are generally controlled by external mass transfer. This results in the ability to measure (1) very insoluble compounds at high resolution and (2) the freely available (bioavailable) contaminant concentration rather than the bulk sediment concentration. The SPME fiber is pre-equilibrated with an appropriate PRC prior to insertion. By measuring the concentration of PRC upon retrieval, the equilibrium percentage can be estimated and concentrations of HOC corrected for non-equilibrium. The SPME fibers were placed parallel in each geochemical cell between the 0.2-µm pore size and 10-µm pore size membrane (Figure 5.1). This allowed for ~8 cm of fiber per sample depth to be deployed. The increased length of fiber per depth increases the sensitivity and allows for monitoring of lower concentrations per depth compared to vertically placed fibers which must integrate multiple depths to achieve similar concentration ranges. Placement of the fibers between the membranes protects them during insertion and does not result in any contaminant uptake resistance. For the sHRPP, we estimated a deployment time of three weeks would be sufficient to reach >50% equilibrium for the highest K_{ow} HOCs (e.g., PCBs) and close to 90% for lower K_{ow} HOCs (e.g., phenanthrene, DDX). Details of the SPME sampling procedure, analysis and detection limits are located in Appendix C.

5.1.3 Pore Water Velocity

Pore water velocity was measured based on the depletion of a conservative tracer (e.g., Br^-) from specialized cells in the sHRPP and established relationships between the measured mass transfer coefficient and pore velocity. The magnitude of the external pore velocity affects the rate of mass transfer of the tracer across the membrane and therefor the equilibrium rate. Cells with large specific surface area (A/V) equilibrate more slowly than cells with small A/V ratios. Each set of velocity cells on the sHRPP is designed with four different A/V ratios (Figure 5.2A) ranging from 1 to 20 cm^3/cm^2, which allows k_m to be measured from a single sHRPP deployment. We determine k_m by fitting a rearranged form of Equation 1 (see Figure 5.2B) to a graph of F (V/A) vs. C/C_o (the ratio of Br^- remaining in the cells versus the initial Br^- added, Figure 5.2B).

Experimental results and field applications yield k_m values increasing from 0.5 to 2.5 cm/d for velocities of 0, 1, 10, 60 and 100 cm/d (Figure 5.2C). These compare well with the results of an analytical model (Equation 2) relating the theoretical impact of pore velocity on the mass transfer coefficient (details of the model are available in SERDP ER-2419 Interim Report 2016).

$$k_m = \frac{D_m}{\delta} e^{\left(\frac{\left(\frac{D_m}{\delta}\right)^2 x}{UD_z}\right)} erfc\left(\frac{D_m}{\delta}\sqrt{\frac{x}{UD_z}}\right) \quad \text{Eq. 2}$$

Where U is the velocity, D_z is the diffusivity through porous media in the z direction, D_m is the membrane diffusivity, δ is the thickness of the membrane boundary layer, and x is the length of the cell opening in the x direction. D_z is defined by the following equation:

$$D_z = \frac{D_w \emptyset}{\tau} + \alpha U \quad \text{Eq. 3}$$

$$\frac{\emptyset}{\tau} = \emptyset^{4/3} \quad \text{Eq. 4}$$

$$\alpha = \frac{d_p}{10} \quad \text{Eq. 5}$$

where D_w is the open water diffusivity of bromide, ϕ, τ, and α are the porosity, tortuosity, and transverse dispersivity of the porous media, and d_p is the average particle diameter.

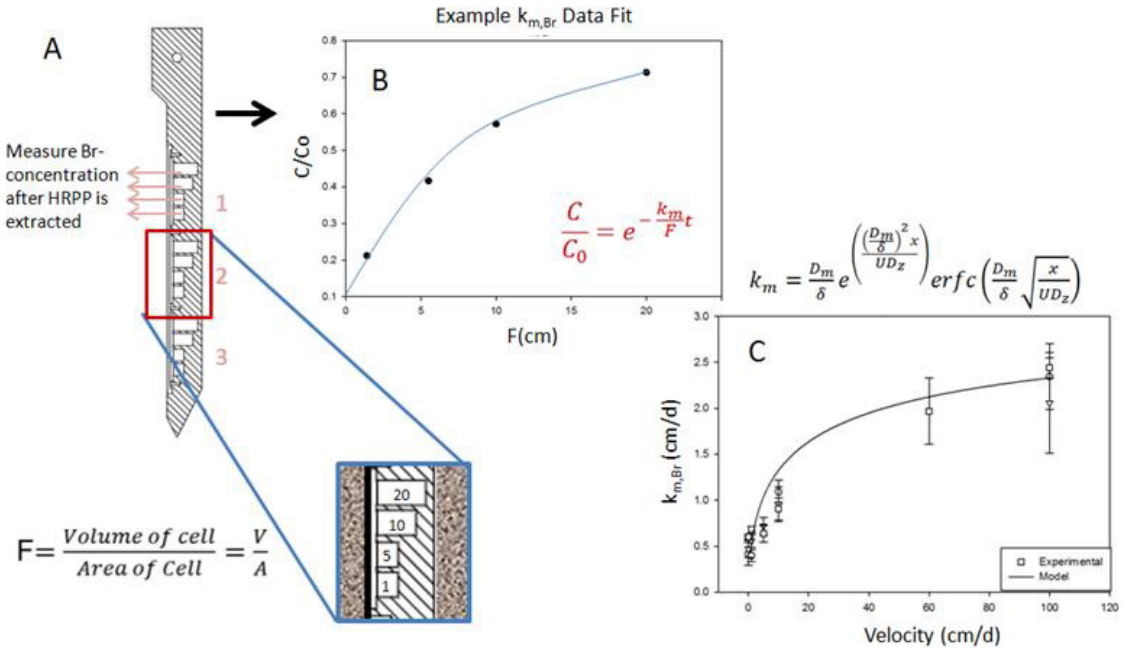


Figure 5.2. sHRPP Diagram.

A) Diagram of sampler showing varying SSA (F) for cells designed to evaluate pore velocity. B) Evaluation of the mass transfer coefficient (K_m) for a single deployment time. C) Pore water velocity determination using an established relationship (lab and field) between the mass transfer co-efficient and pore velocity. The solid line represents the results of an analytical model (Eq. 2) detailed in Appendix D.

5.1.4 Microbial Community Analysis

Microbial community composition was measured using commercially available Bio-Sep beads (Microbial Insights) to create a micro-Bio-Trap. Bio-Traps have been developed during the past decade as a means to characterize microbial communities in groundwater aquifers, and in some cases, to provide evidence of microbial degradation of a target contaminant (Busch-Harris et al., 2008 and references therein). Bio-Traps are placed in groundwater wells, and biofilms grow on the Bio-Sep beads that are then analyzed for microbial community structure and metabolic capability using *q*PCR (Davis et al, 2008). Thus, Bio-Traps represent a versatile approach to assess microbial communities, degradative organisms/genes, and the potential or optimal conditions for contaminant degradation in groundwater. Our SERDP project (ER-2419) has established that the Bio-Sep beads can be incorporated into HRPP samplers and can be used to successfully evaluate complex microbial communities with high resolution. For the current sHRPP application, the Bio-Sep beads were placed in specialized cells (Figure 5.2) on the opposite side of the sampler from the cells designed to evaluate geochemical indicators and HOC concentrations. The beads were covered by a 500-µm pore size nylon mesh to retain them during insertion. Placement of the beads on the opposite face from the SPME fibers prevents the organic Bio-Sep beads from impacting the HOC absorption by the SPME fiber. In the current effort, we focused largely on bacterial communities influencing site geochemistry, such as sulfur-reducing and sulfur-oxidizing bacteria, sulfate-reducing archaea, Mn and Fe oxidizers, Fe reducing bacteria and archaea, methanogens, and denitrifiers.

The following subsections provide a detailed description of the demonstration design and testing that was conducted at each of the four selected sites to address the overall performance objectives described in Section 3.0. Since the goals of implementation, and thus the test design, differs somewhat for each of the four sites due to varying contaminant types and distribution, surface water body types and conditions, prior remedial activities (in some cases), and other logistical characteristics; each site is presented individually below. As will be discussed, field-testing the sHRPPs consisted of two mobilizations to each of the selected sites. The first mobilization at each site consisted of prepping and deploying the sHRPPs, while the second consisted of retrieval/sampling the sHRPPs and advancing sediment cores. Fieldwork at one site was completed prior to moving to the next site. Figure 5.3 presents a summary of the schedule of sHRPP field deployments at all four demonstration sites.

5.2 CANAL CREEK (APG) SITE TESTING

5.2.1 Conceptual Experimental Design

The Canal Creek site was primarily chosen due to the presence of heavy metals within the sediments of the canal and adjacent wetlands. There are also groundwater seeps within this vicinity, which made it an ideal location to demonstrate the utility of the sHRPP. For this site, our implementation goals were as follows:

1. To demonstrate that the sHRPP can produce high resolution spatial concentration profiles of metals with depth with a sensitivity at least equal to methods based on core processing and that concentrations with depth have higher precision (lower variation) than traditional method.
2. To demonstrate that the sHRPP can evaluate the geochemical environment with sufficient spatial resolution to predict changes in metal concentrations and with a spatial resolution that is less than the depth over which redox changes occur and conservative transport occurs.
3. To demonstrate that the sHRPP can measure pore water velocity and upwelling in canal and marsh sediments.
4. To demonstrate the differences in cost and effort between traditional pore water sampling methods and the sHRPP, as well as the increased resolution, quality and reliability of sHRPP produced data.
5. To evaluate the increase in model resolution and confidence for the overall transport of heavy metals to surface receptors using the sHRPP data compared to traditional methods.

The successful completion of these goals would demonstrate the ability of the sHRPP to provide data of sufficient resolution and breadth to predict the exposure, risk, and attenuation of heavy metals over prolonged periods with more precision than traditional methods. The collected data would also demonstrate how the sHRPP could be used to locate hot spots or seeps which could be separately addressed with appropriate technologies to further reduce the risk exposure.

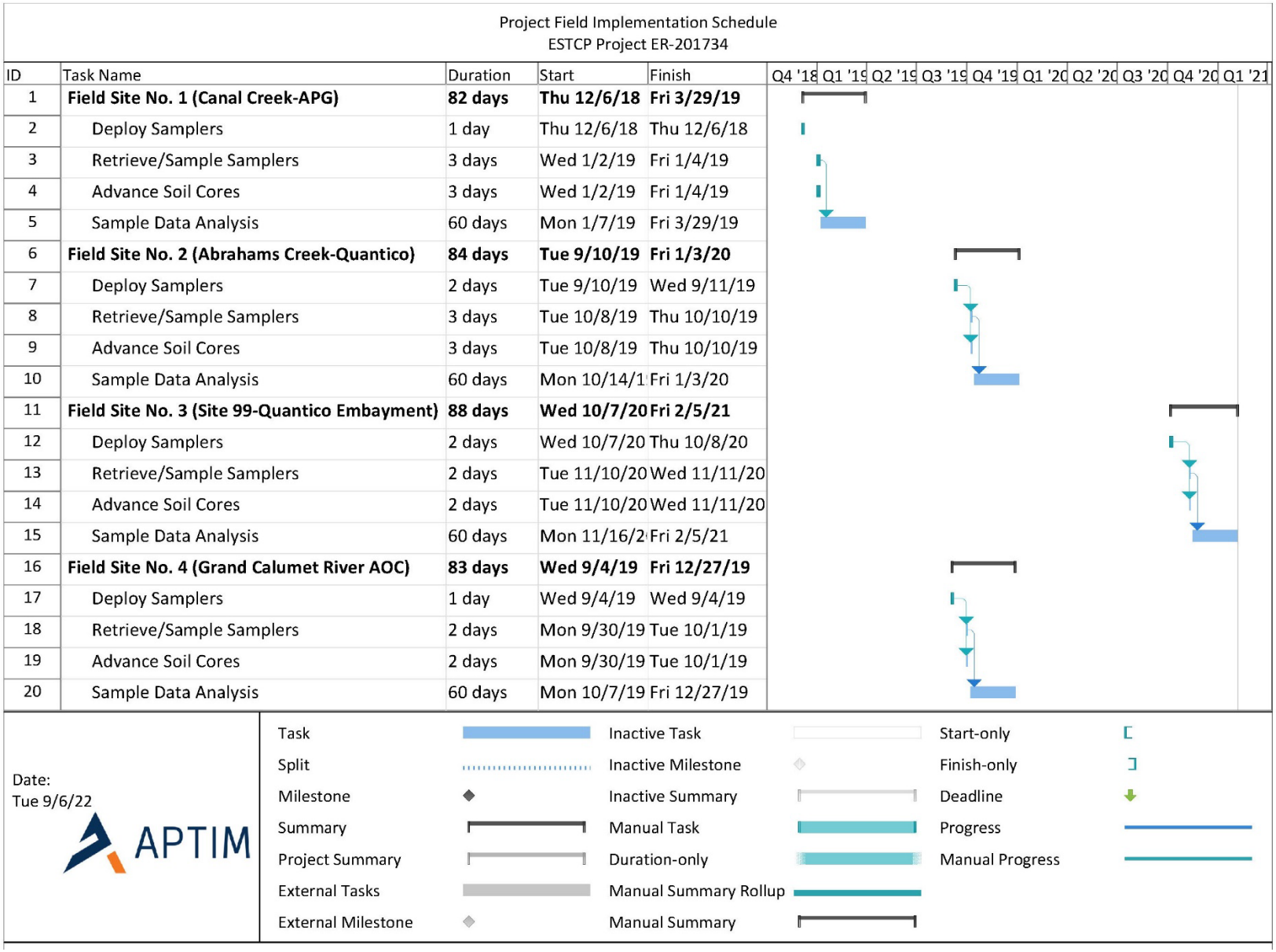


Figure 5.3. sHRPP Field Deployment Schedule

5.2.2 Baseline Characterization

As the demonstrated technology is a site characterization tool, typical baseline characterization activities do not apply. However, as will be discussed in the following subsections, an accepted traditional method of sediment characterization (sediment coring followed by pore water processing) was performed as part of the demonstration for comparison purposes.

5.2.3 Design and Layout of Technology Components

The demonstration at Canal Creek was designed to compare pore water concentrations of heavy metals (As, Pb, Va,, Zn, Cr, Hg), and geochemical indicators (NO_2^-, NO_3^-, FeT, Fe^{+2}, SO_4^{-2}, and S^{-2}) produced by the sHRPP and an accepted traditional method (sediment coring followed by pore water processing). To do this, six sHRPPs were deployed in areas of Canal Creek previously identified as having elevated concentrations of heavy metals in the sediment. The selected sHRPP locations are presented on Figure 5.4. At each of these same locations, we also acquired a sediment core (10 cm diameter). The sHRPP locations, with the exception of sHRPP#4, were in the marsh adjacent to Canal Creek, previously identified as an area of upwelling and elevated metals concentrations. sHRPP#4 was located within the Canal Creek bottom sediments. Although the location coordinates collected in the field depict sHRPP#2 as being in the Canal Creek bottom sediments on Figure 5.4, the location was in the marsh adjacent to the mean low water level.

We anticipated this data set would allow us to do the following:

1. Generate data to compare the cost and time required for each method.
2. Compare each technique's ability to acquire depth dependent non-altered data sets
3. Demonstrate that the sHRPP can capture critical redox and transport processes with sufficient resolution to model and that the sHRPP can capture changes at a resolution less than the depth over which they occur.
4. Allow direct comparisons of spatial profiles of metals including resolution, precision, and magnitude of variance of depth dependent concentrations for each method.
5. Compare sHRPP measured pore velocity to historic averages.
6. Compare model resolution and confidence for each method.

The test location for sHRPP#1 through sHRPP#4 was near a bend in the creek approximately 250 ft (76 m) to the north of recent sediment sampling location 1K-SD110 (see Figure 5.4). This bend has historically elevated concentrations of heavy metals, PAHs, and PCBs (to a lesser extent). It is also the location of two known groundwater seeps, 3-3E and 3-4W.

Contaminant concentrations measured in sediment at 1K-SD109 and 1K-SD110 during a November 2017 sampling event conducted by ECC are summarized in Appendix B (ECC, 2018). The samplers were deployed at the location of Seep 3-3E and near identified metals hot spots based on past sediment sampling. sHRPP#6 and sHRPP#7 were deployed in the marsh/wetland but out of the upwelling area and still in a known hot spot (near historic sampling location 1K-SD109), as shown on Figure 5.4. sHRPP#5 was used as a control and was not deployed at the site.

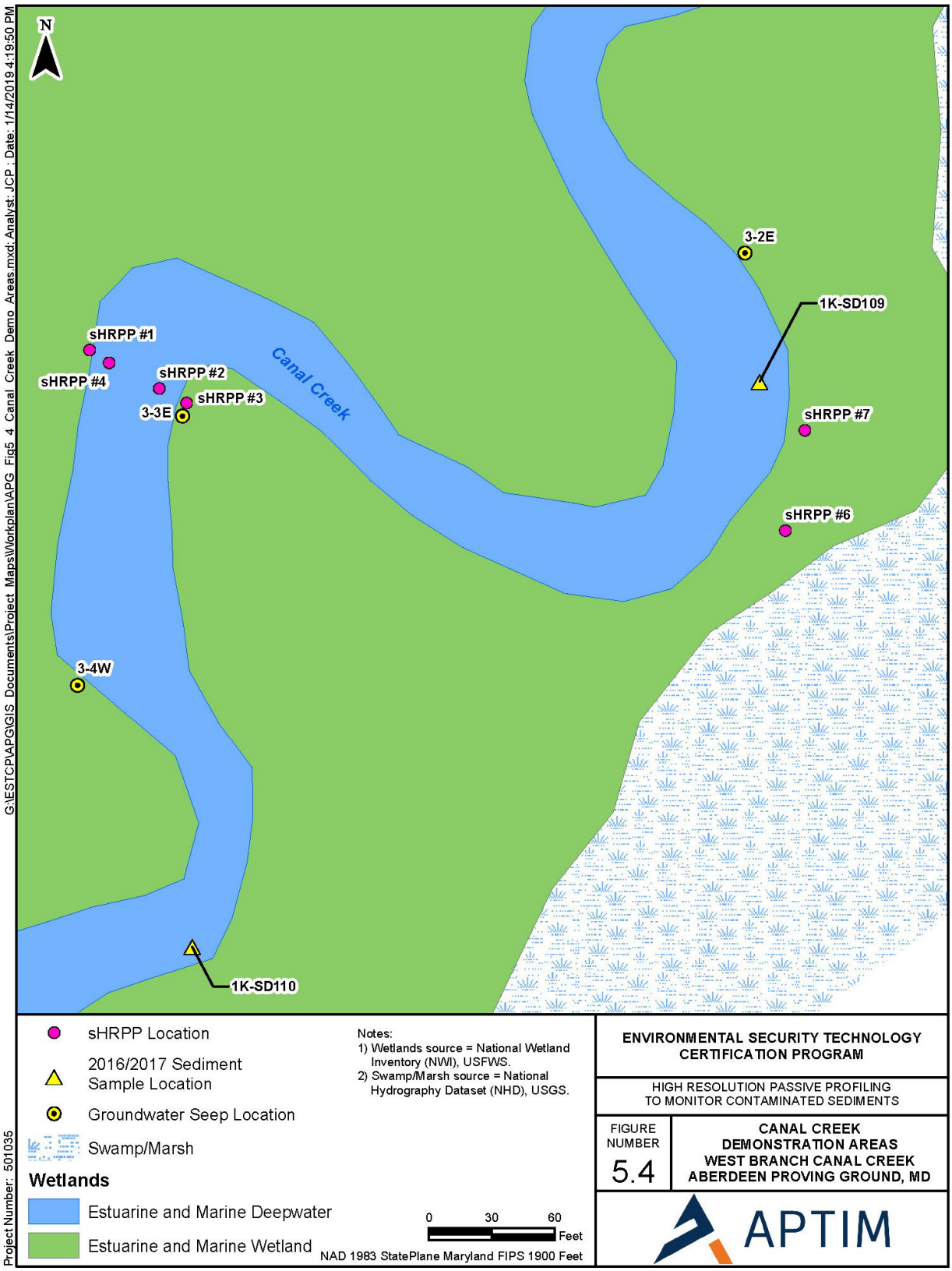


Figure 5.4. Canal Creek Demonstration Areas

The samplers were pushed into the marsh or canal sediment by hand or driven using a slide hammer. In the case of samplers deployed in the marsh, they were advanced up to 1 m below the permanent water surface. If there was standing water, the top cells of the sampler were located within the water or if there was no standing water the top cells were located at the marsh surface. Samplers deployed in the canal sediments were advanced from a boat using a removable extension and fitted with buoys tied to the samplers to aid in retrieval. The top cells were positioned to remain in the bulk canal surface water 3 – 10 cm above the sediment surface. Deployment locations were spaced to maximize separation and allow similar spacing of sHRPPs and sediment cores.

5.2.4 Field Testing

Field-testing the sHRPPs consisted of two mobilizations; the first to prepare and deploy the sHRPPs, and the second to retrieve and sample the sHRPPs, as well as advance/collect the sediment cores. All field activities were conducted in accordance with the Accident Prevention Plan (APP) and associated Site Safety and Health Plan (SSHP), to ensure a safe work environment during the demonstration. Prior to mobilization to the Site, APTIM worked with our point of contact (POC) at APG (Ms. Allison O'Brien) to procure all required base work permits, including an excavation permit and a range control permit. A utility mark-out dig ticket request was also made through Miss Utility MD811 prior to initiating intrusive activities at the site. As part of the initial mobilization, unexploded ordinance (UXO) avoidance procedures (as outlined in the APP) were implemented prior to commencement of intrusive activities. No UXO were detected during the demonstration.

The sHRPP samplers were prepared on shore and carried to the study site for installation. The samplers were prepared by submerging in distilled water spiked with sodium bromide (NaBr) (100 mg/l-Br). The nylon membrane (0.2-µm pore size) and nylon mesh (10-µm pore size) was secured with the cover plates and the sampler was stored (up to ~3 h) submerged until deployment. Water from the sHRPP preparation was subsampled to evaluate any pre-deployment contamination. Bio-Sep beads were placed in compartments within the sHRPP and retained using stainless steel mesh (~100-µm pore size). See Appendix E1 for photographs of pre-deployment sHRPP preparation (Photos 1-3).

As shown above, each of the samplers is designed to assess pore water over an approximately 1.0 m vertical interval. Table 5.1 presents the total number and types of samples collected.

To deploy the samplers, a rope was first attached to the hole machined into the top of the sampler. An extension rod was then positioned over the top of the sampler (not connected to the sampler), and the unit was pushed/driven into the marsh/canal sediment to the proper depth (as discussed in Section 5.2.3). The extension rod was then removed, and a marker buoy was attached to the tag end of the rope to assist in locating the sampler during retrieval. The samplers remained in the marsh/canal sediment for approximately four weeks. See Appendix E1 for photographs of sHRPP deployment activities (Photos 4-9).

Table 5.1. Total Number and Types of Samples Collected (Canal Creek)

Matrix	Number of sHRPPs / Samples per sHRPP	Total Number of Samples	Analyte	Location
sHRPP Pore Water	6 / 48 6 / 48 6 / 48 6 / 6	288 288 288 36	Metals Total Mercury Anions Pore Water Velocity	sHRPP#1 through sHRPP#4, sHRPP#6, and sHRPP#7
Soil Core Pore Water	6 / 30 6 / 30 6 / 30 3 / 3	180 180 180 9	Metals Total Mercury Anions Microbial Community	
sHRPP Preparation Water	1 / 6 1 / 6 1 / 6	6 6 6	Metals Total Mercury Anions	Control sHRPP#5 (not deployed at site)

5.2.5 Sampling Methods

5.2.5.1 sHRPP Retrieval and Sampling

After approximately four weeks of equilibration, the samplers were removed by hand pulling. The samplers were transported by small boat to shore where a large, high-roof cargo van was outfitted with tables to aid in the sampling process (See Appendix E1 for photographs of sHRPP retrieval and sampling activities (Photos 10-15)). The equilibration cells and velocity cells were sampled first. A pre-cleaned glass syringe with 18-gauge needle was inserted through the membrane and water removed by suction. A second needle was placed through the membrane to relieve any vacuum and prevent any outside water from being pulled through the membrane. Water from each cell was placed in an appropriate container, as summarized in Table 5.2, for analysis for total metals (Pb, Zn, Cr, As, CrT), total mercury, and anions (Br^- NO_2^-, NO_3^-, SO_4^{-2}). Standard operating procedures (SOPs) for each analyte including preservation, analysis, QA/QC, and detection limits are located in Appendix C.

Table 5.2. Sample Analytical Methods, Volume, Preservation, and Containers

Analyte	Method/ Laboratory	Sample Volume	Preservative	Bottle
Metals (Pb, Zn, Cr, As, Cr_T)	EPA 200.8 Texas Tech	5 mL	4°C with HNO_3	5 mL glass vial (x1)
Total Mercury	EPA 1631B Texas Tech	2 mL	4°C with HCl	5 mL glass vial (x1)
Anions (Br^-, NO_2^-, NO_3^-, SO_4^{-2})	EPA 300.0 Texas Tech	2 mL	4°C	5 mL glass vial (x1)
On-Site Testing (Fe^{+2}, FeT, total sulfide)	Hach 8133 and 8146 Field Test Kits	3 mL	On Site Only	5 mL glass vial (x1) or direct analysis

All total metals, mercury and anion samples were shipped on ice in a cooler to Texas Tech for analysis. The remaining solution (in equilibrium cells) were used for on-site testing (Fe^{+2}, FeT, total sulfide) using field test kits (Hach Methods).

5.2.5.2 Sediment Core Collection

During sampler retrieval, we also collected soil cores using either a 5-cm diameter direct push coring device (Multi-Stage Sludge/Sediment Sampler, manufactured by AMS, Inc.) or larger diameter (10-cm) aluminum sleeve, depending on field site conditions at each location. The cores were advanced by hand or driven into the sediment using a slide hammer to a depth of approximately 0.5 to 0.8 m.

The AMS soil sampler's "valved core tip" fills the sampler without losing the sample upon retrieval. The sampler uses a disposable plastic soil catcher that fits on the end of a 5 x 30 cm plastic liner. The core tip allows the plastic soil core catcher and liner to fit snuggly over the lip of the core tip. Once the soil core catcher and liner are placed on the core tip, they are loaded into a stainless steel multi-stage base section and screwed together. During deployment, the flap cap opens and allows excess air and water to escape through the top of the sampler, eliminating pressure buildup. The sediment enters and fills the liner. When the sampler is lifted, the flap closes and creates suction to assist the soil core catcher in retaining the sample. The top of the core is then capped and sealed, and the core removed from the multi-stage base section. The bottom of the core is then capped and sealed.

At locations where field site conditions required a larger diameter core for sediment retrieval (highly vegetated marsh locations), a 10-cm diameter, 0.6-m long aluminum sleeve was implemented. The sleeve was advanced to depth by hand, and a thin-blade shovel was used along the outside of the sleeve to access the bottom of the sleeve by hand to ensure minimal sediment loss during hand removal of the sleeve. Each end of the sleeve was then capped and sealed.

A soil core was collected at each sHRPP location, approximately 0.3 m from the sHRPP. Each sealed core was shipped on ice in a cooler to Texas Tech, where the cores were sectioned at 15-cm intervals and the core material transferred to a centrifuge bottle. All processing was conducted within a glove bag which was purged with N_2 gas. Pore water was separated from sediment by centrifuging. The centrate was filtered through a 0.2µm polysulfone filter and the resulting solution analyzed for parameters listed in Table 5.1.

5.2.6 Sampling Results

There were 6 sample sites evaluated using the sHRPP. Four sHRPP were located along a transect (~15m) that reached from the west bank to the east bank, with 3 sHRPP placed in the marsh and one within Canal Creek channel (Figure 5.4). The other two sHRPP (6 and 7) were placed at an upstream location on the east bank close to the creek channel. Results from each location are described individually followed by the presentation of a qualitative site model and synthesized discussion of all results with respect to the site model. Laboratory analytical results are tabulated in Appendix F1. Finally, we discuss the performance of the sHRPP relative to other available methods.

5.2.6.1 Location Specific Results

5.2.6.1.1 Canal Channel Site 1 Location 4 (sHRPP 4)

Sampler sHRPP 4 was deployed within the Canal Creek channel (see Figures 5.4 and 5.5). The sHRPP was deployed to a depth of ~50cm below the sediment interface (BSI) with ~20 cm of the sHRPP in the overlying water. Depths are approximate with respect to the sediment interface (SI), as the interface is ill defined due to the presence of a low density suspension that transitions to a more consolidated material. Chloride depth profiles were used to further establish depth of deployment based on changes from bulk solution at the sediment interface.

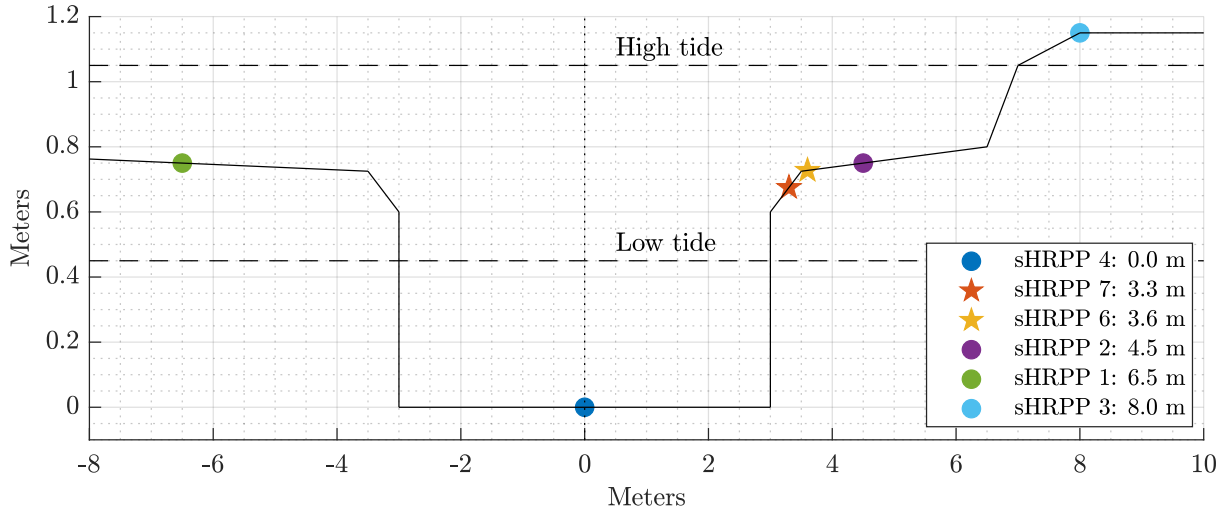


Figure 5.5. Cross-Section of Canal Creek Channel

Shows the approximate distance from creek channel and low/high tide elevations. Note that both sites are represented on cross section but sHRPP 6 and 7 were deployed at a separate upstream location (Figure 5.4).

The overlying water 0 to 20 cm above the SI was characterized by depth independent concentrations of all constituents except the metals As, Pb, and Zn, which slightly increased towards the SI (see Figure 5.6). Below the SI, Cl^- concentrations (~55 mg/l) were slightly higher than surface water (~45 mg/l) and unvarying to 10 cm BSI. Below this depth, Cl^- concentrations increased to a maximum (~160 mg/l) at ~30cm BSI and then slowly decreased at lower depths. All cells above the SI interface and to10 cm BSI were 100% equilibrated based on Br^- loss. Depths below 10 cm were > 85% equilibrated. The estimated pore velocity at lower depths (> 26cm BSI) were near 1 cm/d, below the sampler resolution. In the bulk water, the estimated velocity was > 100 cm/d and at the interface (~2cm BSI) 12 cm/d. Based on the Cl^- profiles, pore velocities, and cell equilibrium extents, it appears that a mixed zone exists below the SI to a depth of ~10 cm. Below this mixed zone, there is minimal advective flux.

The bulk surface water appears largely oxic based on the presence of NO_3^-, SO_4^{-2} and lack of dissolved Fe (Figure 5.6). Below the SI, NO_3^- is not detected, SO_4^{-2} concentrations rapidly reduce from ~17 mg/l at the SI to ~5 mg/l at 4 cm BSI, fluctuate until 9 cm BSI, decrease to a minimum (≤ 2 mg/l) at 15 cm BSI, and remain constant at lower depths.

Conversely, Fe^{+2} concentrations increased to 8 mg/l from 0 to 4 cm BSI, remained constant to a depth of 10 cm, and then increase to a maximum at 37 cm BSI, below which they declined. Sulfide concentrations peaked (~80 ug/l) at 8 cm BSI, and then decreased but remained elevated to a depth of 30 cm, before sharply declining to a constant concentration <25 ug/l. Results support a surface water source of SO_4^{-2}, which is being rapidly reduced between 0 and 9 cm BSI, corresponding to the zone of rapid mixing. Sulfide in this zone was low likely due to oxidation from the rapid mixing of surface water and possible sequestration by FeS. Once SO_4^{-2} is depleted (> 12cm BSI), Fe concentrations increase likely due to lower S^{-2} production.

Pb and Zn concentrations decreased rapidly from a peak in bulk water at the SI to a depth of ~10 cm BSI, the same depths over which SO_4^{-2} is reduced (Figure 5.6). Hg concentrations were generally unvarying with depth and similar to bulk water concentrations in Canal creek (~3 ng/l). Arsenic concentrations mirrored Zn and Pb concentration profiles. Arsenic concentrations were lowest in the creek water, increased from 0 to ~10 cm BSI, remained constant until 15cm and then declined to a depth of 30cm BSI below which it remained constant. No data is available on sediment bulk metal concentrations as the core did not remain intact in shipping.

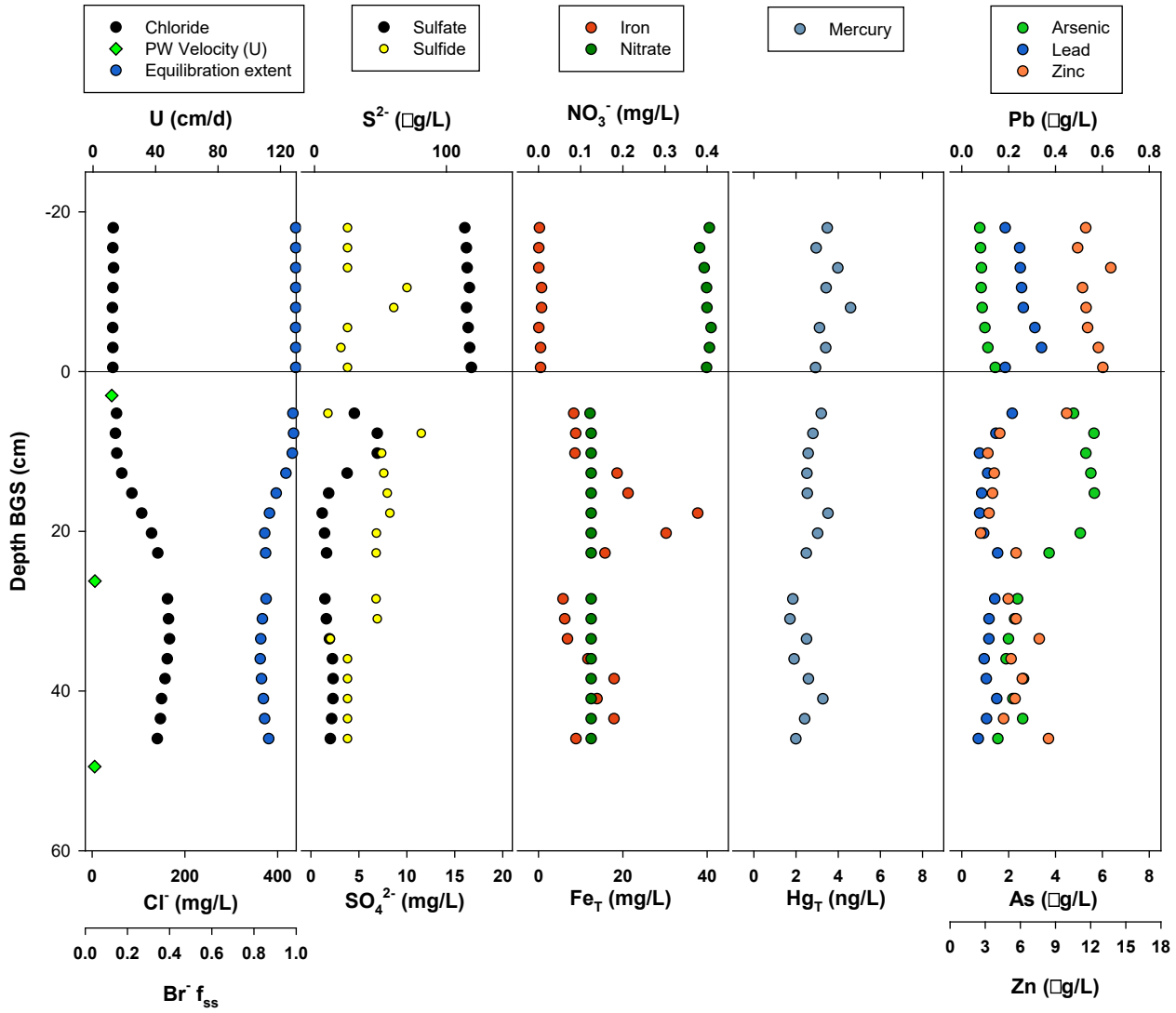


Figure 5.6. Pore Water Concentrations of Evaluated Species, Pore Velocities and Equilibrium Cell Extent for sHRPP 4

Installed within the canal bank at Site 1.

5.2.6.1.2 Marsh Bank Site 1 Location 2 (sHRPP 2)

Sampler sHRPP 2 was deployed ~2m from the creek bank at low tide but within the creek bank at high tide (see Figures 5.4 and 5.5). The sHRPP was deployed from the marsh surface to a depth of 65 cm BSI. All cells were 88% equilibrated based on Br^- loss. Cl^- concentrations in pore water rapidly increase at the SI from ~41 mg/l in bulk surface water to 121 mg/l at the SI. Concentrations slowly increased to a depth of 16 cm BSI, below which they rapidly increased to a peak concentration of 390 mg/l at a depth of 40 cm BSI. Concentrations then gradually decreased for all deeper depths (Figure 5.7). The estimated pore velocity at all depths were 40-60 cm/d. Based on the Cl^- profiles, pore velocities, and cell equilibrium extents, it appears that a mixed zone exists below the SI to a depth of ~20cm, consistent with the location being within the tidal zone. The high Cl^- values between 20 and 40 cm, which were ~10X greater than surface water and ~4X greater than the deepest pore water, may be due to evapotranspiration. Given the relatively high measured velocities and Cl^- profile, the flow direction may be lateral rather than vertical due to bank drainage at low tide.

Below the SI, NO_3 was not detected, SO_4^{-2} concentrations rapidly reduced from ~17 mg/l at the SI to ~5 mg/l at 9 cm BSI, remained constant until 16 cm BSI, and then decreased to < 2 mg/l at 30cm and remained constant for lower depths (Figure 5.7). Conversely, Fe^{+2} concentrations increased rapidly to ~20 mg/l at 9 cm BSI, remained constant to a depth of 19 cm, and then increased to a maximum (64 mg/l) at 40 cm BSI, below which they declined. Sulfide concentrations were < 25 ug/l to a depth of 9 cm and remained relatively constant (~30-40 ug/l) to a depth of 50 cm, below which they were highly variable. Results support a surface source of SO_4^{-2} from the bulk water which was being rapidly reduced between 0 and 9 cm BSI. Lower depths were dominated by iron reduction.

Pb and Zn concentrations decreased rapidly from a peak at the SI to a depth of ~10 cm BSI, the same depths over which SO_4^{-2} was reduced. Lead concentrations at the SI were higher and Zn lower in the overlying water than pore water at the SI. Hg concentrations were generally unvarying with depth and lower than the bulk water concentrations. As concentrations mirrored Zn and Pb concentration profiles at depths near the SI and then decreased similar to Zn and Pb, to a depth of 16 cm, below which As concentrations increased to a maximum (~7 ug/l) at 60 cm BSI. Concentrations of Hg, As, Pb, and Zn in bulk solids were slightly lower at depths > 30 cm BSI with maximum concentrations at ~ 10cm BSI (see Figure 5.8).

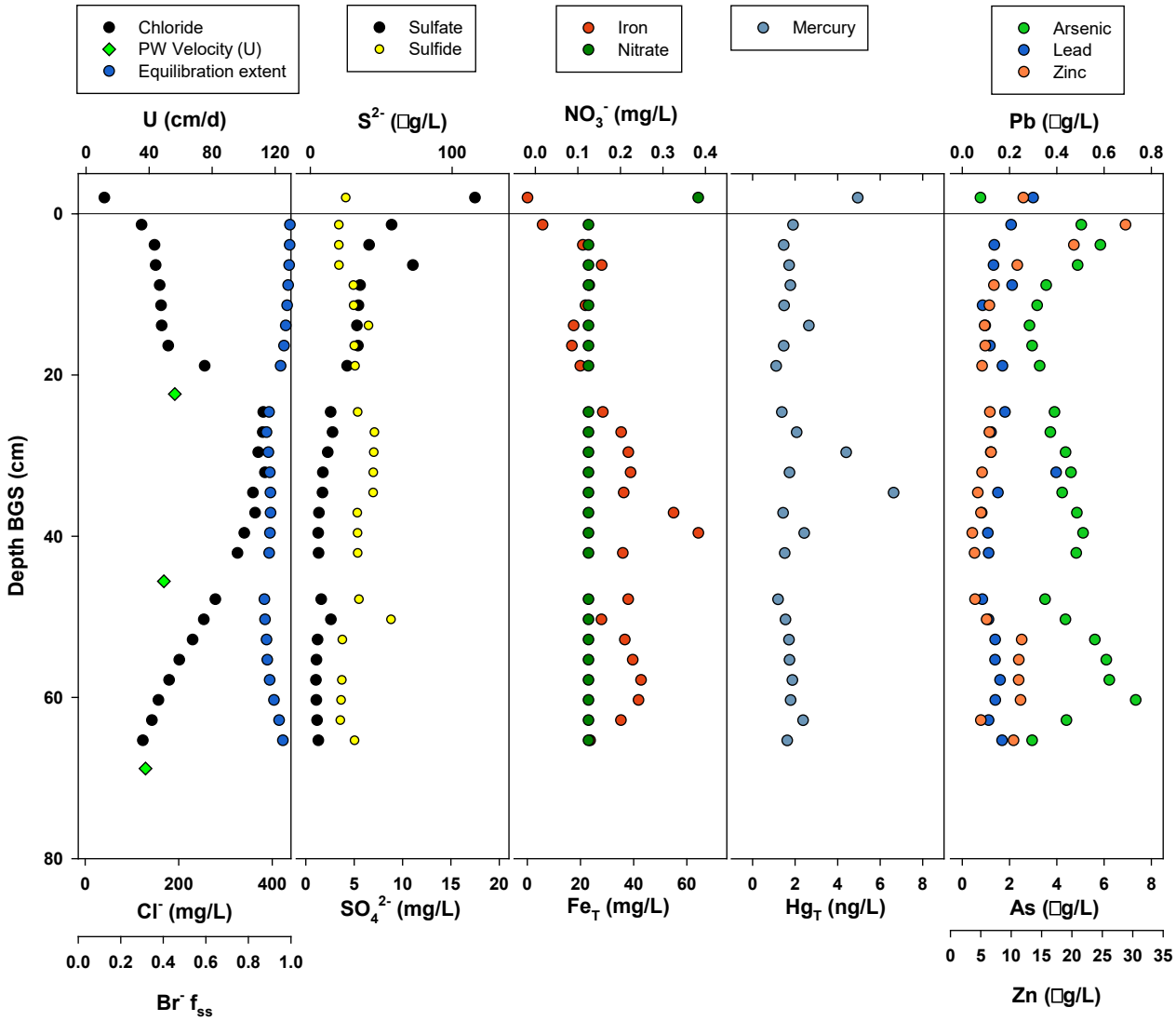


Figure 5.7. Pore Water Concentrations of Evaluated Species, Pore Velocities and Equilibrium Cell Extent for sHRPP 2

Installed 2m from creek bank at Site 1.

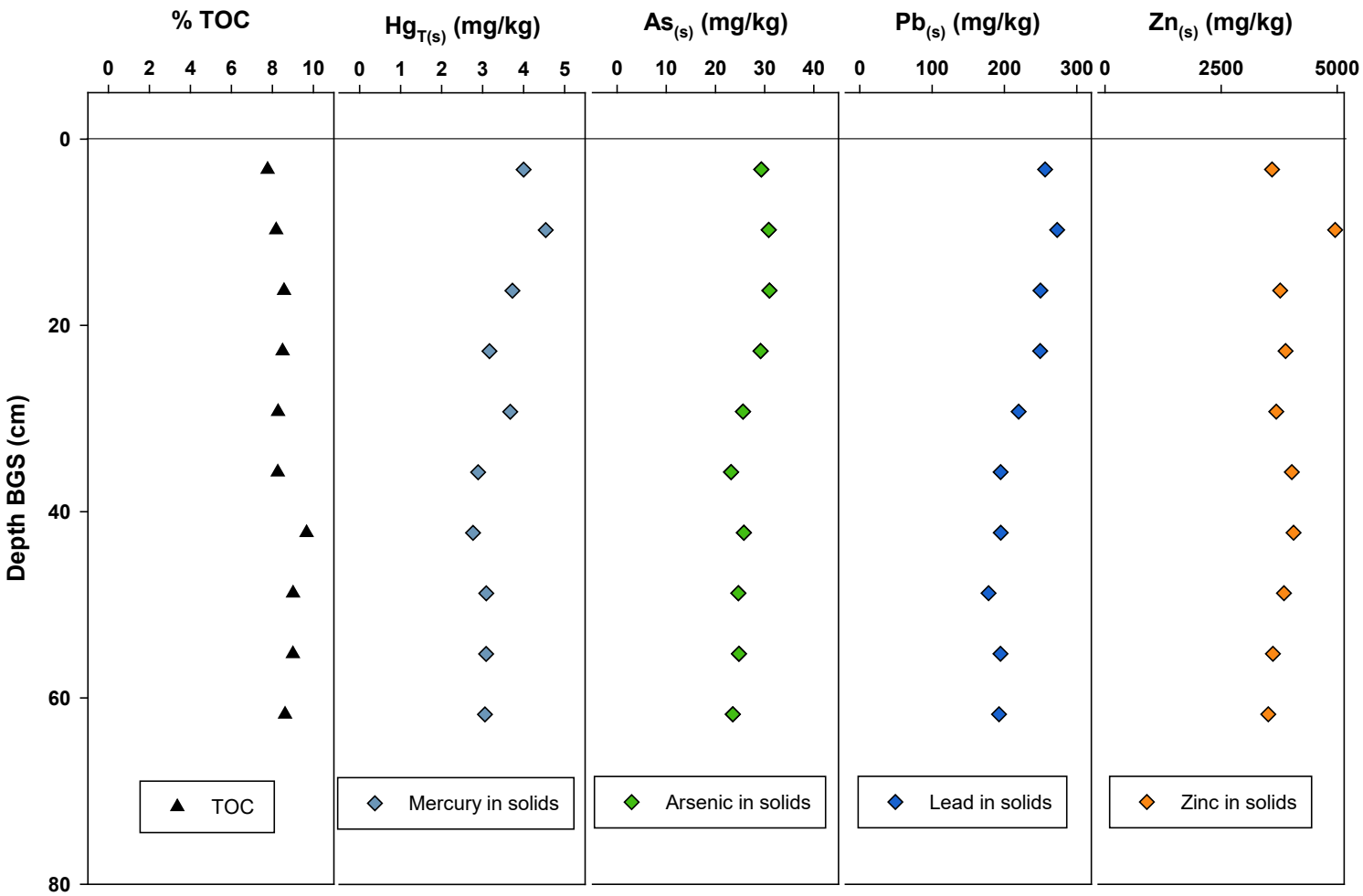


Figure 5.8. Metals Concentrations in Bulk Sediment from Site 1 Location 2

5.2.6.1.3 Marsh Bank Site 1 Location 1 (sHRPP 1)

Sampler sHRPP 1 was deployed ~3.5m from the creek bank at low tide and at an elevation lower than the creek bank at high tide (see Figures 5.4 and 5.5). The sHRPP was deployed from the marsh surface to a depth of 65 cm BSI. All cells were >80% equilibrated based on Br^- loss, with cells within 25cm BSI more equilibrated than lower cells. Cl^- concentrations in pore water rapidly increased from the bulk surface water concentration (~41 mg/l) to 130 mg/l at 2 cm BSI. Concentrations slowly increased (260 mg/l) to a depth of 18 cm, increased rapidly to peak concentrations (560 mg/l) at depths between 30-50 cm BSI, and then gradually decreased for all deeper depths (Figure 5.9). The estimated pore velocity at depths above 23 cm BSI were > 9 cm/d and < 4 cm/d at lower depths. Based on the Cl^- profiles, pore velocities, and cell equilibrium extents, it appears that porewater exchange occurs at depths within 20 cm BSI. The flow direction may be lateral rather than vertical based on low velocities at depth.

Below the SI, NO_3^- was not detected, SO_4^{-2} concentrations rapidly reduced from ~17 mg/l in the bulk water to ~2 mg/l at 4 cm BSI, below which they remain constant for lower depths. Conversely, Fe^{+2} concentrations increased rapidly to ~20 mg/l at 4 cm BSI, decreased to a minimum (7 mg/l) at 25 cm BSI, and then increased with depth to maximums (> 30 mg/l) at the lowest depths. Sulfide concentrations were < 25 µg/l to a depth of 2 cm BSI, increased to 90 mg/l at 7 cm BSI, decreased to < 25 µg/l at depths 17-25 cm BSI, and then increased but remain variable (48-266 µg/l) at lower depths. Results support a surface source of SO_4^{-2} from bulk overlying water which was being rapidly reduced between 0 and 9 cm BSI. Lower depths are dominated by iron reduction.

Lead, Zn, and As concentrations were higher in pore water below the SI than in the overlying water. Lead, Zn, and As concentrations decreased rapidly from a peak at 2 cm to a depth of ~10 cm, the same depths over which SO_4^{-2} is reduced and S^{-2} concentrations increase, and remain constant at lower depths. Hg concentrations were generally unvarying with depth and lower than bulk water concentrations. Peak concentrations at the SI are likely due to oxidation of existing metal sulfides. Concentrations of metals in bulk solids were lower at lower depths (>30 cm BSI) with peak concentrations for Hg, Pb, and As at depths of 15-18 cm BSI, with peak concentrations of Zn at 2cm BSI (see Figure 5.10).

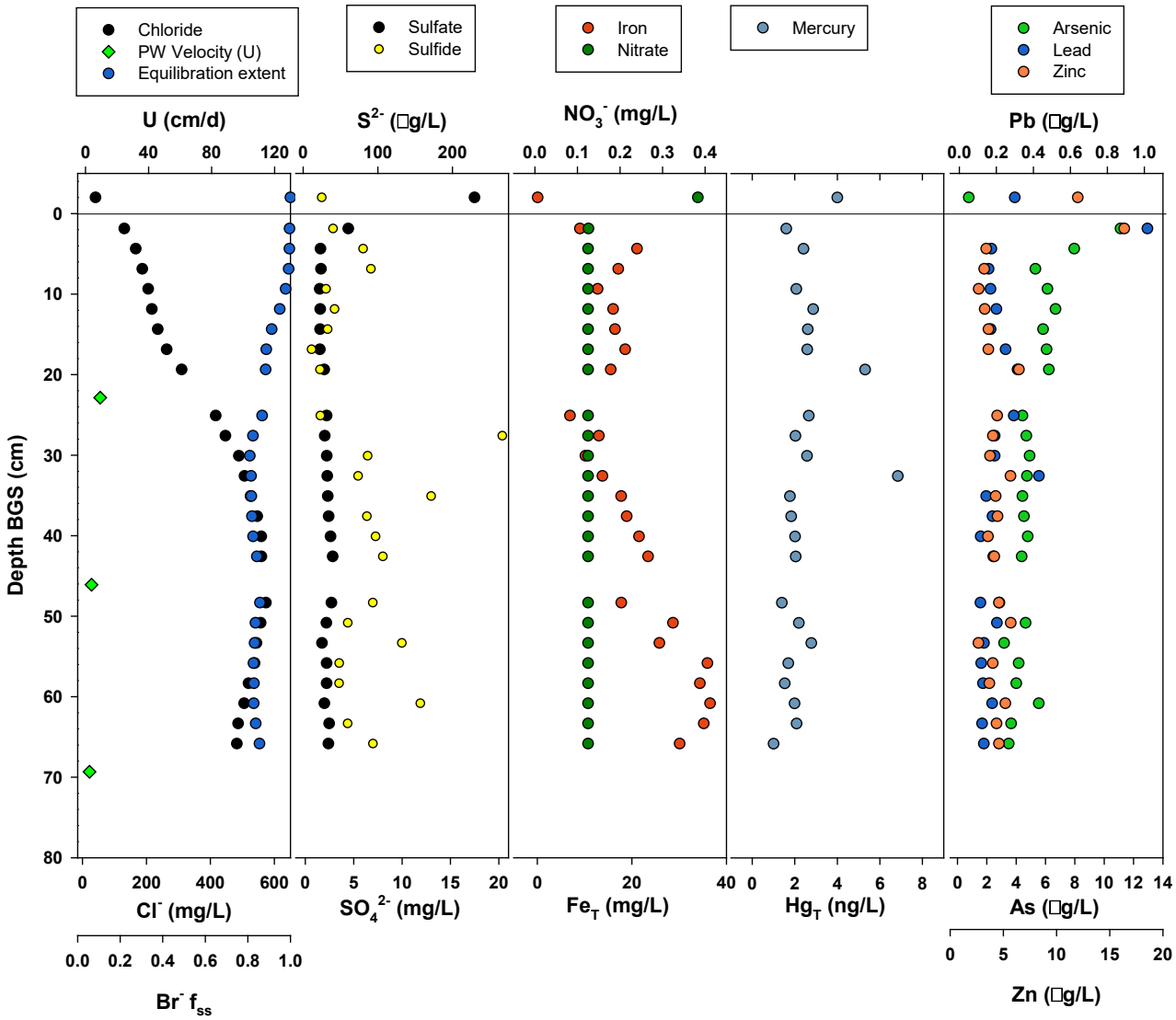


Figure 5.9. Pore Water Concentrations of Evaluated Species, Pore Velocities and Equilibrium Cell Extent for sHRPP 1

Installed 3m from creek bank at Site 1.

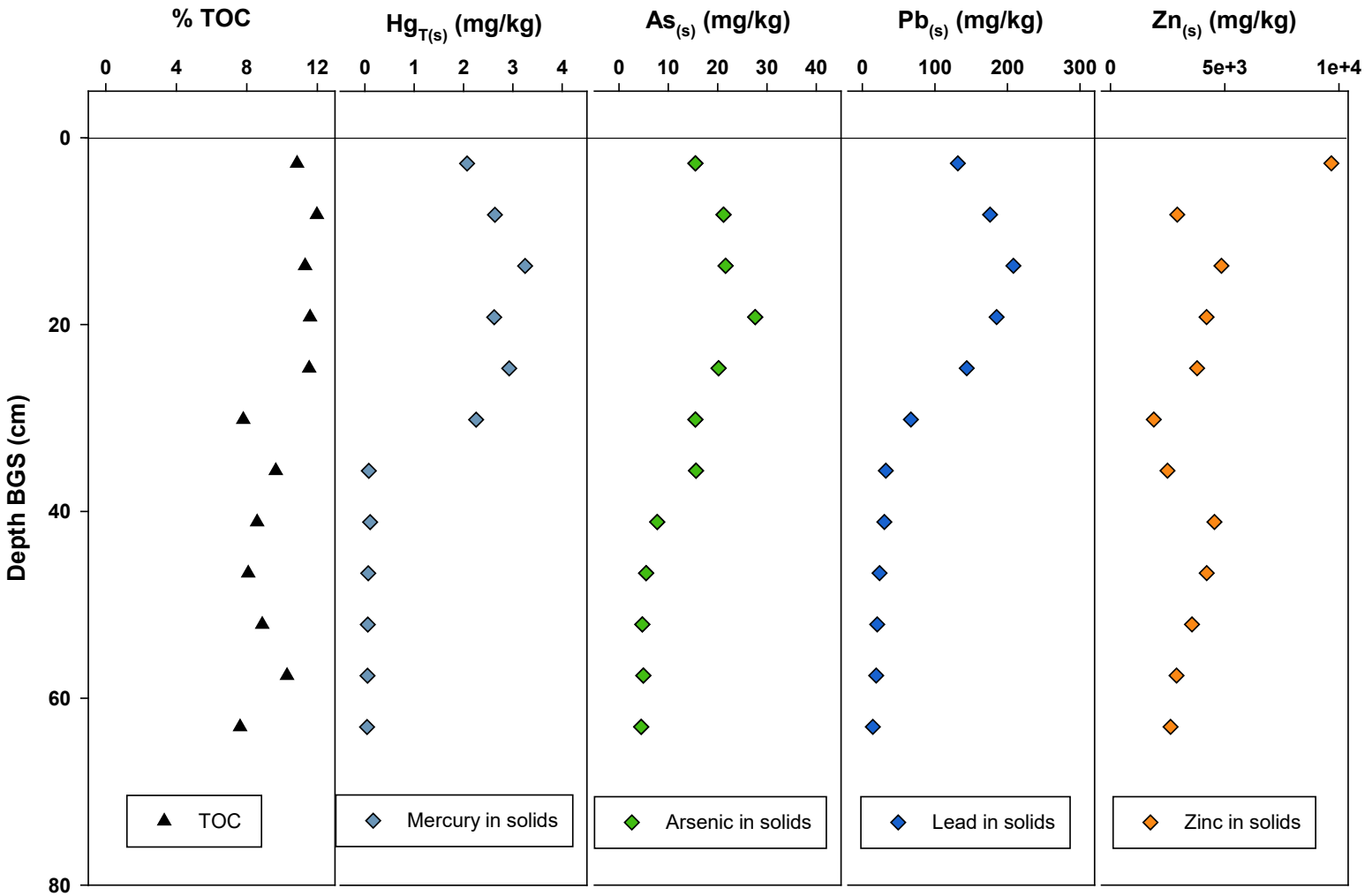


Figure 5.10. Metals Concentrations in Bulk Sediment from Site 1 Location 1

5.2.6.1.4 Marsh Bank Site 1 Location 3 (sHRPP 3)

Sampler sHRPP 3 was deployed ~5m from the creek bank at low tide and at an elevation above the creek bank at high tide (see Figures 5.4 and 5.5). The sHRPP was deployed just above the marsh surface to a depth of 64 cm BSI. All cells were >80% equilibrated based on Br^- loss. Chloride concentrations in pore water slowly increase from the bulk surface water concentration (~41 mg/l) to 230 mg/l at 17 cm BSI. Concentrations then rapidly increased to peak concentrations (800 mg/l) at depths > 45 cm BSI, below which they remained constant (Figure 5.11). It should be noted that it did not appear that surface water inundated this site during low tide, although it is possible that inundation did occur during rain events. The estimated pore velocity at depths above 60 cm BSI were ~10 cm/d, and ~5 cm/d at depths > 60 cm BSI. Based on the Cl^- profiles, pore velocities, and cell equilibrium extents, it appears that porewater exchange (lateral or during rain events) occurred at depths within 20 cm BSI, but deeper depths were advectively isolated with diffusional exchange to upper depths. The flow direction may have been lateral rather than vertical based on low velocities at depth.

Below the SI, NO_3^- is not detected, but unlike other sites below the high tide line, SO_4^{-2} concentrations were highest at the SI interface to a depth of 5 cm. This concentration is greater than measured surface water but, as mentioned, it is unclear if inundation occurs at this site. Below 5 cm SO_4^{-2} concentrations rapidly decreased to a depth of 10 cm, below which they remained constant for lower depths. Conversely, Fe concentrations were < 0.2 mg/l to a depth of 3 cm BSI and increased rapidly to ~20-40 mg/l at depths > 9cm BSI. Sulfide concentrations were < 25 ug/l at all depths. Results suggest that SO_4^{-2} concentrations in pore water at the SI interface were generated from oxidation of solid metal sulfides which were rapidly reduced at lower depths. Lower depths were dominated by iron reduction.

Zinc concentrations are highest near the SI and then rapidly decrease similar to SO_4^{-2} concentrations (Figure 5.11). Lead concentrations in porewater were generally constant BSI. Arsenic concentrations increased to a depth of 20 cm similar to Fe^{+2} and then remained elevated but variable at lower depths, generally increasing and decreasing with Fe concentrations. Hg concentrations were generally unvarying with depth and lower than bulk water concentrations. Concentrations of Hg, Pb, and As in bulk solids were higher at deeper depths > 30cm BSI, while Zn concentrations were generally similar (Figure 5.12).

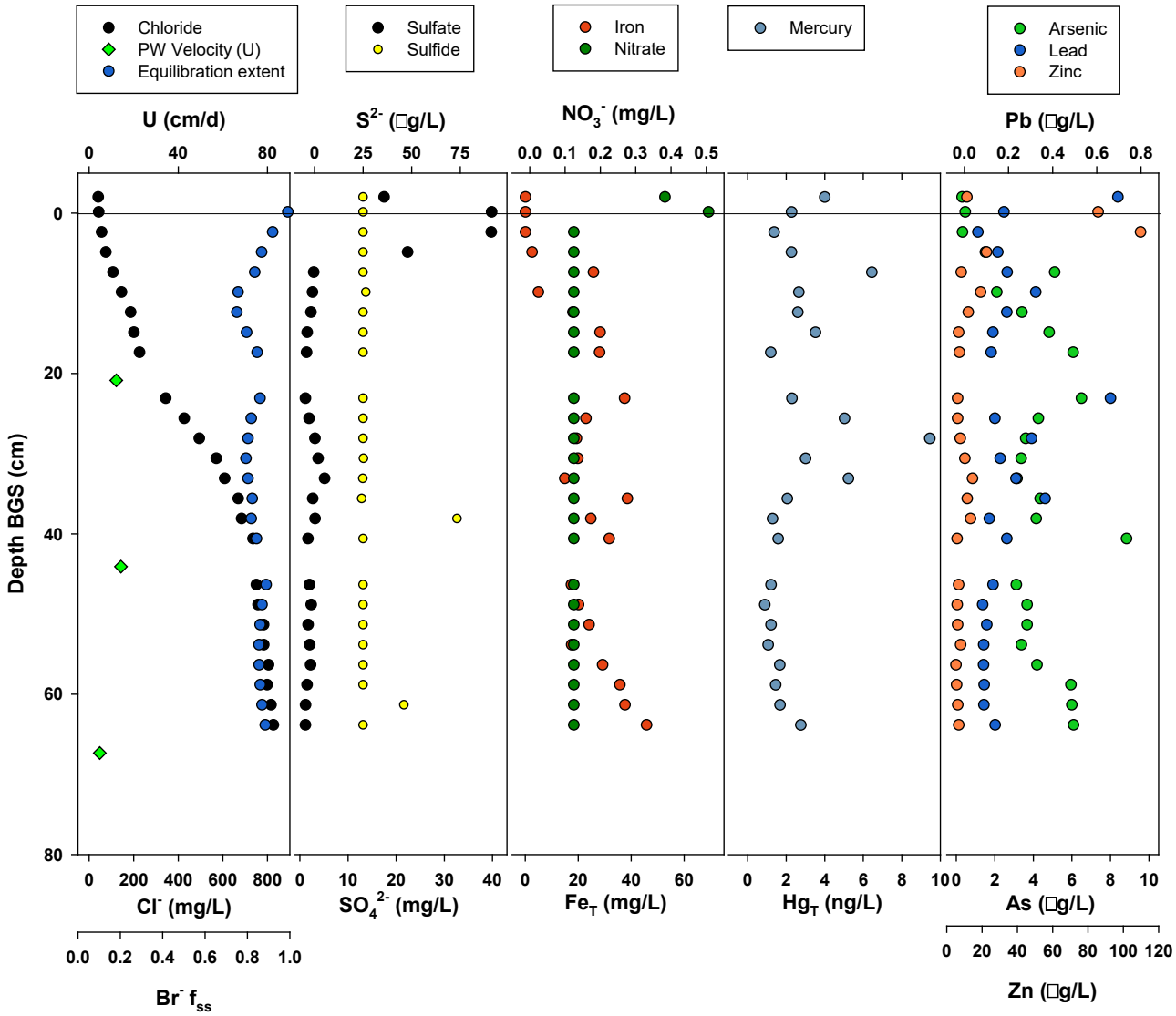


Figure 5.11. Pore Water Concentrations of Evaluated Species, Pore Velocities and Equilibrium Cell Extent for sHRPP 3

Installed 5m from creek bank at Site 1.

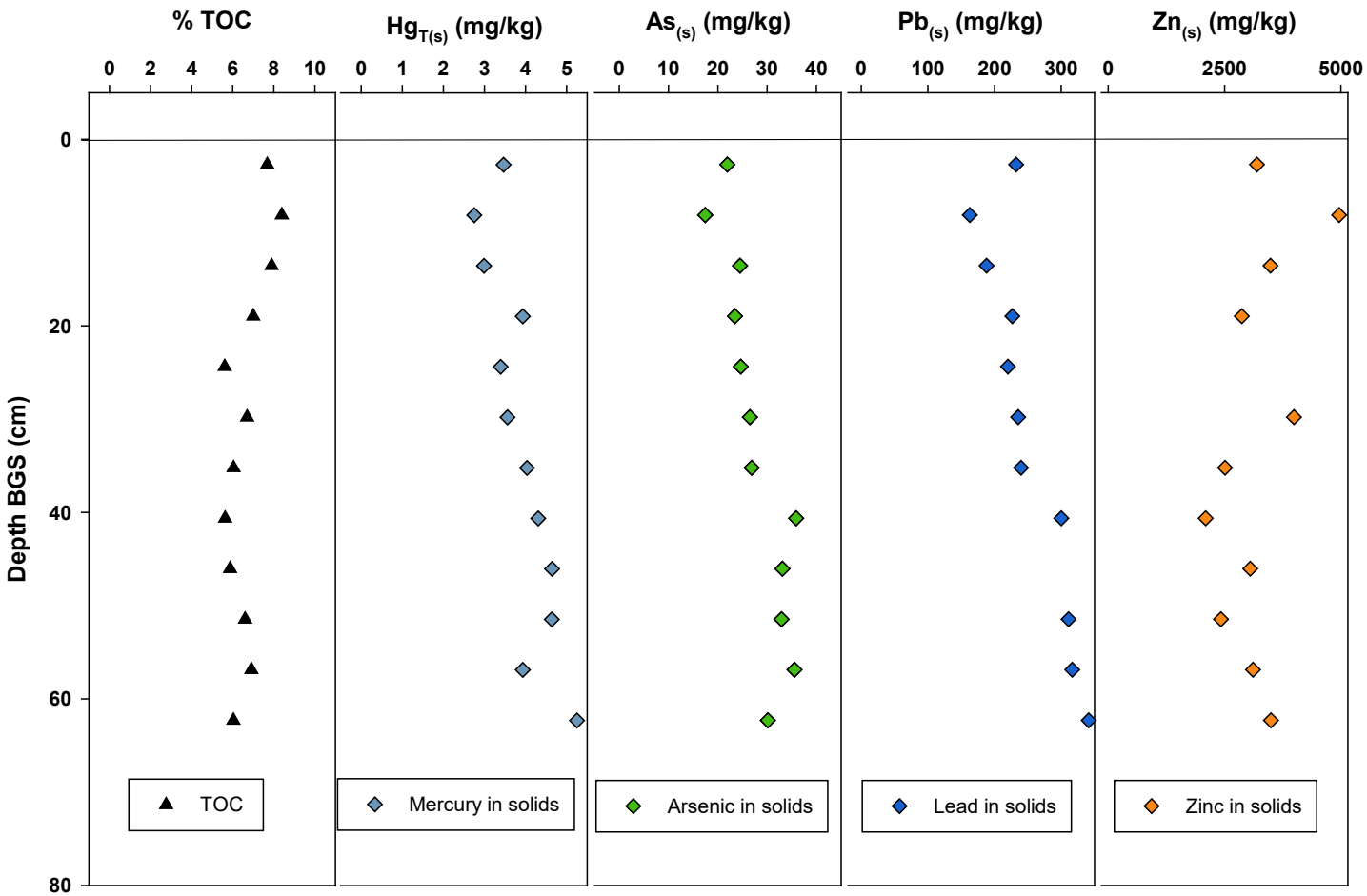


Figure 5.12. Metals Concentrations in Bulk Sediment from Site 1 Location 3

5.2.6.1.5 Marsh Bank Site 2 Location 7 (sHRPP 7)

Sampler sHRPP 7 was deployed <1m from the creek bank at low tide and at an elevation below the creek bank at high tide (see Figures 5.4 and 5.5). The sHRPP was deployed 7 cm BSI to a depth of 71 cm. All cells were >80% equilibrated based on Br^- loss. Chloride concentrations in pore water slowly increased from bulk surface water concentration (~41 mg/l) to 90 mg/l at 25cm BSI. Concentrations then rapidly increase to peak concentrations (300 mg/l) at a depth of 45 cm BSI, below which they decrease and remain constant at the lowest sampled depths (>63 cm BSI) (Figure 5.13). The estimated pore velocity was relatively high at shallow depths (~40 cm/d at 30 cm BSI) and much lower at deeper depths (<6 cm/d). Based on the Cl^- profiles, pore velocities, and cell equilibrium extents, it appears that porewater exchange with surface water rapidly occurred at depths within 30 cm BSI, but deeper depths are dominated by diffusional exchange to upper depths. The flow direction may be lateral (bank drainage) rather than vertical based on low velocities at depth.

NO_3^- concentrations decreased from the bulk water to les than the detection level (DL) at a depth of 7 cm BSI, just above the depth (12 cm BSI) at which SO_4^{-2} concentrations peaked (55 mg/l) (Figure 5.13). SO_4^{-2} concentrations decreased to a depth of 30 cm BSI, below which they remained constant for lower depths before slightly increasing at the lowest depths sampled (>65 cm BSI). Conversely, Fe concentrations (< 1 mg/l) remained low to a depth of 17 cm and then increased to a peak concentration (~22 mg/l) at a depth of 30 cm, and then decreased to a depth of 50 cm, below which they remain relatively constant (2-4 mg/l). Sulfide concentrations were < 25 ug/l to a depth of 47 cm BSI where they rapidly increased and then varied (8-160 ug/l) at lower depths. Results suggest that depths above 7 cm BSI are less reduced and maximum SO_4^{-2} concentrations were due to oxidation of solid sulfides. Sulfate reduction dominates at depths between 8 cm and 25 cm due to available SO_4^{-2}, and possibly below 66 cm from a deeper groundwater source. Fe reduction dominated at middle depths.

Zn concentrations followed a similar trend as SO_4^{-2} with peak (237 ug/l) concentrations ~ 9 cm BSI and decreasing concentrations above and below (Figure 5.13). Pb concentrations in porewater were variable with depth. As concentrations generally tracked Fe^{+2} concentrations, with low concentrations at shallow depths and deepest depths where iron concentrations were lowest, and highest As concentrations at middle depths where Fe concentrations were highest. Hg concentrations were generally unvarying with depth although concentrations sporadically increased between 30 and 45 cm BSI, depths at which SO_4^{-2} reduction was at a minimum and Fe at maximum. Concentrations of Zn, Pb, As, and Hg in bulk solids were generally constant with depth to 30cm BSI, below which they decreased to a depth of 50 cm and then increased to values similar to the upper depths (Figure 5.14).

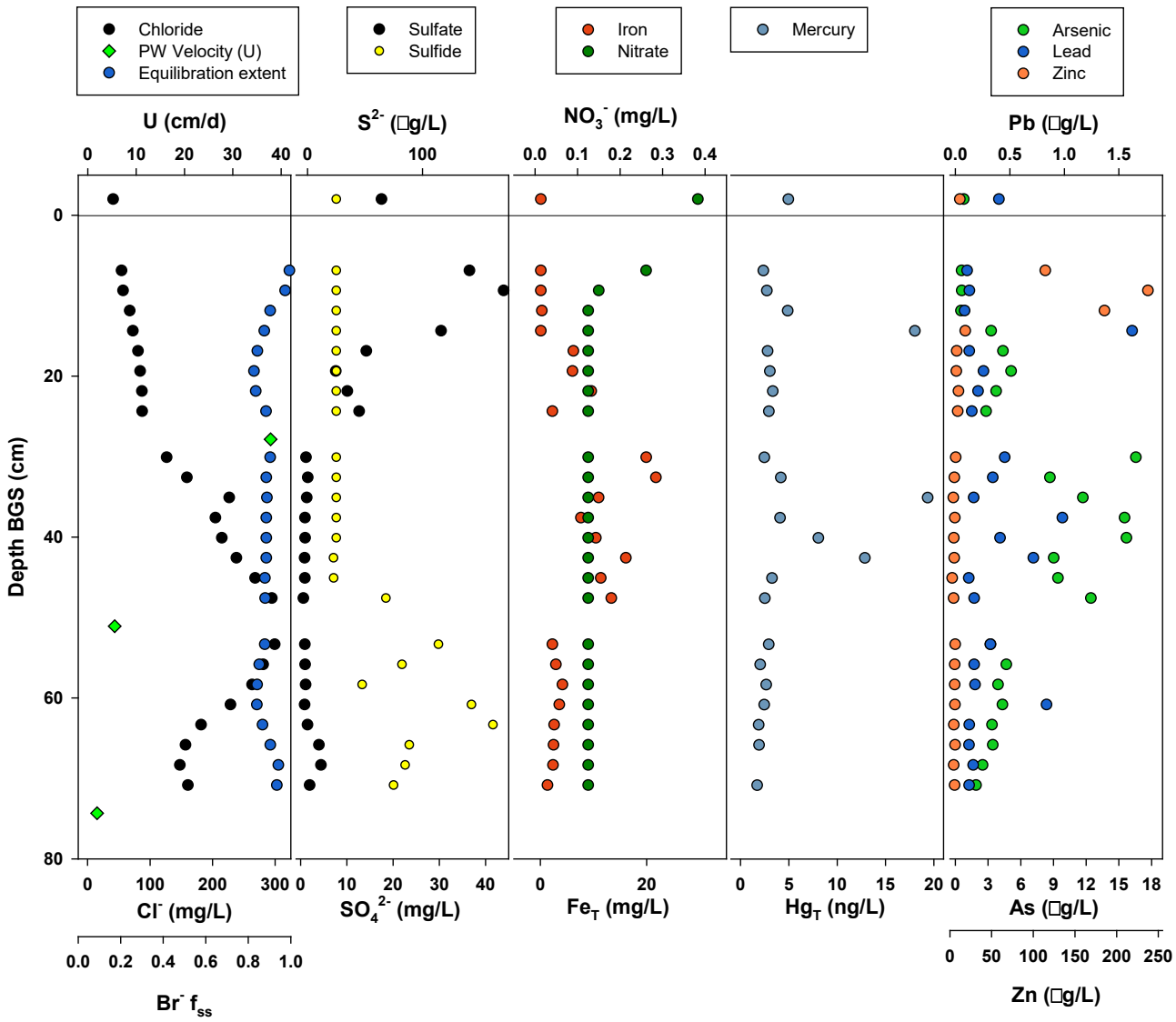


Figure 5.13. Pore Water Concentrations of Evaluated Species, Pore Velocities and Equilibrium Cell Extent for sHRPP 7

Installed 1m from creek bank at Site 2.

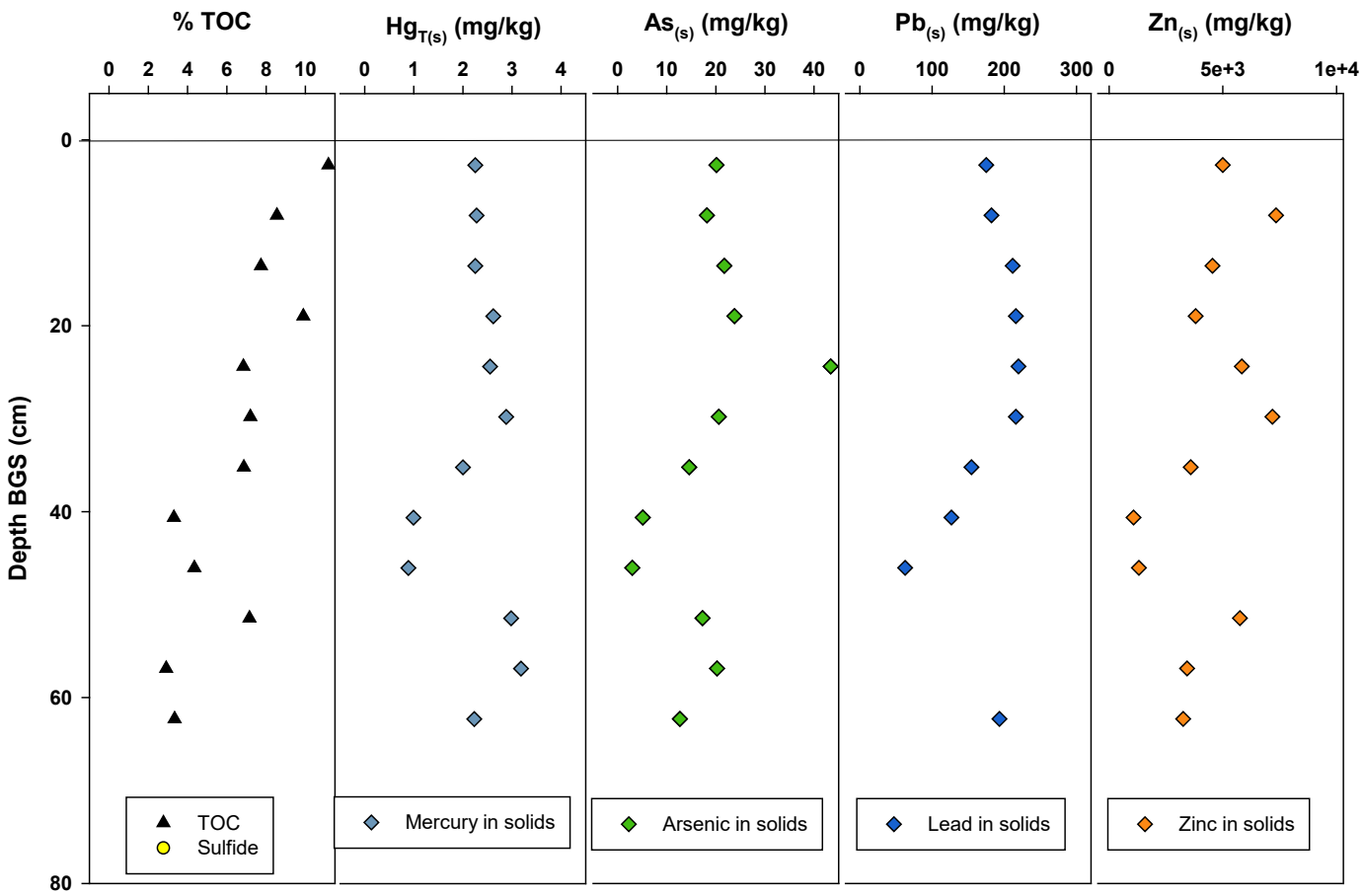


Figure 5.14. Metals Concentrations in Bulk Sediment from Site 2 Location 7

5.2.6.1.6 Marsh Bank Site 2 Location 6 (sHRPP 6)

Sampler sHRPP 6 was deployed <1m from the creek bank at low tide and at an elevation below the creek bank at high tide (see Figures 5.4 and 5.5). The sHRPP was deployed 0 cm BSI to a depth of 64 cm. All cells from 0-20 cm BSI were ~100% equilibrated with lower equilibration extents at deeper depths (>80%). Chloride concentrations in pore water slowly but constantly increased from the bulk surface water concentration (~41 mg/l) to 90 mg/l at 17 cm BSI. Concentrations then more rapidly increased to peak concentrations (290 mg/l) at a depth of 49 cm BSI, below which they decreased (Figure 5.15). The estimated pore velocity at all depths below 20 cm BSI were ≤ 5 cm/d. Based on the Cl^- profiles, pore velocities, and cell equilibrium extents, it appears that porewater exchange rapidly occurred with surface water at depths within 20 cm BSI but deeper depths were advectively isolated with diffusional exchange to upper depths. The flow direction may be lateral rather than vertical based on low velocities at depth.

NO_3^- concentrations decreased from the bulk water to < DL at a depth of 5 cm BSI (Figure 5.15). SO_4^{-2} concentrations increased from the bulk water (18 mg/l) to a peak concentration (104 mg/l) at 12 cm BSI. SO_4^{-2} concentrations then rapidly decreased to 3 mg/l at a depth of 23 cm BSI and then slowly decreased to a constant concentration (1-2 mg/l) at depths below 35 cm BSI. Conversely, Fe^{+2} concentrations remained low (< 1 mg/l) to a depth of 12 cm (depth of SO_4^{-2} maximum), increased to ~3 mg/l at depths between 12-18 cm BSI (depths of maximum SO_4^{-2} reduction), sharply increased to a maximum (42 mg/l) at 33 cm BSI, and then slowly decrease at lower depths. Sulfide concentrations were < 25 ug/l to a depth of 12 cm BSI where they rapidly increased to a maximum (110 ug/l) and then decreased but were variable at lower depths. Given that Cl^- concentrations only increased by a factor of 2 but SO_4^{-2} increases by a factor of 6 at depths down to 12 cm BSI, suggest that SO_4^{-2} is being produced in situ (S^{-2} oxidation). At depths 12-20 cm BSI, SO_4^{-2} is rapidly reduced leading to peak S^{-2} concentrations. At depths lower than 20 cm BSI, Fe reduction generally dominates.

Zn concentrations (32 mg/l) in the SI pore water were higher than surface water (12 mg/l), increased to 50 mg/l at a depth of 3 cm BSI and remain relatively constant to a depth of 7 cm BSI. Zn concentrations then rapidly decline to < 3 µg/l at a depth of 17 cm and remain constant at lower depths. Pb concentrations were highest in surface water. As concentrations generally tracked Fe concentrations with low concentrations at shallow depths and deepest depths where Fe concentrations were lowest, and highest concentrations of As and Fe at middle depths. Porewater Hg concentrations generally increased with depth. Concentrations of Zn, Pb, As, and Hg in bulk solids were generally constant with depth to 30 cm BSI, below which they decreased to a depth of 40 cm and remained constant (Figure 5.16).

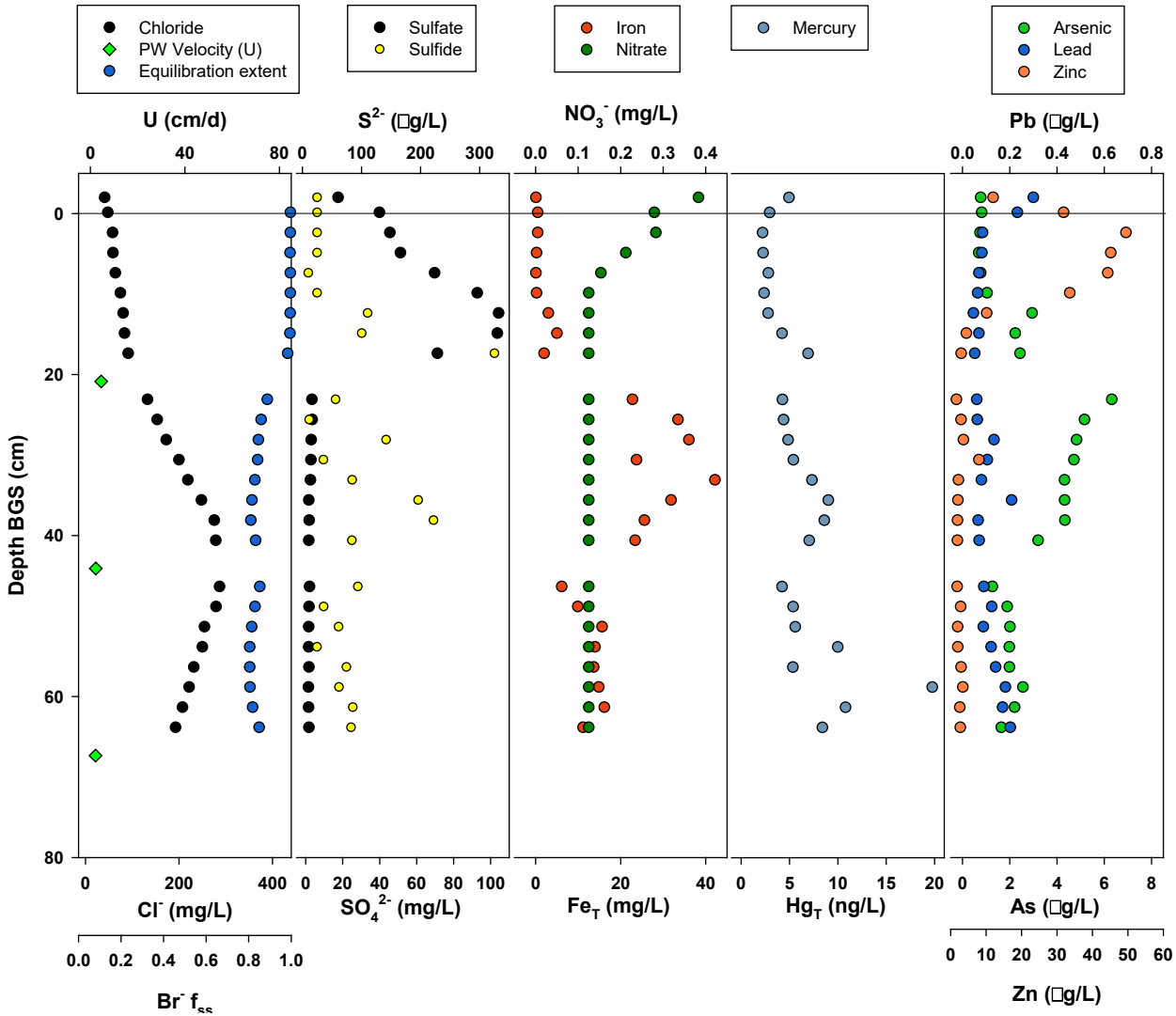


Figure 5.15. Pore Water Concentrations of Evaluated Species, Pore Velocities and Equilibrium Cell Extent for sHRPP 6

Installed 1m from creek bank at Site 2.

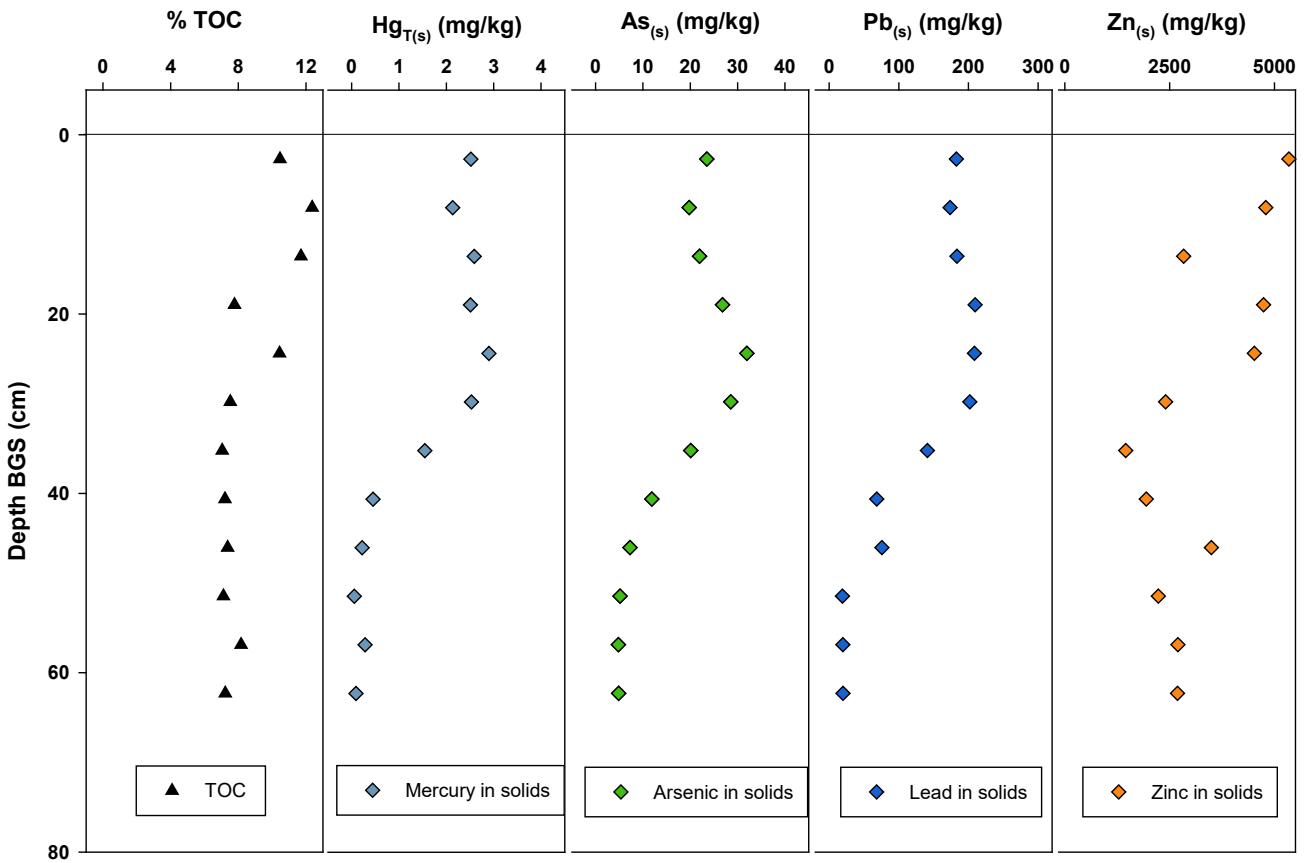


Figure 5.16. Metals Concentrations in Bulk Sediment from Site 2 Location 6

5.2.6.2 Comparison of Porewater Concentrations Produced by sHRPP and Cores

At each location where a sHRPP was installed, we attempted to acquire a sediment core. Initially we tried to use a hand driven (slide hammer) drive device with plastic sleeves and a core catcher. However, due to the consistency of the marsh surface and thick interwoven root system of the plants, no core could be retrieved. We then used 4" thin-walled metal tubes, which were hand pressed while rotating to cut into the marsh material. A hole next to the core was then dug and the core removed. At all locations except in the channel of Canal Creek, we were able to retrieve an ~60 cm core. It should be noted that in some cases the core was compressed and in most cases some drainage occurred before the cores could be sealed. Cores were shipped back to the lab and extruded into a glove bag purged with N_2 gas to limit O_2. Core sectioning (5 cm intervals) and homogenization was difficult due to the thick fibrous nature of the plant roots. Homogenized material was placed in centrifuge bottles and, after centrifugation, filtered. However, as discussed below, based on SO_4^{-2} concentrations, oxidation of core material occurred during shipping and/or processing. Due to the clear evidence of sulfide oxidation, core extracts were not run for metals, as the data would have little value. For Hg, subsamples of homogenized core sections were sealed in glass vials in the glove bag and DGT button samplers emplaced to measure ex situ pore water concentrations.

Chloride concentrations in porewater from cores generally (sHRPP 1, 6, 7) spanned the range of Cl^- concentrations produced by sHRPP (Figure 5.17). While concentration profiles were similar, peak concentrations occurred at deeper depths possibly due to drainage of pore water. In two profiles (sHRPP 2, 3) concentration profiles were less pronounced. Overall, it appears that core shipping/processing led to mixing of porewater and loss of concentration profiles. Sulfate concentrations in core pore water generally did not match those produced by sHRPP (Figure 5.18). Concentrations from core pore water were often 2 to 3 orders of magnitude greater than sHRPP profiles. In addition, SO_4^{-2} concentrations based on soil cores usually increased or remained elevated with depth, which should not be possible given the reduced nature of the sediment. It appears that soil core processing led to oxidation of sulfides that caused large increases in SO_4^{-2} concentrations and would have also produced increased metal porewater concentrations, due to oxidation of metal sulfides. Hg concentrations predicted by DGT ex situ samplers were very similar to porewater concentrations for some sHRPP (1,2) throughout the depth evaluated (Figure 5.19). In two cases concentrations were much higher (~10X) in the upper core but similar at lower depths. Differences could be due to ex situ measurements compared to in situ, as ex situ do not incorporate loss of mass from pore water due to advection and diffusional losses or even in situ production of S^{-2} due to sulfate reduction (SO_4^{-2} is not resupplied in ex situ measurements). Alternatively, higher concentrations could be due to oxidation of core material during processing, although in both cores (sHRPP 6 and 7) with highest ex situ pore water Hg concentrations, porewater SO_4^{-2} was lower or equal to SO_4^{-2} in sHRPP samples at most depths where ex situ Hg was highest.

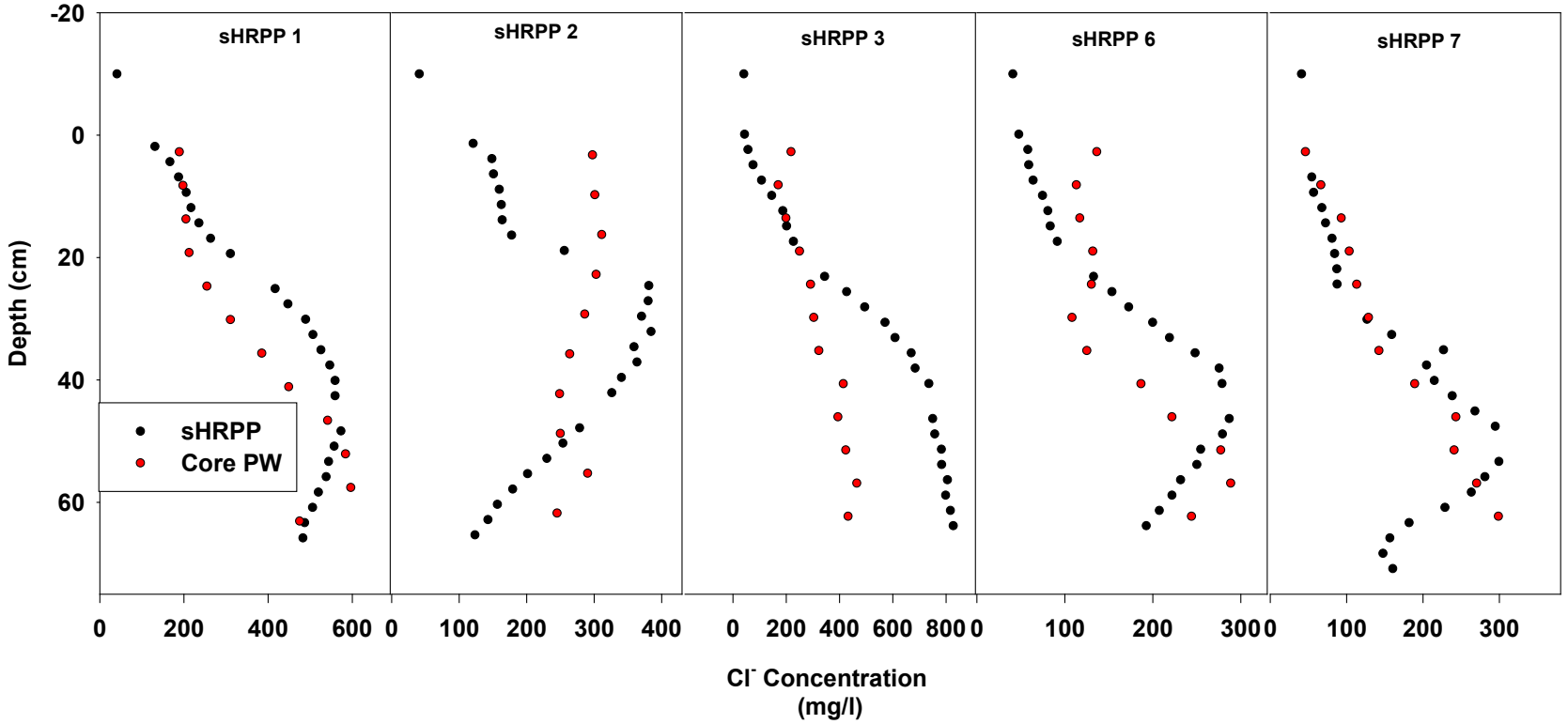


Figure 5.17. Comparison of Porewater Chloride Measured in sHRPP Samples or in Porewater Obtained from Cores

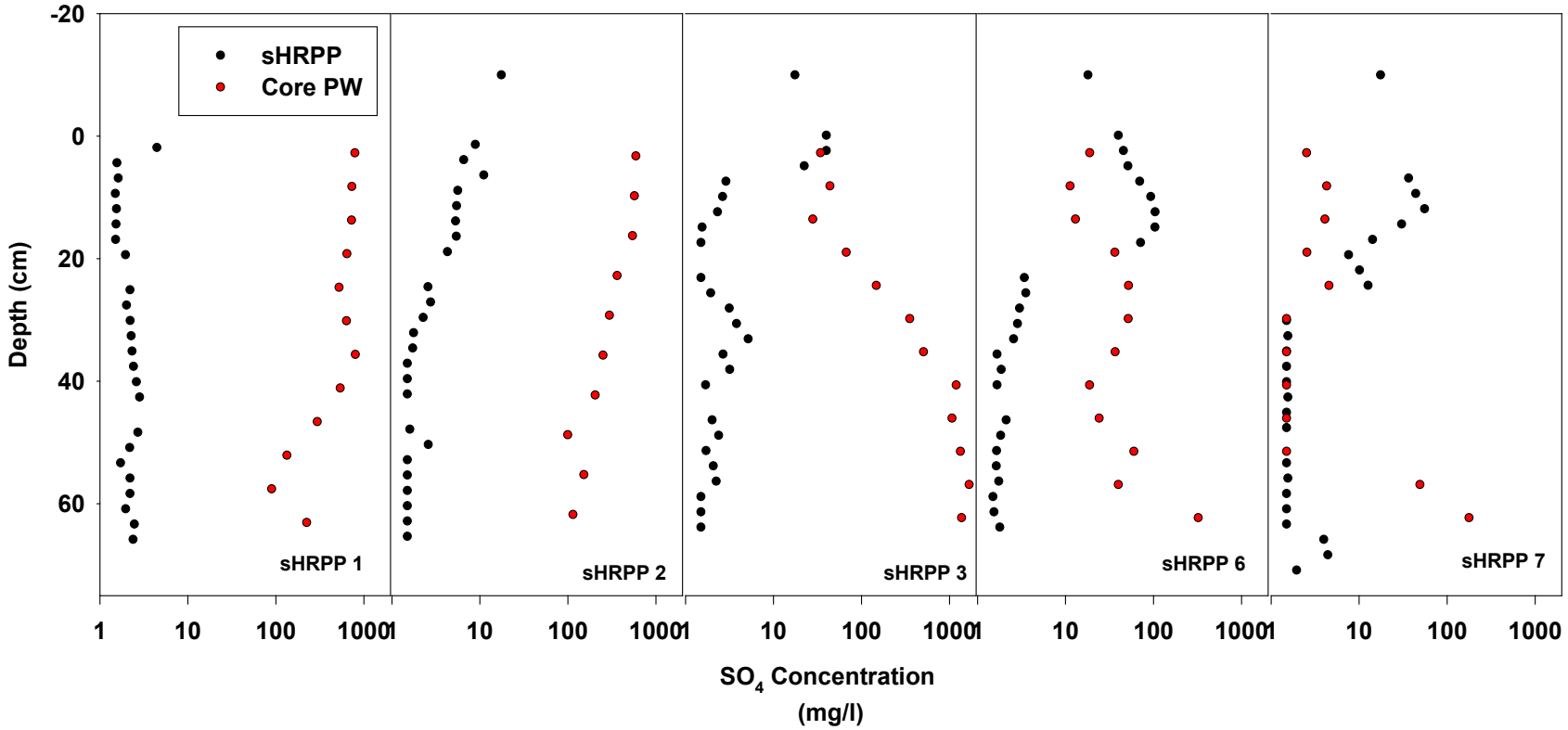


Figure 5.18. Comparison of Porewater Sulfate Measured in sHRPP Samples or in Porewater Obtained from Cores

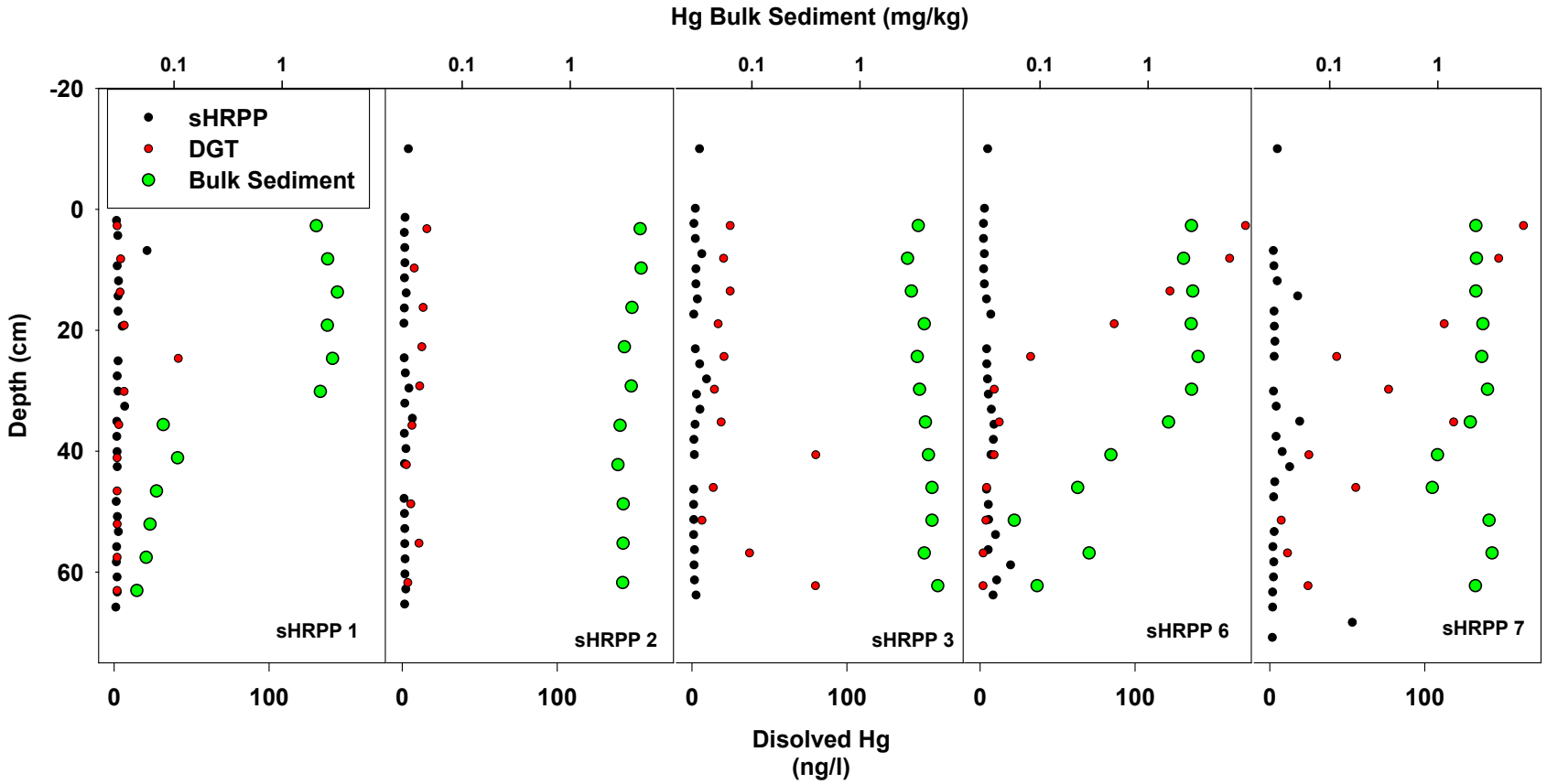


Figure 5.19. Comparison of Porewater Hg Measured in sHRPP Samples and Predicted from DGT Ex situ Measurements of Core Material As Well As Bulk Hg Concentrations in Core Material.

Resolution between the two methods, sHRPP and cores, is somewhat difficult to compare. sHRPP produce data at 2.5cm intervals. Cores may be able to be sectioned at this interval if first frozen. If so, this would produce > 30 ml of solution per 2.5 cm segment assuming 50% of the water could be recovered as free water. However, this would require the core to be cut in a N_2 atmosphere to prevent oxidation of the core surface and additional handling time to either cut or thaw the core to allow transfer to centrifuge bottles. Regardless, for at least some marsh sites (all locations in this study) acquiring a core produced some compression and some drainage of pore water. Cores also increase the time between sample acquisition and sample preservation. For sHRPP samples, the solution can be removed and placed in appropriate preservatives or measured on site within ~30 minutes. For cores, shipment is almost always a requirement and thus processing could not occur until the following day and depending on the number of cores could take an additional day at least. As such, redox sensitive parameters can be affected either by oxidation, due to input of O_2 or by reduction in sediments that were oxic but due to being sealed off from the atmosphere during shipping became reduced. Direct comparison on sensitivity, and time and cost, will be made in a later section (Section 6.0) but results indicate the difficulty in obtaining unaltered metal or geochemical profiles with cores and highlight the resolution and sensitivity that can be achieved by the sHRPP. We also demonstrate how orders of magnitude changes in metal concentrations can occur over very small depths and that metal availability is highly associated with geochemical indicators primarily SO_4^{-2}, S^{-2} and Fe^{+2}. Finally, in support of site models, the sHRPP produces multiple measures of transport including conservative Cl^- profiles and direct measures of pore velocity (unique to the sHRPP). Combining transport and availability data with geochemical indicators can lead to improved models of contaminant source and availability as discussed below.

5.2.6.3 Conceptual Model Based on sHRPP High Resolution Data

The objective of this research was to evaluate how the sHRPP high resolution data can facilitate the understanding of metal availability in comparison to other methods of porewater analysis. An individual sHRPP can be used to understand metal availability and transport at specific locations. Additionally, by evaluating multiple sites simultaneously, a larger conceptual model of the site (e.g., Canal Creek Marsh) can be developed to understand the environmental controls of metal availability. Individual sites clearly show that the near surface (~20 cm BSI) can experience rapid pore water exchange with associated impacts on geochemistry and metal availability with depth and that there is little evidence of upwelling (at least over this deployment period) at any location. Chloride profiles also suggest that a process is active to concentrate Cl^- below the sediment interface even though surface and deeper pore water is lower in Cl^- concentration.

In Canal Creek Marsh sediments, Cl^- concentration profiles for samplers installed in marsh locations below the high tide line increase with depth from surface water concentrations (~45 mg/l) to peak concentrations at ~40-50 cm BSI, and then decrease to concentrations similar to pore water at the deepest depths of the sHRPP located within Canal Creek (Figure 5.20), possibly representative of groundwater. Peak Cl^- concentrations increase with distance from the canal bank. For sHRPP 3 located furthest from the canal and at a surface marsh elevation greater than the high tide elevation, Cl^- concentrations increase throughout the depth profile. Peak Cl^- concentrations also increase with distance from the creek bank. At locations closest to the bank (<2 m), the rate of Cl^- concentration increase with depth is similar at depths <20 cm BSI and less than the rate of increase at depths > 20cm up to the maximum concentrations.

At locations > 3m from the creek bank the rate of increase from the surface to the maximum concentration is similar to the higher rate of increase at locations near the creek bank. The rate of decrease in Cl^- concentration below the peak concentrations are similar for all profiles and to the higher rate of increase at lower depths. Based on these observations, it appears that evapotranspiration has produced a zone of increased Cl^-, with the peak located perhaps near the maximum root density. The concentration of Cl^- increases with distance from the creek likely due to the reduced dilution produced by the higher elevation (less tidal drainage and flushing) as well as distance from creek (low concentration boundary). The low rate of Cl^- increase at locations near the creek is likely due to rapid flushing at depths down to the low tide elevation (supported by velocity measurements). The higher rate of increase at deeper depths and at locations further from the bank where bank drainage will be dampened, as well as the matching decrease below the concentration maximum, is likely due to diffusional processes. Due to the fact that samplers were only deployed at one time of year (December) it is unclear the extent to which Cl^- concentrations increase during peak evapotranspiration months or dissipate during plant senescence. We propose that marsh drainage and recharge, due to low and high tide, combined with the distance from the creek bank, diffusion, and evapotranspiration can reasonably explain the observed individual and combined profiles. Figure 5.21 is a conceptual drawing of the marsh channel and sHRPP locations both with respect to distance from the creek and depth above the creek bottom. We have included samplers from both sites in a common transect to demonstrate the consistency of sites at similar lateral distance from the canal.

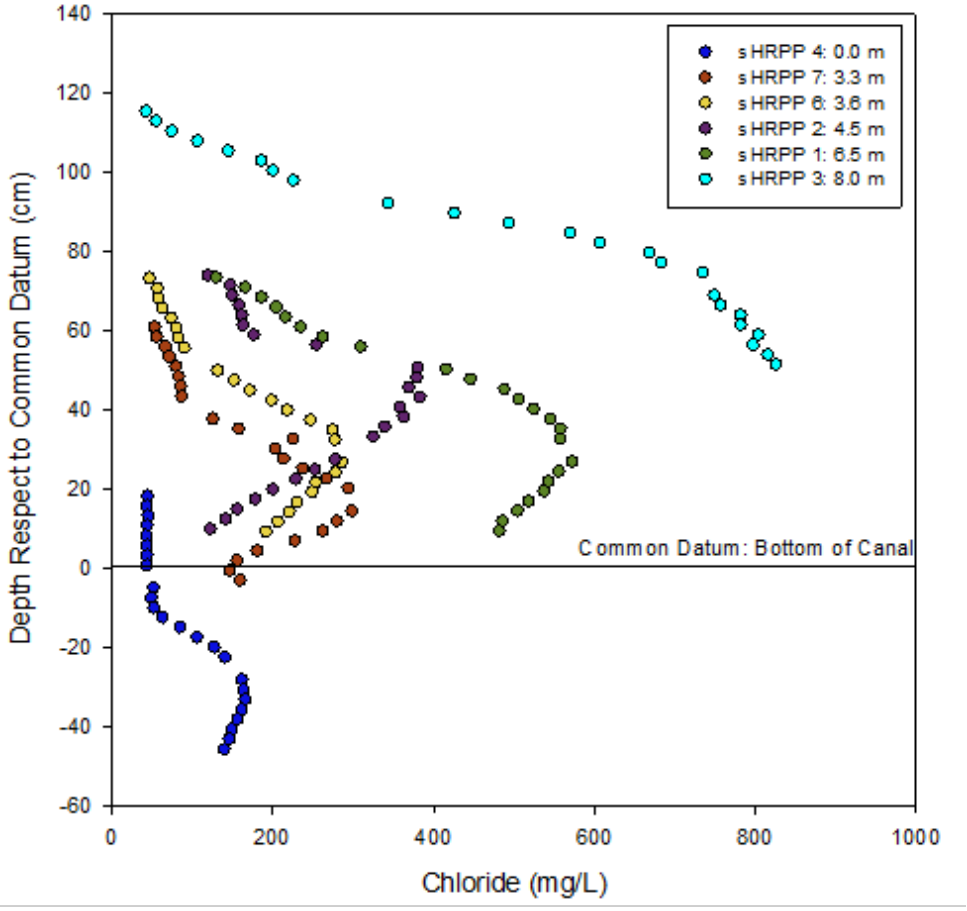


Figure 5.20. Pore Water Chloride Concentrations

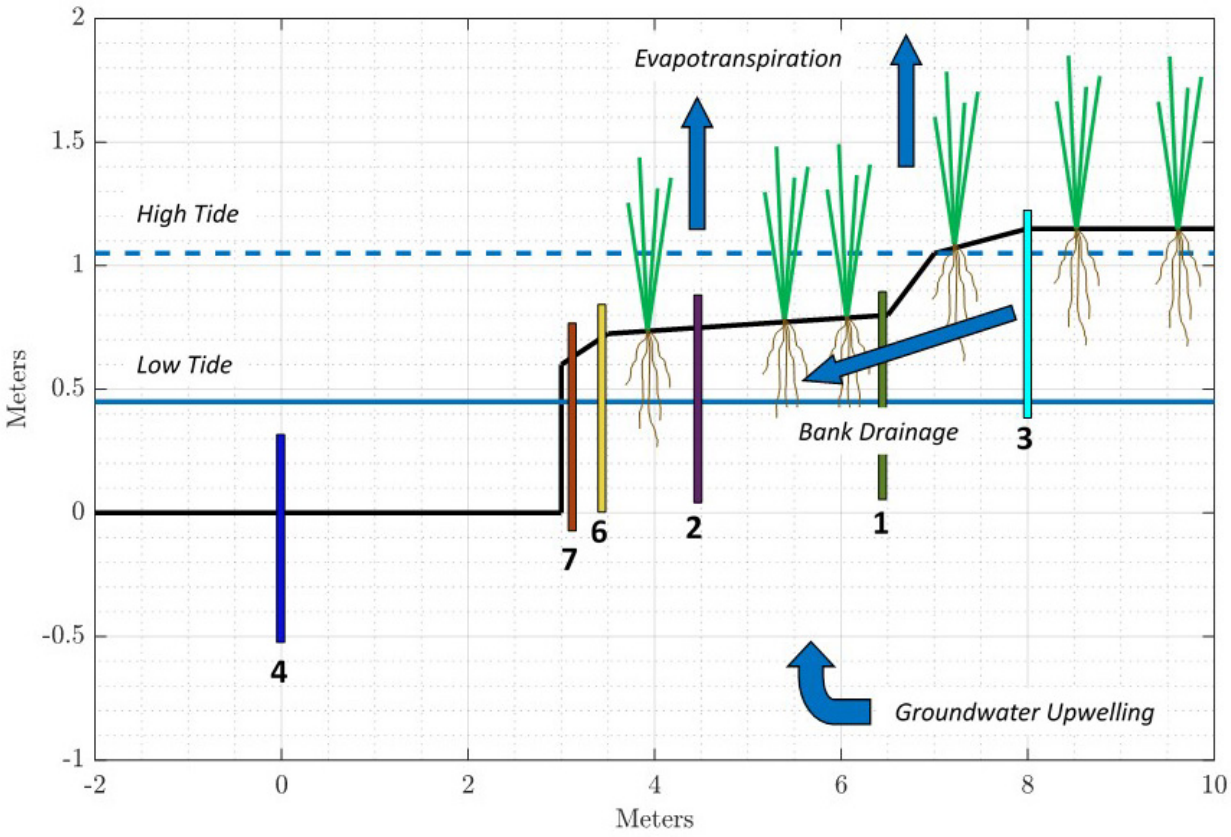


Figure 5.21. Conceptual Drawing of the Marsh Channel and sHRPP Locations

Non-conservative species do not reflect this evapotranspiration effect. For SO_4^{-2}, reduction can occur, which produces sulfides, while metals can form insoluble metal sulfide precipitates. If SO_4^{-2} was not reduced, based on Cl^- concentration profiles, SO_4^{-2} concentrations would be expected to increase with depth and distance from the creek, reaching concentrations up to 20X higher than surface water concentrations. However, SO_4^{-2} concentration profiles do not match Cl^- profiles, in fact SO_4^{-2} is not present at depths greater than 20 cm BSI, the maximum depth of rapid pore water change based on Cl^- profiles and velocity measurements. In locations near the creek (sHRPP 6 and 7), there appears to be a zone near the surface (~12cm) in which solid sulfides are oxidized leading to peak SO_4^{-2} concentrations above surface water concentrations (5-10X) at depths much closer to the interface than depths at which the Cl^- maximum occurs. At other locations, SO_4^{-2} is slightly greater or less than surface water at the interface. Peak SO_4^{-2} concentrations occur where bank drainage is predicted to be greatest based on Cl^- concentrations which would lead to oxidizing conditions at deeper depths. Sulfate profiles, therefore, represent both loss of SO_4^{-2} due to reduction but also production due to oxidation solid sulfides. This has a major impact on Zn porewater concentrations (Figure 5.22). Porewater concentrations of Zn are greater (2-20X) than surface water concentrations at every marsh site, but not the creek bottom sediments where there is no air interface or bank drainage (sHRPP 4). Peak concentrations occur at the same or shallower depth than SO_4^{-2} but decrease similar to SO_4^{-2} at depths below the peak SO_4^{-2} concentration. This highlights the role of near surface redox conditions and their relation to spatial parameters (e.g., distance from the creek).

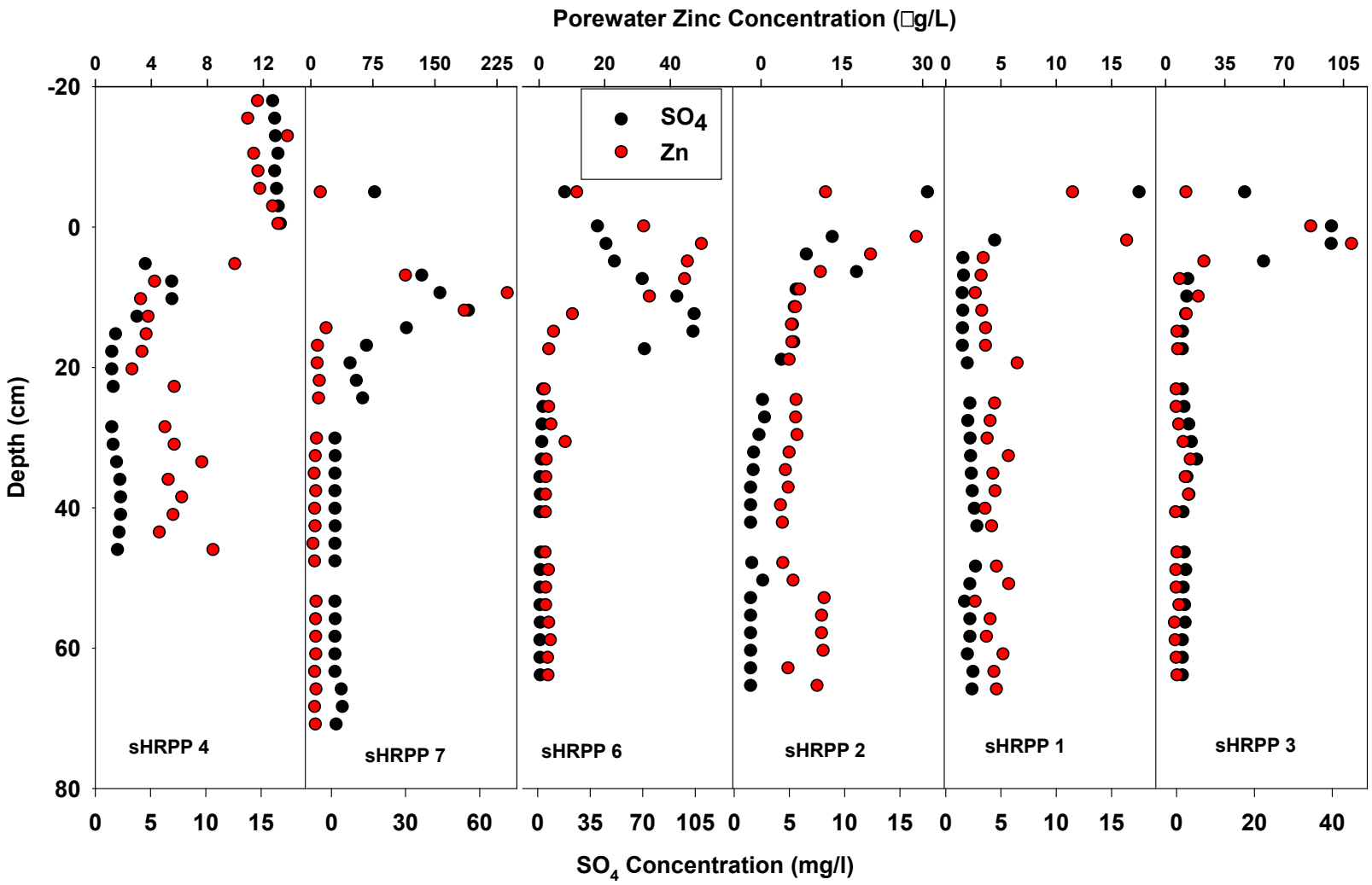


Figure 5.22. Pore Water Zinc and Sulfate Concentrations

The Cl^- accumulation is important as it not only can help define and limit transport parameters, but it also infers that in months with active transpiration, substantial water is pumped to deeper depths increasing the flux of oxygen, nitrate, and sulfate to lower depths and impacting the geochemistry and associated metal availability. Conditions can be very different throughout the year based on plant activity, hydraulic conditions (tides, rainfall), and temperature. A single deployment even of multiple samplers is not capable of recreating the full transport and biogeochemistry which produced the current geochemical depth profiles. However, the current profiles do suggest that sequestration of metals (Zn, Pb, and As) into the sediments is possible. Based on the Cl^- accumulations there is a net flux of water into the marsh. Given the loss of SO_4^{-2} and subsequent production of sulfides, metals in surface water would be sequestered in the sediment. Depending on the back flux of metals to surface water during oxidation events, metal concentrations in sediments may be partly due to enhanced capture.

This high resolution data set highlights the dynamic processes that can occur in sediments with respect to metal availability. Critical variations in concentration profiles can occur over depths < 5 cm limiting the ability to understand metal availability by using other porewater techniques (e.g., cores). In addition, the redox sensitive species (Fe, S^{-2}, metals, SO_4^{-2}) are not likely stable over the time period required to ship and process the core, and the processing of the core is likely to alter the redox parameters.

5.3 ABRAHAM'S CREEK (QUANTICO) SITE TESTING

5.3.1 Conceptual Experimental Design

The Abraham's Creek location at MCB Quantico, was chosen due to the presence of PCBs and the past application of active sequestration and biocatalytic sequestration activities from a previous ESTCP study ER-201215; summarized in Sowers et. al., 2017. The site includes four test areas (plots): Plot 1, the control plot; Plot 2, an activated carbon amended plot; and Plots 3 and 4, replicate biocatalytic activated carbon (seeded with a PCB dehalogenating consortium) amended plots. A site location map and plot layout drawing are presented as Figures 5.23 and 5.24, respectively. These plots were established in April 2015 and extensive pre-and post-amendment evaluations of PCB concentrations are available. Due to these prior activities, the site was considered ideal to demonstrate the ability of the sampler to simultaneously evaluate numerous performance objectives. For this site our implementation goals were:

1. To demonstrate that the sHRPP can produce high resolution spatial concentration profiles of pore water PCBs with depth at a sensitivity comparable to or greater than traditional 1D vertical SPME sampling and is capable of evaluating the impact of treatments (biocatalytic activated carbon and controls) with more sensitivity (less variance more statistical power). Impacts are defined as decreased pore water concentrations at depth and increased ratios/concentrations of lower chlorinated PCBs.
2. To demonstrate that the sHRPP can measure the presence and abundance of the bioaugmented PCB consortium with depth as well as general capacity for reductive dechlorination with as much or more sensitivity than core samples.
3. To demonstrate that the sHRPP can, simultaneously with goals 1 and 2, measure the geochemical sediment conditions that can be used to predict potential dechlorinating activity by measuring major redox transitions and conservative tracer transport at a scale which is less than the depth over which the transition takes place.

4. To demonstrate the differences in cost and effort between traditional pore water sampling methods and the sHRPP, as well as the increased resolution, quality and reliability of sHRPP produced data.

Figure 5.23. Site Location Map

(Sowers et. al., 2017) *Treatment site located just south of an access road (A); treatment plots marked with 1" PVC pipe (B).*

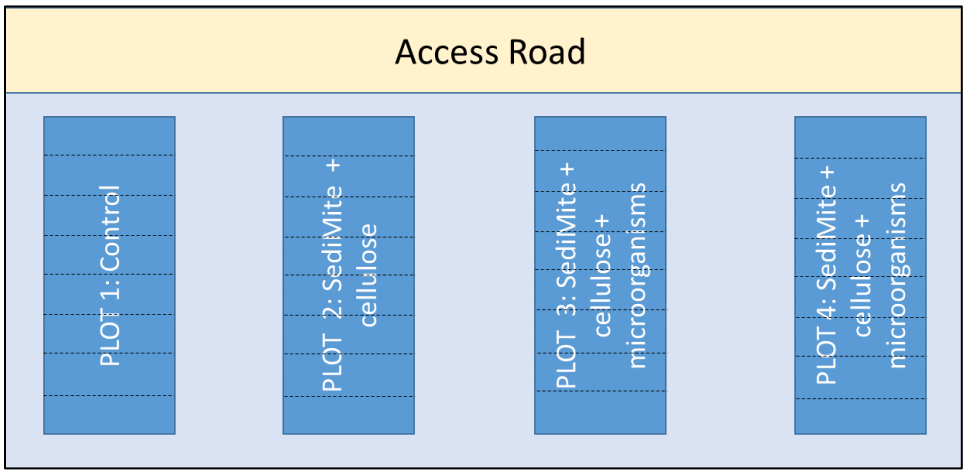


Figure 5.24. Existing Treatment Plot Layout

(Sowers et. al., 2017) Four 400 m^2 treatment plots

The successful completion of these goals would demonstrate the ability of the sHRPP to provide data to qualitatively predict the long-term efficacy of active sediment remediation and bioremediation strategies for PCBs and with more statistical power to observe differences than traditional measurement techniques.

5.3.2 Baseline Characterization

As the demonstrated technology is a site characterization tool, typical baseline characterization activities do not apply. However, as mentioned and will be discussed in the following subsections, there is sufficient pre-capping and post capping data to serve as baselines and accepted traditional methods of sediment characterization (*in-situ* SPME sampling with a "T Bar" sampler) were performed as part of the demonstration for comparison purposes.

5.3.3 Design and Layout of Technology Components

We compared pore water concentrations of PCBs produced by analysis of the SPME fibers within the sHRPP with an accepted passive sampling method, *in-situ* 1D vertical SPME analysis with a T Bar sampler (see SOP, Appendix C). For *in-situ* measurements, T Bar samplers were co-deployed with the sHRPPs. These T Bar samplers contained a SPME fiber oriented along the sampler length and provided ~5cm resolution. They were directly pushed into the sediment. The sHRPP equilibrium cells were also used to measure anions and general geochemical indicators (Cl^-, dissolved organic carbon (DOC), NO_2^-, NO_3^-, FeT, Fe^{+2}, SO_4^{-2}, and S^{-2}). As diffusion-based samplers are the accepted method for these species, they were not measured by an alternate method. We also attempted to measure and compare microbial community structure (see description below) produced by the sHRPP and an accepted traditional method (coring and subsampling sediment). However, due to impacts of the Coronavirus pandemic (COVID) the cores were not able to be evaluated for community structure.

To complete the objectives, three sHRPPs were deployed in the control test plot (Plot 1), three in the plot amended with activated carbon only (Plot 2), and three in one of the replicate biocatalytic activated carbon amended plots, (i.e., one seeded with a PCB dehalogenating consortium; Plot 3). The sampler deployment locations are presented on Figure 5.25. At each location where a sHRPP is deployed, one 5 cm diameter direct push core was collected within 0.3 m of the sHRPP. The cores were obtained during sHRPP and T Bar retrieval (rather than placement) to minimize disruption of the sediments/cap in the vicinity of the samplers. Each core was used to major geochemical processes such as nitrate reduction, sulfate reduction, iron reduction, and methanogenesis, as well as various reductive dechlorinators/reductase enzymes.

We anticipated that this data set would allow us to do the following:

1. Allow direct comparisons of spatial profiles of PCBs and for each method including the variance associated with each measurement type.
2. Evaluate the potential for PCB degradation based on geochemical conditions with depth.
3. Compare each techniques' ability to acquire depth-dependent data sets that allow for site interpretation and statistical testing of remediation impacts (e.g., ANOVA or other test based on data normality).
4. Generate data to compare the cost and time required for each method.

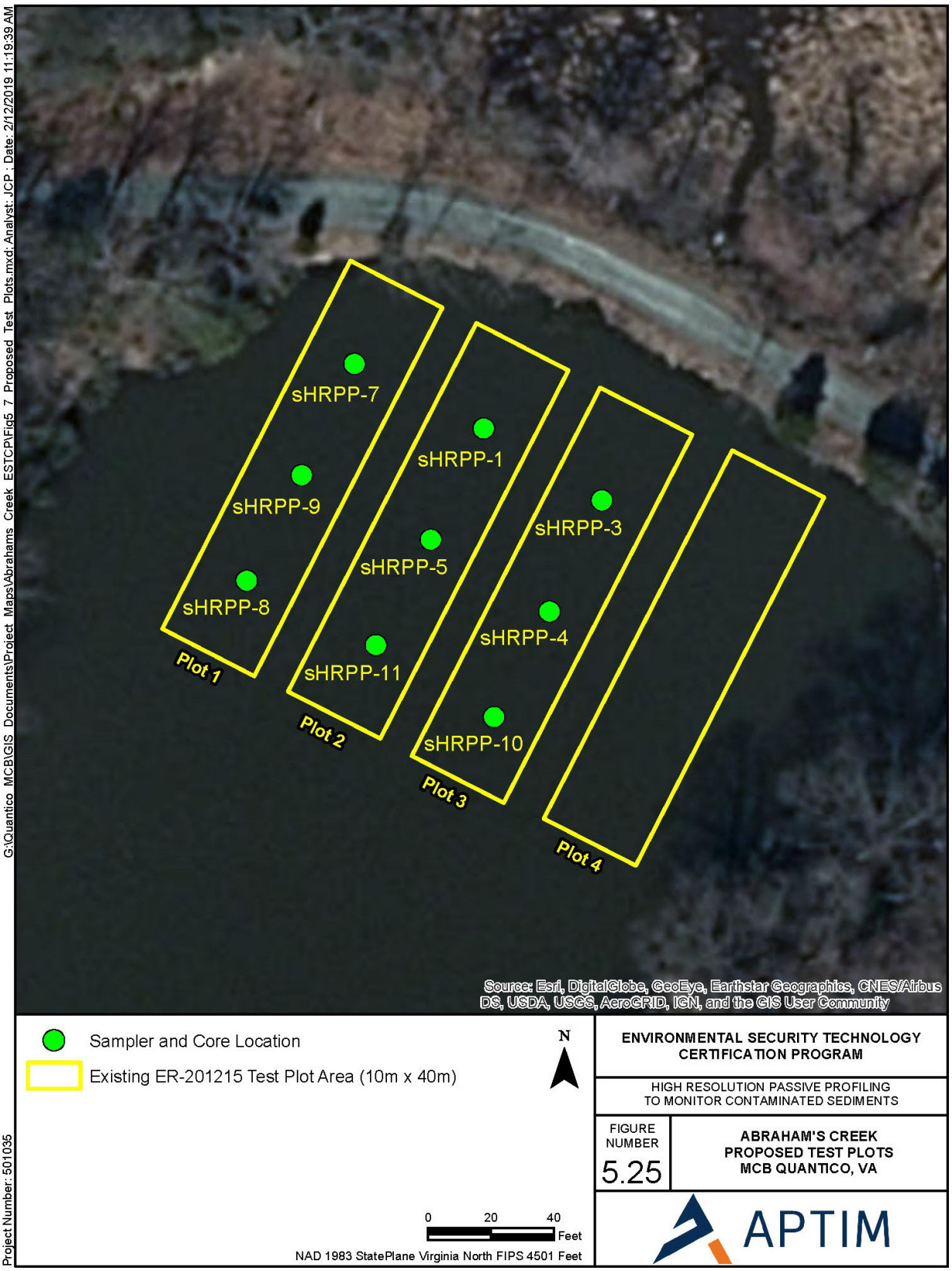


Figure 5.25. Abraham's Creek Demonstration Area

5.3.4 Field Testing

Field-testing the sHRPPs consisted of two mobilizations; the first to prepare and deploy the sHRPPs and T Bar samplers, and the second to retrieve and sample the sHRPPs and T Bar samplers, as well as advance/collect the sediment cores. All field activities were conducted in accordance with a site-specific APP/SSHP, to ensure a safe work environment during the demonstration. Prior to mobilization to the Site, APTIM worked with our POC at MCB Quantico (Mr. Rodney Aguirre) to procure all required base work permits including a NAVFAC work request and base excavation permit. A utility mark-out dig ticket request was also made through Miss Utility VA811 prior to initiating intrusive activities at the site.

The sHRPPs and T Bar samplers were prepared on shore and carried to the site for installation. The sHRPPs were prepared by submerging in distilled water spiked with NaBr (100 mg/l-Br). The nylon membrane (0.2µm pore size) stainless steel mesh (50µm pore size) and coarse stainless mesh (500µm) or stainless steel sintered membrane (Pall) and coarse stainless mesh were secured with cover plates and the sampler stored (~up to 12 hours) submerged until deployment. SPME fibers (~8cm) pre-equilibrated with PRCs were placed over select equilibration cells, sandwiched between the fine stainless mesh and coarse mesh or stainless membrane and coarse mesh. SPME were secured using a trace of silicone. Water and additional SMPE fibers placed in Br^- water were subsampled to evaluate any pre-deployment contamination (see SOP Appendix C). See Appendix E2 for photographs of pre-deployment sHRPP preparation (Photos 1-3).

As shown in Section 5.1, each of the samplers is designed to assess pore water over an approximately 1.0 m vertical interval. Table 5.3 presents the total number and types of samples that were collected within the test plots. sHRPP#2 was used as a control and was not deployed at the site.

Table 5.3. Nominal Total Number and Types of Samples Collected (Abraham's Creek)

Matrix	Number of sHRPPs / Samples per sHRPP	Total Number of Samples	Analyte	Location
Test Plot #1				
sHRPP SPME Fiber	3 / 21-23	65	PCBs	sHRPP-7 sHRPP-8
sHRPP Pore Water	3 / 24	72	Anions	sHRPP-9
	3 / 24	72	DOC	
	3 / 3-4	10	DHC, DECO, BPH4	
	3 / 3-4	10	Pore Water Velocity	
in-situ SPME Sampling (T Bar)	3 / 10-12	33	PCBs	
Soil Core Sediment	3 / 9	27	PCB-Degraders	

Table 5.3. Total Number and Types of Samples (cont'd)

Matrix	Anticipated Number of sHRPPs / Samples per sHRPP	Total Number of Samples	Analyte	Location
Test Plot #2				
sHRPP SPME Fiber	3 / 22-24	70	PCBs	sHRPP-1 sHRPP-5
sHRPP Pore Water	3 / 24	72	Anions	sHRPP-11
	3 / 24	72	DOC	
	3 / 3-4	10	DHC, DECO, BPH4	
	3 / 3-4	10	Pore Water Velocity	
in-situ SPME Sampling (T Bar)	3 / 11	33	PCBs	
Soil Core Sediment	3 / 9	27	QuantArray PCB-Degraders	
Test Plot #3				
sHRPP SPME Fiber	3 / 22-24	70	PCBs	sHRPP-3 sHRPP-4
sHRPP Pore Water	3 / 24	72	Anions	sHRPP-10
	3 / 24	72	DOC	
	3 / 3	9	DHC, DECO, BPH4	
	3 / 3-4	10	Pore Water Velocity	
in-situ SPME Sampling (T Bar)	3 / 9-11	30	PCBs	
Soil Core Sediment	3 / 9	27	QuantArray PCB-Degraders	
Control				
sHRPP SPME Fiber	1 / 6	6	PCBs	Control sHRPP-2 (not deployed at site)
sHRPP Preparation Water	1 / 6	6	Anions	
	1 / 6	6	DOC	
	1 / 1	1	QuantArray	
	1 / 1	1	PCB-Degraders	
in-situ SPME Sampling (T Bar)	1 / 6	6	PCBs	

To deploy the samplers, a rope was first attached to the hole machined into the top of the sampler. An extension rod was then positioned over the top of the sampler (not connected to the sampler), and the unit is pushed/driven into the cap/underlying sediment to the proper depth (as discussed in Section 5.3.3). The extension rod was then removed, and a marker buoy was attached to the tag end of the rope to assist in locating the sampler during retrieval. The T-Bar samplers were also pushed into the cap/underlying sediment using the extension rod, with a rope tied to the sHRPP buoy to aid in retrieval.

The sHRPPs and T-Bar samplers remained in the cap/sediment for approximately four weeks. See Appendix E2 for photographs of sHRPP deployment activities (Photos 4-9).

5.3.5 Sampling Methods

5.3.5.1 sHRPP and T-Bar Retrieval and Sampling

After approximately four weeks of equilibration, the sHRPPs and T-Bar samplers were removed by hand pulling. The samplers were transported by small boat to shore where a large, high-roof cargo van was outfitted with tables to aid in the sampling process (See Appendix E2 for photographs of sHRPP retrieval and sampling activities (Photos 10-18)). The equilibration cells and velocity cells were sampled first. A pre-cleaned glass syringe with 18-gauge needle was inserted through the membrane and water removed by suction. A second needle was placed through the membrane to relieve any vacuum and prevent any outside water from being pulled through the membrane. Water from each cell was placed in an appropriate container, as summarized in Table 5.4, for analysis of anions (Cl^-, NO_2^-, NO_3^-, SO_4^{-2}), and DOC. After the equilibration cells were sampled, the velocity cells were sampled in a similar manner with the total volume of each cell placed in a separate glass vial for Br^- analysis.

SPME fibers were retrieved by removing the top cover plate and pulling off the coarse stainless mesh while retrieving the fibers with tweezers as each cell was uncovered. The SPME fibers were gently rinsed in DI water, wiped with a clean kimwipe and placed in vials prefilled with hexane. The SPME fibers from the T Bar samplers were sampled by removing the fiber from the vertical slot, gently rinsed with water and sectioned in 5cm increments. Each 5cm increment was placed in hexane in the field and shipped back to the TTU lab. Details of sampling are available in the SOP presented in Appendix C.

Table 5.4. Sample Analytical Methods, Volume, Preservation, and Containers

Analyte	Method/Laboratory	Sample Volume	Preservative	Bottle
PCBs	EPA 8082A Texas Tech	SPME	4°C	5 mL glass vial w/ hexane (x1)
Anions (Br^-, NO_2^-, NO_3^-, SO_4^{-2})	EPA 300.0 Texas Tech	2 mL	4°C	5 mL glass vial (x1)
DOC	EPA 415.3 Texas Tech	2 mL	4°C with H_2SO_4	5 mL glass vial (x1)
Microbial Community (Pore Water)	QuantArray Microbial Insights	20 biosep beads	4°C	15 mL conical (x1)
Microbial Community (sediment)	QuantArray Microbial Insights	8 oz.	4°C	8 oz. glass jar (x1)
On-Site Testing (Fe^{+2}, total sulfide)	Hach 8133 and 8146 Field Test Kits	3 mL	On Site Only	5 mL glass vial (x1) or direct analysis

For microbial community analysis, the Bio-Sep beads were sampled by: (1) removing the retaining cover; (2) removing the beads with an alcohol-sterilized spatula; (3) placing beads in a sterile saline solution and gently rinsing to remove sediment; and (4) placing beads in sterile 15-mL conical tubes, as summarized in Table 5.4. The beads were stored at -80°C, and down-selected for microbial analysis based on the contaminant and geochemical data as discussed in Section 5.3.6.

The remaining solution (in equilibrium cells) was used for on-site testing (Fe^{+2}, total sulfide) using field test kits (Hach Methods).

5.3.5.2 Sediment Core Collection

During sampler retrieval, we also collected soil cores using a 5-cm diameter direct push-coring device (Multi-Stage Sludge/Sediment Sampler, manufactured by AMS, Inc.). The cores were advanced by hand or driven into the sediment using a slide hammer to a depth of approximately 0.8 m. The soil sampler's "valved core tip" fills the sampler without losing the sample upon retrieval. The sampler uses a disposable plastic soil catcher that fits on the end of a 5 x 30 cm plastic liner. The core tip allows the plastic soil core catcher and liner to fit snuggly over the lip of the core tip. Once the soil core catcher and liner are placed on the core tip, they are loaded into a stainless steel multi-stage base section and screwed together. During deployment, the flap cap opens and allows excess air and water to escape through the top of the sampler, eliminating pressure buildup. The sediment enters and fills the liner. When the sampler is lifted, the flap closes and creates suction to assist the soil core catcher in retaining the sample. The top of the core is then capped and sealed, and the core removed from the multi-stage base section. The bottom of the core is then capped and sealed.

Three 30-cm base sections were threaded together and used to acquire a 0.9 m long soil core at each sHRPP location, spaced (~ 0.3 m) from the sHRPP. Each sealed core was shipped on ice to Dr. Sowers lab where they were frozen. Dr. Sower was originally supposed to analyze the cores for the bio-amended culture but do to COVID this analysis was never able to be performed. The cores were then shipped to TTU where they were sectioned and placed in 8 oz. soil jars. This material was used to perform ex situ SPME analysis of PSB concentrations.

5.3.6 Sampling Results

Three sHRPPs and three T-Bar SPME samplers were deployed in each of the three test plots (control, Sedimite, and Sedimite-bioaugmented). Each sHRPP produced high resolution data on geochemistry (SO_4^{-2}, S^{-2}, and Fe^{+2}), dechlorination microbial abundance, transport indicators (in situ conservative tracers (Cl^-), pore velocity, fraction of steady state) and porewater concentrations of PCBs. T-bar samplers only produced data on porewater PCB concentrations. Cores (three form each plot) were also obtained and evaluated for ex situ porewater PCB concentrations, and sediment characteristics/texture. Laboratory analytical results are tabulated in Appendix F2.

5.3.6.1 Transport Indicators

Core texture analysis indicated that the top ~10-20 cm of the core was mainly composed of silt (Table 5.5). The total depth of this layer is unclear due to substantial compression of the fluff layer. Core samplers were driven to obtain 90 cm cores, but recoveries were ≤ to 60 cm, suggesting significant compression of core material. The lower depths varied in texture but were generally silty clay, clayey silt, or clay with the presence of some sand and, in one core, sand and gravel. There are three measured parameters that relate to transport of porewater. In some cases, Cl^- profiles can indicate advective or diffusive dominated transport when a gradient in surface water and pore water and/or a gradient in porewater and deeper groundwater occurs.

At this site Cl^- concentration profiles did not vary substantially with depth. Surface water had very low Cl^- concentrations and concentrations rapidly increased with depth over the upper ~5 cm. Below that, Cl^- profiles varied with location but concentrations did increase slowly to maximum concentrations at depths > 20 cm BSI (Figure 5.26). Variations are most likely due to differences in sediment material and possibly impacts of lateral water movement. Upwelling or downwelling is unlikely as velocity profiles at the deepest depth were all very low. Pore velocities at upper depths, excluding those near the surface interface which can be very high due to lower porosity and bioturbation, mainly varied from ~2 cm/d to 10 cm/d with a few locations as high as 15 cm/d with no clear relationship to cell, location or even texture (Figure 5.26). Equilibrium cell fraction of steady state decreased from ~100% to ~80% at the lowest depths for all plots and samplers (Figure 5.26). This most probably indicated an increase in sediment density with depth and subsequent decrease in porosity. Overall transport indicators suggest no clear role for advective transport, supporting a diffusive dominated transport regime.

5.3.6.2 Biogeochemistry

For all plots and replicate locations within plots, SO_4^{-2} concentrations in surface water (1-2 mg/l) were reduced below the detection limit (0.5 mg/l) within a few cm of the surface interface (Figure 5.27). Sulfide concentrations were uniformly low <200 µg/l (Figure 5.27). On the other hand, Fe^{+2} concentrations rapidly increased with depth below the sediment water interface to a depth of ~5-10 cm and then remained constant, though high varying from 40-90 mg/l (Figure 5.27). Concentrations in the Sedimite + Bioaugmentation plots were uniformly lower than the Control and Sedimite plots. The sediment appears to be reduced.

Abundances of two bacterial species capable of dehalogenation were measured in each treatment (Figure 5.28). Both species were present at all depths, but there was no difference in abundances between treatments at any depth.

Table 5.5. Soil Core Texture Analysis

Plot Type	Location	Depth Range (cm below interface)	Texture	Velocity
Control	North	0-8	Silt	7
		23-38	Clay	6
		38-53	Clayey Silt	7
		>53		1
	Central	0-14	Fine Silt	80
		27-42	Silty Clay	4
		42-57	Clayey Silt	2
		>57		
	South	0-12	Silt	40
		23-33	Sandy Clay	12
		33-43	Silty Clay	3
		>43		1
Sedimite	North	0-14	Silty Clay	50
		32-43	Coarse Sand-gravel	8
		43-55	Coarse Sand Gravel	14
		>55		1
	Central	0-12	Silt	70
		24-33	Silty Clay	14
		33-42	Silty Clay	5
		>42		1
	South	0-13	Silt	20
		26-36	Clay	6
		36-46	Silty Clay	1
		>46		
Sedimite +Bioaugmentation	North	0-19		70
		10-19	Silty Sand	6
		19-45	Clayey Silt	2
		45-71	Clayey Silt	0
	Central	0-16	Silty Sand	>100
		30-47	Silty Clay	5
		47-65	Clay	2
		>65		1
	South	0-15	Silty Sand	3
		31-46	Clayey Silt	13
		46-61	Sandy Clay	0
		>61		

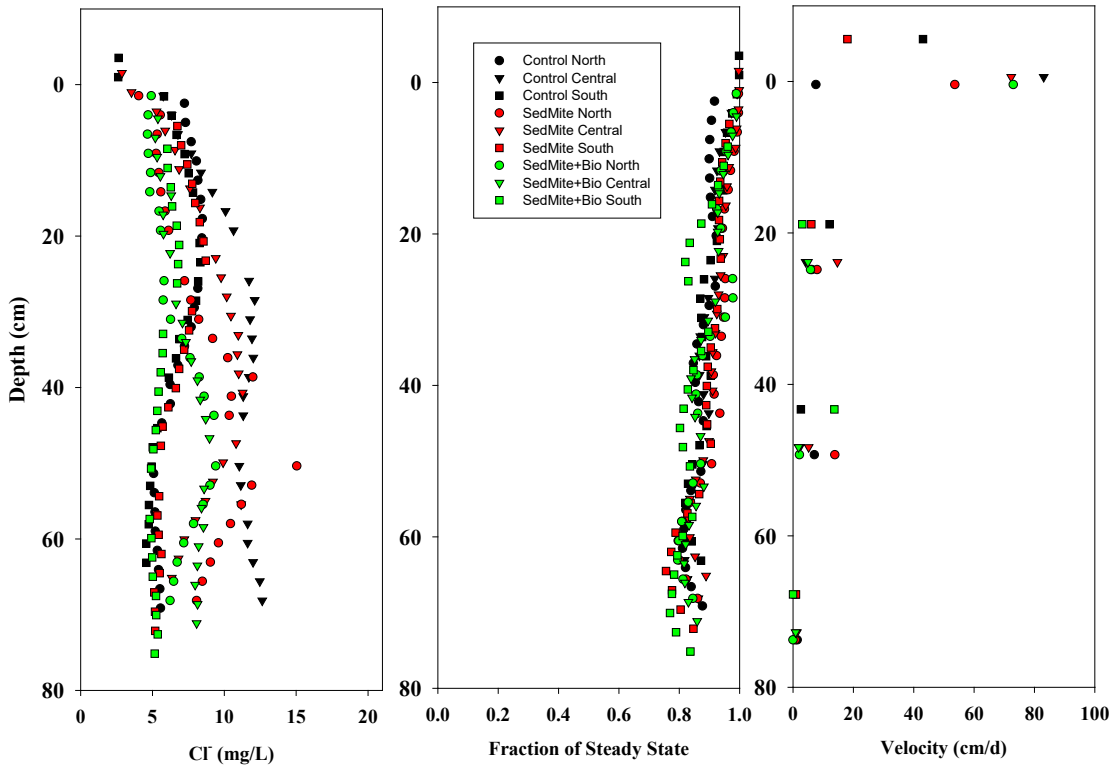


Figure 5.26. Cl^-, Fraction of Steady State and Velocity Profiles

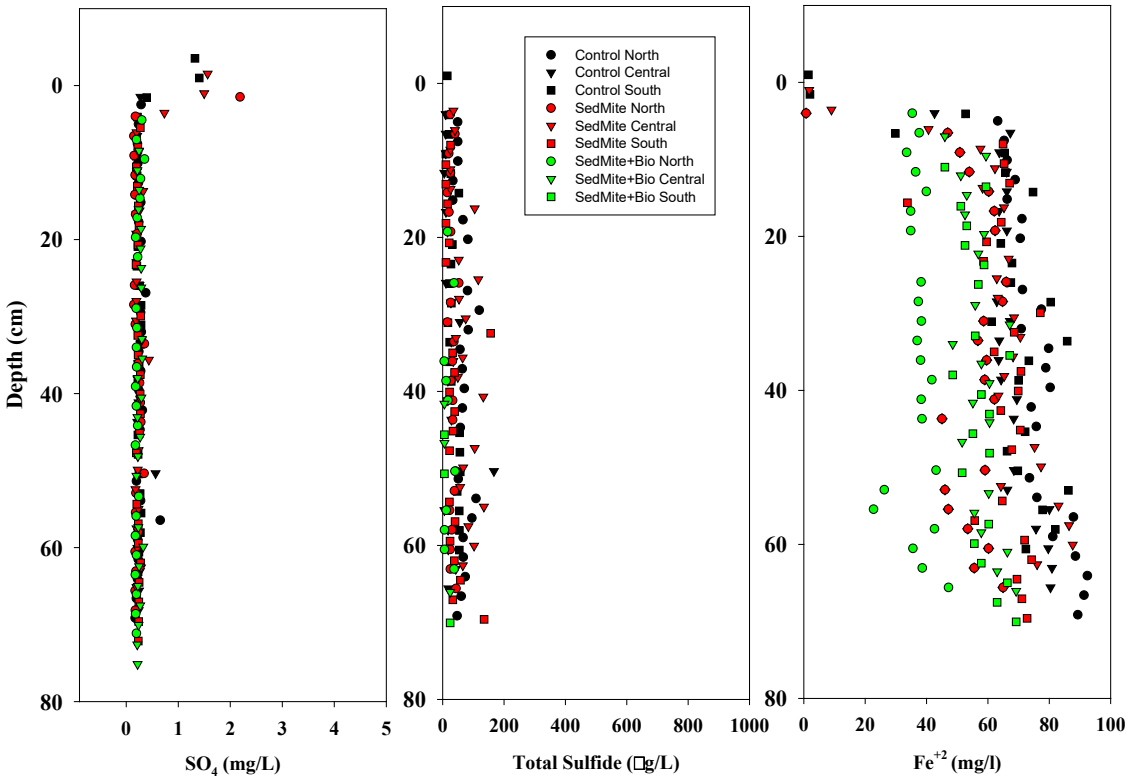


Figure 5.27. Concentration Distribution of Sulfate, Sulfide and Fe^{+2} with Depth

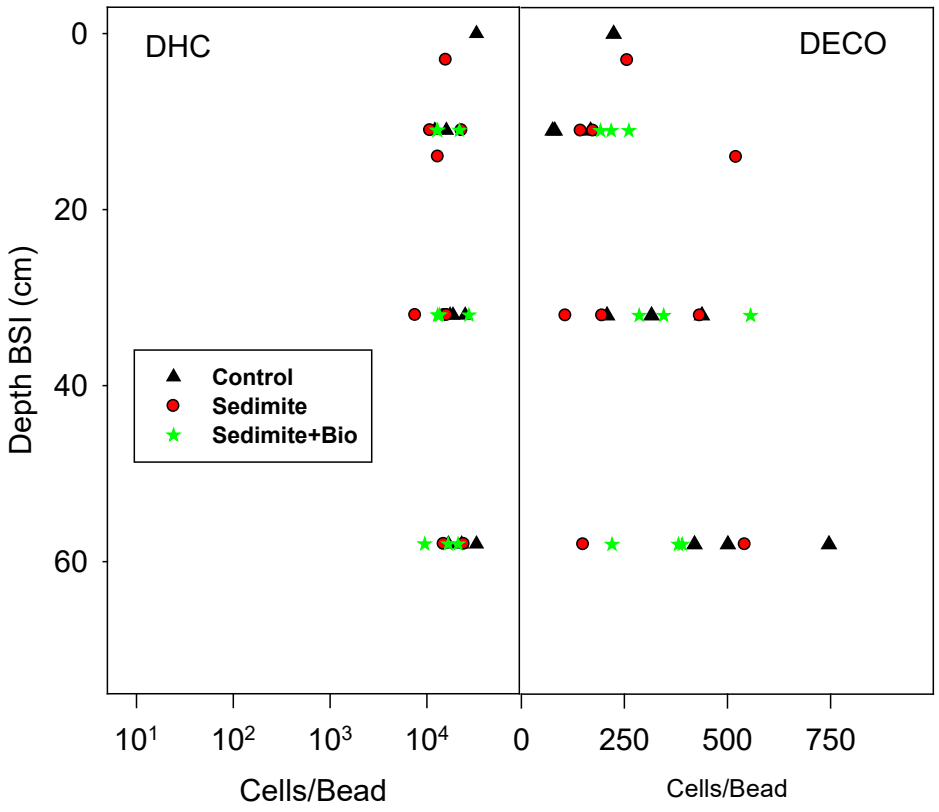


Figure 5.28. Abundances of DHC and DECO with Depth

5.3.6.3 PCB Concentrations

5.3.6.3.1 PRC Fraction of Steady State

The SPME method like other polymeric sampling methods uses Performance Reference Compounds (PRC) to evaluate the fraction of steady state (fss) achieved between the pore water concentrations and polymer concentration. This value is used to correct for any dis-equilibrium. For PCBs, six ^{13}C PCB compounds (Figure 5.29) were used representing a range of log K_{ow} (5.67-7.36). For this effort we compared the fss achieved by each type of sampler in each plot. In general, higher fss reduce the error associated with pore water concentration corrections.

For the sHRPP samplers, the SPME fibers fss varied from 90 to 20% with decreasing fss with increasing PRC K_{ow} (Figure 5.29). Variation in fss for any given PRC was generally low (25 and 75 percentile < ±0.1 of average fss). The fss values for PRCs were very similar for sHRPP deployed in the Sedimite and Sedimite + Bioaugmentation plots. For sHRPP deployed in the control plots fss values were generally lower (~10-20%) for PCB 28, 52, and 101, with smaller differences for more hydrophobic PRCs. While laboratory tests had shown that the nylon membrane underlying the stainless steel mesh would not impact the SPME fiber equilibrium, we further tested this issue in the field. Three sHRPP (one per plot type), were installed with a stainless steel sintered membrane (no nylon present). These three sHRPP had fss values similar to sHRPP with nylon (Figure 5.29).

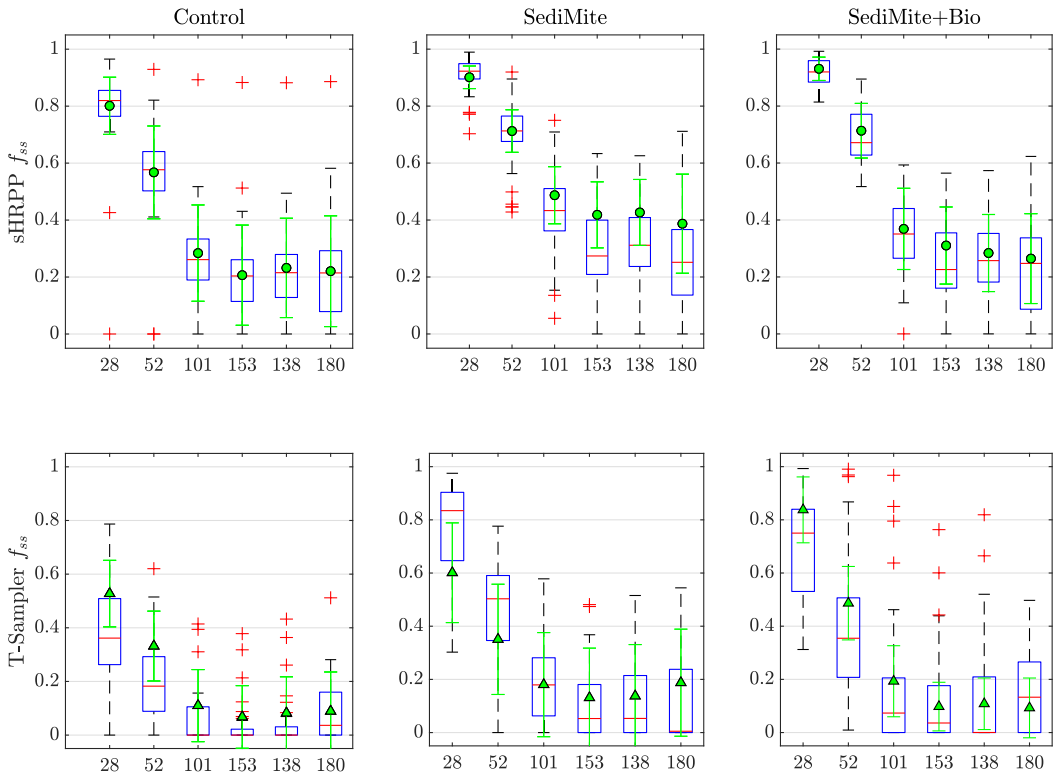


Figure 5.29. Distribution of fss Values for Each PRC

Distribution of fss values (all depths and locations within plot type combined) for each PRC within each plot type (Control, Sedimite, and Sedimite + Bioaugmented). Green circles and triangles represent the average (±stdev) fss value for sHRPP with stainless steel membrane and unsheathed T-Bar samplers, respectively.

For the T- samplers, fss were uniformly lower than sHRPP. The fss values generally declined as expected with increasing PRC K_{ow} values with the exception of PCB 180. The fss values for the control plot were lower than both the Sedimite and Sedimite Bioaugmented similar to results for the sHRPP, although the magnitude of the reduction was greater, particularly for the lower K_{ow} PRCs. The very low fss values after 4 weeks of deployment for the T-Bar samplers is difficult to explain. One possible contribution was the use of a sheath over the samplers. The sheath is meant to protect the samplers but perhaps blocked the sediment from coming in close contact with the fiber. Three of the T-Bar samplers were installed without the sheath. These three samplers 1 per plot type, did generally have greater great fss values for all PRCs than sheathed T-Bar samplers but were not always higher. It is not clear what caused the very low PRC equilibrium of the T-Bar samplers. The fibers were sourced from the exact same batch of PRC equilibrated fibers.

The anomaly of the low T-bar fss values created problems for comparing PCB porewater concentrations between methods. In order to make comparisons we considered a number of factors. First, the sHRPP fss values appear reasonable based on previous work with in situ SPME PRC equilibrium in sediments which should range from 0.9-0.20 after a 4 week deployment (Lampert et al., 2015). The overall T-Bar sampler fss equilibrium was low compared to previous work. Secondly, four locations (Sedimite-North, Center, and South and Sedimite + Bioaugmentation North) had similar sHRPP and T-Bar fss values. These four locations also had T-Bar fss values > 10% for all PRCs and fiber PCB concentrations (uncorrected) were often in the same order of magnitude regardless of differences in PRC equilibrium. Due to these observations, we compared PCB concentrations in sediment porewater in two ways. First, we used the average fss of each PRC determined using only the sHRPP data to calculate the PCB porewater concentration. While this may cause inaccuracies for the T-Bar samplers it is reasonable given that SPME fibers in co-located sediments should equilibrate similarly and T-Bar sample fss are unrealistic but PCB concentrations in fibers (similar uptake) are similar between sample methods. In addition, given that all depth dependent data is corrected using the same fss values, the two sampling methods can be compared qualitatively even if absolute concentrations are incorrect. In other words, correcting by a consistent set of fss, allows the accumulation of PCBs to be evaluated irrespective of the true porewater concentration. Secondly, we compared only the four locations for which fss values were similar between sHRPP and T-Bar samplers. For these locations, PCB porewater concentrations were calculated by using the average fss value calculated from each sampler separately. For instance, for location Sedimite North, the average fss with respect to K_{ow} was predicted using the measured values of fss for each PRC from the T-Bar and sHRPP separately and the interpolated fss values for each sampler used to calculate the porewater concentration at each depth for each type of sampler. As a final comparison, in situ porewater concentrations from each method were also compared to ex situ measurements from cores. Ex situ fss values were very similar to sHRPP for all plots and to T-Bar for the 4 plots for which T-Bar and sHRPP fss values generally matched (Figure 5.30).

5.3.6.3.2 PCB Porewater Concentrations

Twenty nine PCB congeners were quantitated (Table 5.6) based on NOAA guidance and the site manager's recommendations. T-Bar sampler fibers were cut into 5cm lengths representing 5 cm of depth. sHRPP fibers were 6 cm in length but represented a single depth. For the sHRPP samplers, only half of the sHRPP cells were used for SPME sampling resulting in a resolution of ~2.5cm. If desired, the resolution can be increased to 1.25cm. Detection limits for PCBS are identical based on the same fiber length but given the slightly longer fiber used for sHRPP the practical quantitation level (PQL) as shown below (Figures 5.31 through 5.33) is lower for sHRPP than T-Bar. For ex situ analysis, cores were sectioned into ~thirds and 20 cm of fiber exposed to the homogenized sediment for 50 days. Ex situ detection limits (porewater) were the same as the sHRPP as fiber solvent extracts were not concentrated. While 29 congeners were evaluated, only a few were consistently detected in the majority of locations by both sHRPP and T-Bar samplers. Due the very large number of samples, only PCBs with average concentrations above the MDL for both sHRPP and T-Bar for the most locations are discussed (see highlighted congeners in Table 5.6). Twelve PCBs are discussed below representing a K_{ow} range of 5.8 to 7.3. Lower molecular weight PCBs (congener numbers < 52) were generally not detected above the PQL. The concentrations of all 29 congeners for both samplers are reported in Appendix F2.

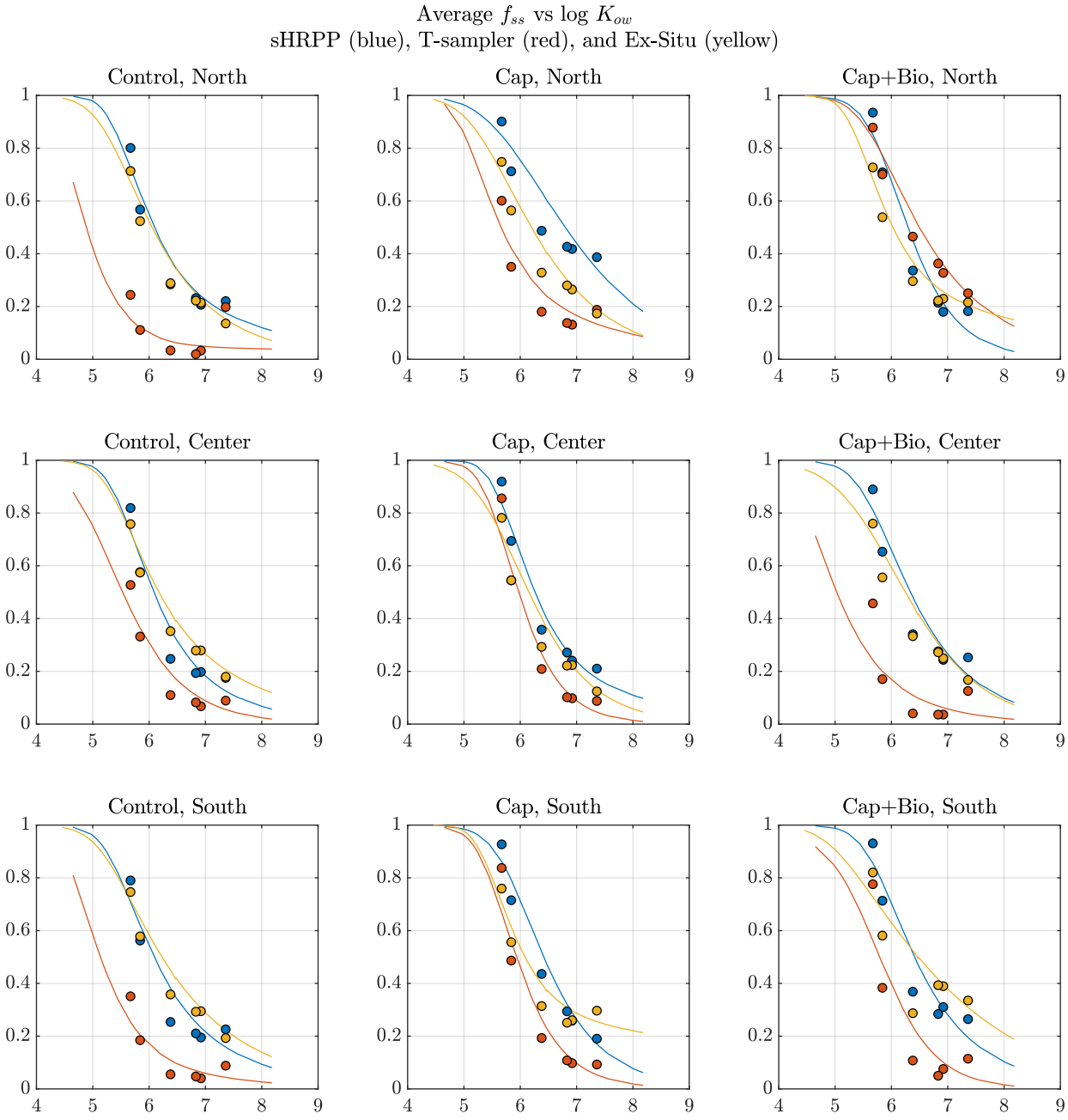


Figure 5.30. Distribution of Average fss Values for Each Location

Distribution of average fss values (all depths combined) for each location (North, Central, and South) for each plot. Blue, yellow, and red symbols represent sHRPP, ex situ, and T-Bar values, respectively. Lines are the modeled relationship between fss and K_{ow}.

Table 5.6. PCB Congeners Analyzed

Highlighted cells indicate PCBs used for discussion due to their frequency of detection above the PQL.

8	5	18	16	2	28	52
44	66	101	110	118	153	132
105	164	138	126	187	183	128+167
174	180	169	170	195	206	209

5.3.6.3.3 PCB Distributions with Depth

There are a large number of possible comparisons given the 9 total locations and 12 PCBs at concentrations generally greater than the PQL. With so many comparisons, synthesizing the overall outcomes can be difficult. We present the PCB concentration distribution in a number of ways. First, we present the PCB depth concentration distribution produced by both the sHRPP and T-Bar samplers for each plot (Control, Sedimite, Sedimite+ Bioaugmentation) with all concentrations corrected for fss using only the sHRPP PRCs. In addition, we also compare the concentration distributions for the four plots for which T-Bar fss were similar to sHRPP fss and near expected values, as well as above 10% equilibrium, with each concentration distribution corrected by the individual samplers PRC fss. Secondly, we do a more rigorous comparison by combing replicate locations within each treatment to evaluate any systematic differences in distribution due to sampler type absent of spatial variation. This analysis also includes the ex situ results.

5.3.6.3.4 Individual PCB Distributions for each Treatment

Due to the potential for treatment effects, the distribution between T-Bar and sHRPP samplers is first compared within each treatment plot separately. As spatial resolution was one of the attributes to be demonstrated, we present the detailed depth concentration distributions. In this case our purpose is less to compare quantitative differences in concentrations but rather to compare the distribution profiles with depth, differences in concentration are discussed in the next section. For each PCB discussed we present two illustrations of the concentration distribution with depth. As discussed above, in the first case the fss values for the sHRPP were used to correct both sHRPP and T-Bar values and all 12 locations are displayed. In the second case, only 4 locations with similar sHRPP and T-Bar fss values are displayed.

5.3.6.3.5 PCB Distribution for each Plot

PCB concentration distributions for all treatments are displayed in Figures 5.31 through 5.33. There are three panels (A, B, C) for the North, Central, and South sampler locations for each treatment. Panel A, B, and C represent PCBs 52, 101, 110, and 118; 153, 132, 164, and 138; and 187, 183, 174, and 170, respectively. Solid lines represent the distribution predicted by the T-Bar samplers and dashed lines represent the distribution by the sHRPP. There are a few observations that can be made concerning all profiles. First, the resolution of the sHRPP is ~ 2x that of the T-Bar samplers. The sHRPP concentrations represent a discrete depth but integrate ~6cm across this depth. T-Bar samplers represent 5 cm of continuous depth but a single point at each depth.

Therefor the samplers predict slightly different concentrations, with the T-Bar representing depth integrated concentrations (~5cm) while the sHRPP integrates more sediment at given depths with a resolution of 2.5 cm. The sHRPP can therefore capture changes in concentration with depth at higher resolution and should be more representative of the variation but can also have greater variability as they do not integrate depths. The other major issue is that the assigned depth is uncertain particularly with the T-Bar samplers. Samplers were installed based on the measured water depth. However, the sediment interface can be nebulous depending on the sediment type and depth of the fluff layer. At Abrahams Creek the top sediment is very soft and given the depth of water (> 10ft), the T-Bar sampler could have been deployed above or more probably below the top of the fluff layer. This depth off-set could be large, up to 15-30 cm. The sHRPP have a two other means of defining the true sediment interface which can allow for more accurate depth determinations relative to the sediment interface. First the samplers will develop an oxidation stain located at the sediment-bulk water interface due the sharp transition between oxic and anoxic conditions (see Photo 11 in Appendix E3). Secondly, the concentrations of Cl^{-}, SO_4^{-2}, Fe^{+2} or other geochemical parameters measured by the equilibrium cells can also be used to define the interface based on the rapid change in transport (free water diffusion) as well as measured change in redox (see Figures 5.26 and 5.27). Combined these offer a relatively robust means (~ ±5cm) to define the sediment interface layer. Due to the differing precision in depth estimates, profiles may be shifted as discussed below.

In the control plot, PCBs (52, 101, 110, and 118) with lower K_{ow} had similar shaped profiles but varied in absolute concentration (Figure 5.31). The main exception to this observation was PCB 118 concentrations, which did not generally co-vary. PCBs tended to increase in concentration with depth and differences in concentration distribution were larger between control replicate locations than between samplers. For instance, T-Bar and sHRPP PCB 101 concentrations were similar for each location (N, C, S) but between the north and central locations the concentrations could vary by an order of magnitude. These general observations are even more pronounced for PCBs with higher K_{ow}s (Figure 31 Panels B and C). For PCBs (153, 132, 164, 138, 187, 183, 174, and 170) the concentration distribution variations with depth are highly similar regardless of sampler, sHRPP and T-Bar. Peak concentrations are generally similar between replicate locations (N, C, S).

In the Sedimite treatment plot, the same major observations also occur (Figure 5.32). Most PCBs co-vary (except 118). For some locations (N and S) it is clear that the sampler depths are off set as discussed above. If the T-Bar sampler for the North replicate was down shifted by 10 cm the profiles produced by either sampler would be nearly identical with a pronounced peak of concentrations at ~ 60 cm BSI. The same is also true for the South replicate location, for which a ~ 20 cm downward shift in depth for the T-Bar samplers would create nearly identical profiles in shape with increases in concentration to depths of 50-60cm BSI below which concentrations declined.

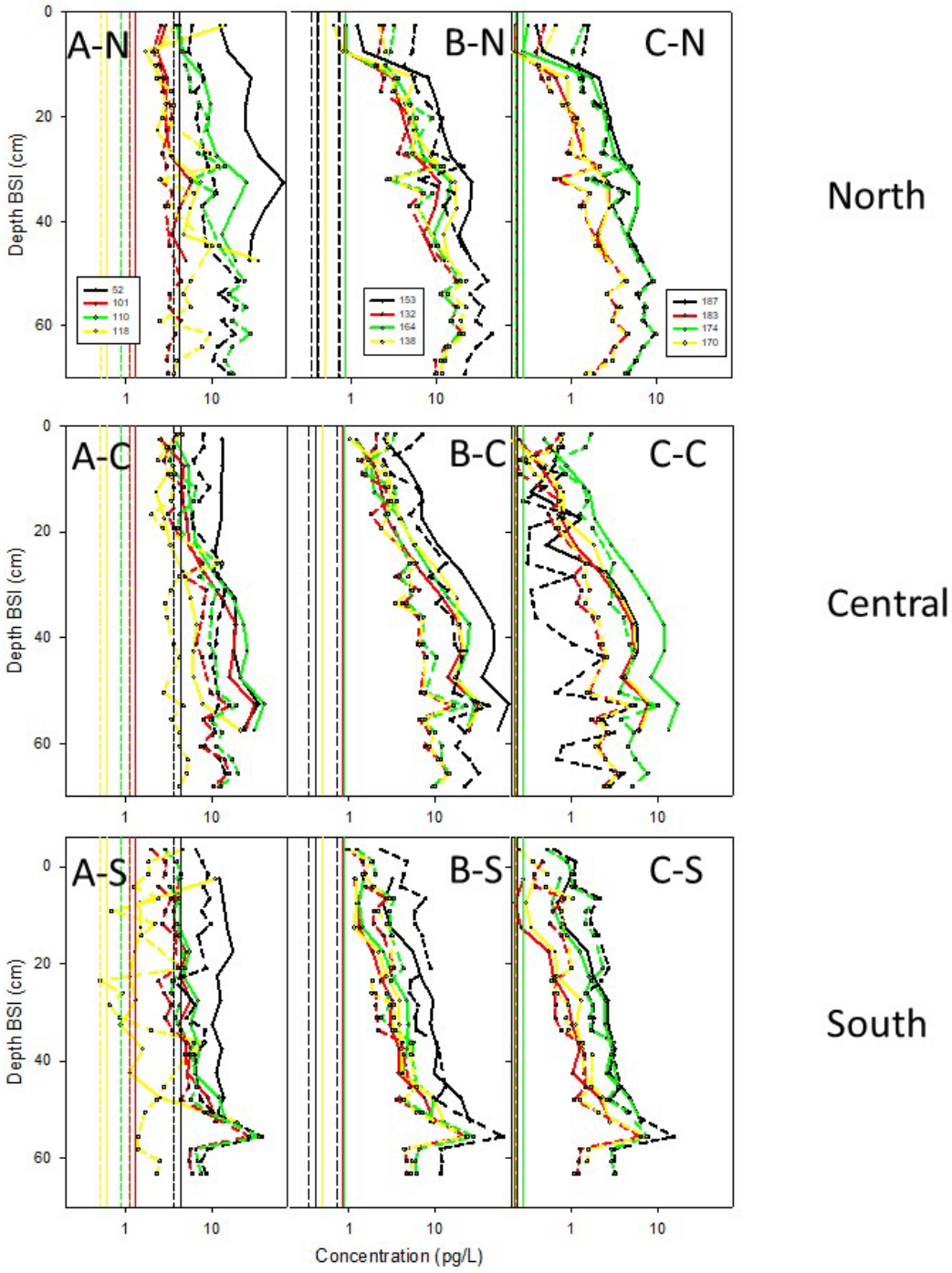


Figure 5.31. PCB Concentration Distribution with Depth for the Control Plot North, Central and South Sub-Locations

Figures A-N, C, S represent PCBs 52, 101, 110, and 118; figures B-N, C, S represent PCBS 153, 132, 164, and 138; and figures C-N, C, S represent PCBs 187, 183, 174, 170 with each individual PCB denoted by color in the legend of the topmost figure. Dashed lines represent the distribution produced by the sHRPP and solid lines represent the distribution produced by the T-Bar samplers.

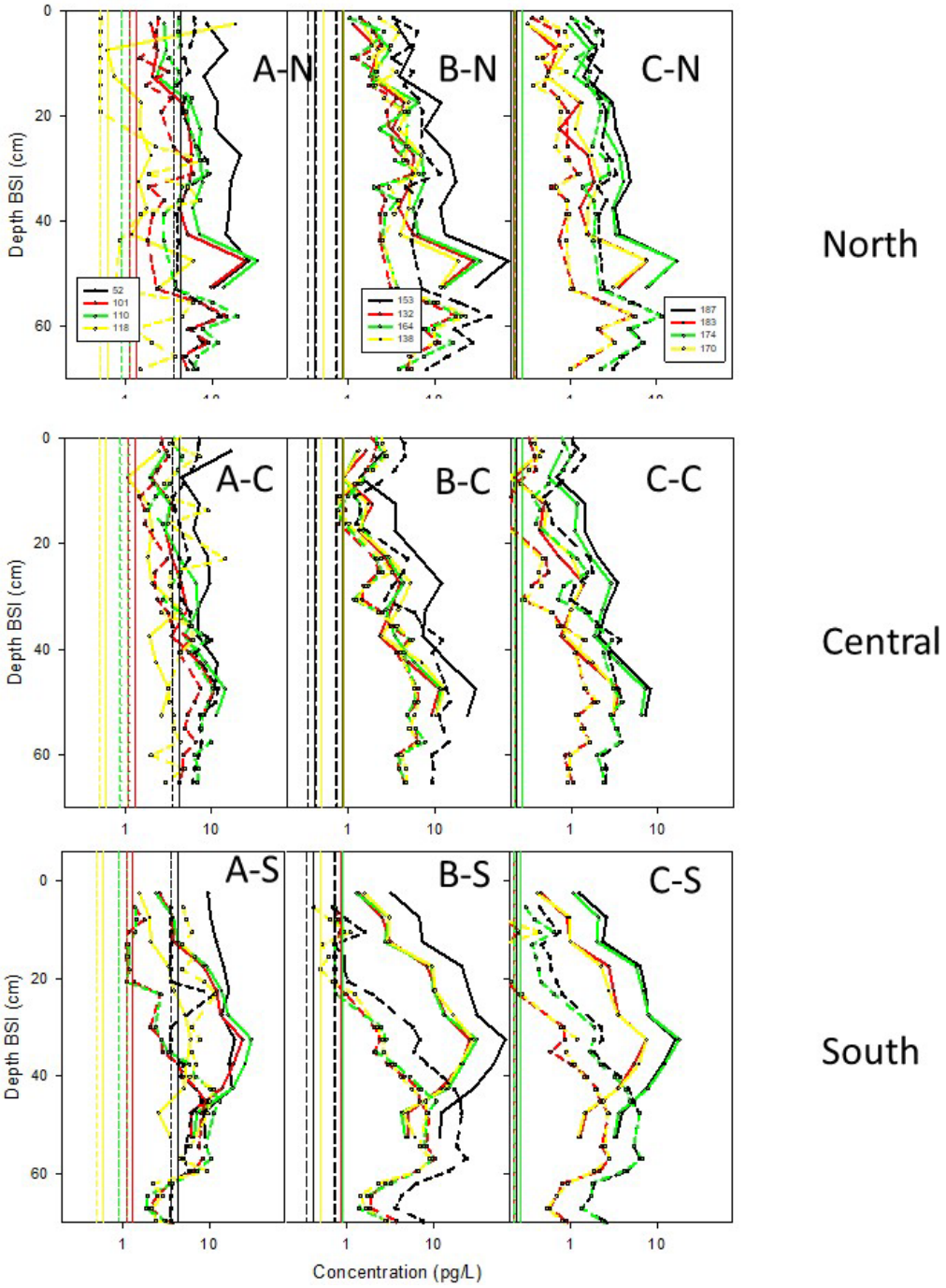


Figure 5.32. PCB Concentration Distribution with Depth for the Sedimite Plot North, Central and South Sub-Locations

Figures A-N, C, S represent PCBs 52, 101, 110, and 118; figures B-N, C, S represent PCBS 153, 132, 164, and 138; and figures C-N, C, S represent PCBs 187, 183, 174, 170 with each individual PCB denoted by color in the legend of the topmost figure. Dashed lines represent the distribution produced by the sHRPP and solid lines represent the distribution produced by the T-Bar samplers.

In the Sedimite + Bioaugmentation treatment plot, distributions varied between replicate locations (Figure 5.33). In the north location, with a few exceptions (PCB 52 and 118), concentrations were similar at depths above 20 cm. PCB concentrations measured by the sHRPP then increase down to depths of ~30cm BSI, remain constant until depths of ~60cm, and decreased at depths >60cm. However, T-Bar concentrations decreased dramatically starting ~20 cm BSI to a minimum at ~30cm BSI and then increased rapidly back to concentrations similar to those measured by the sHRPP at a depth of ~40cm BSI. The large dip in concentrations at depths between 20 and 40 cm are not likely due to an analytical error as they include multiple data points but could be due to a sampling artifact such as the T-Bar sampler not being in good contact with the sediment or even some anomaly in the sediment at that location. The distribution profiles for the Central and South replicate locations also have substantial differences between the North location as well as between samplers. The T-Bar PCB distribution for the Central location has a peak near the surface and steadily declines with depth, which is different than almost all other locations. The PCB sHRPP distribution is more typical with low concentrations near the interface that increase to a peak at lower depths and then remain fairly constant. For the South replicate, the T-Bar concentration distribution also exhibits a peak near the sediment interface but does increase at lower depths. Excluding the shallowest T-Bar depth, concentration profiles would be very similar between samplers down to a depth of ~40cm. Overall, sHRPP PCB concentration profiles were very similar for all three replicate locations, while there was a substantial variation in T-Bar profiles. While some differences certainly exist between T-Bar and sHRPP predicted concentration profiles, taking into account potential depth off-sets, the samplers predicted reasonably similar concentration profiles.

As a second method to compare samplers, 4 locations (Sedimite N, C, and S and Sedimite + Bioaugmentation N) with T-Bar fss values similar to sHRPP and above 0.1 (10% equilibrium), were compared by correcting concentrations to each sampler's (T-Bar and sHRPP) PRC fss values. In order to simplify the discussion, all PCBs that co-varied (excludes 52 and 118) were summed as they have near identical distributions with depth. Concentration distributions based on T-Bar fibers were similar regardless of which fss values (sHRPP or T-Bar) were used to correct (Figure 5.34) Observations comparing T-Bar and sHRPP concentration distributions are therefore unchanged from the discussion above.

Finally, to allow more quantitative comparisons between T-Bar and sHRPP distributions, we calculated average depth distributions for each treatment. This was accomplished by combining all PCB concentrations for a given congener over a depth range for all replicate locations. The depth range was broken into 15 cm intervals. The data is displayed as box and whisker plots in order to allow visual examination of the data variation (Figures 5.35 through 5.38). In addition, we plot the ex situ predicted concentrations which represent depth ranges of 8 to 15 cm and are displayed at the mid-point of the sampled depth.

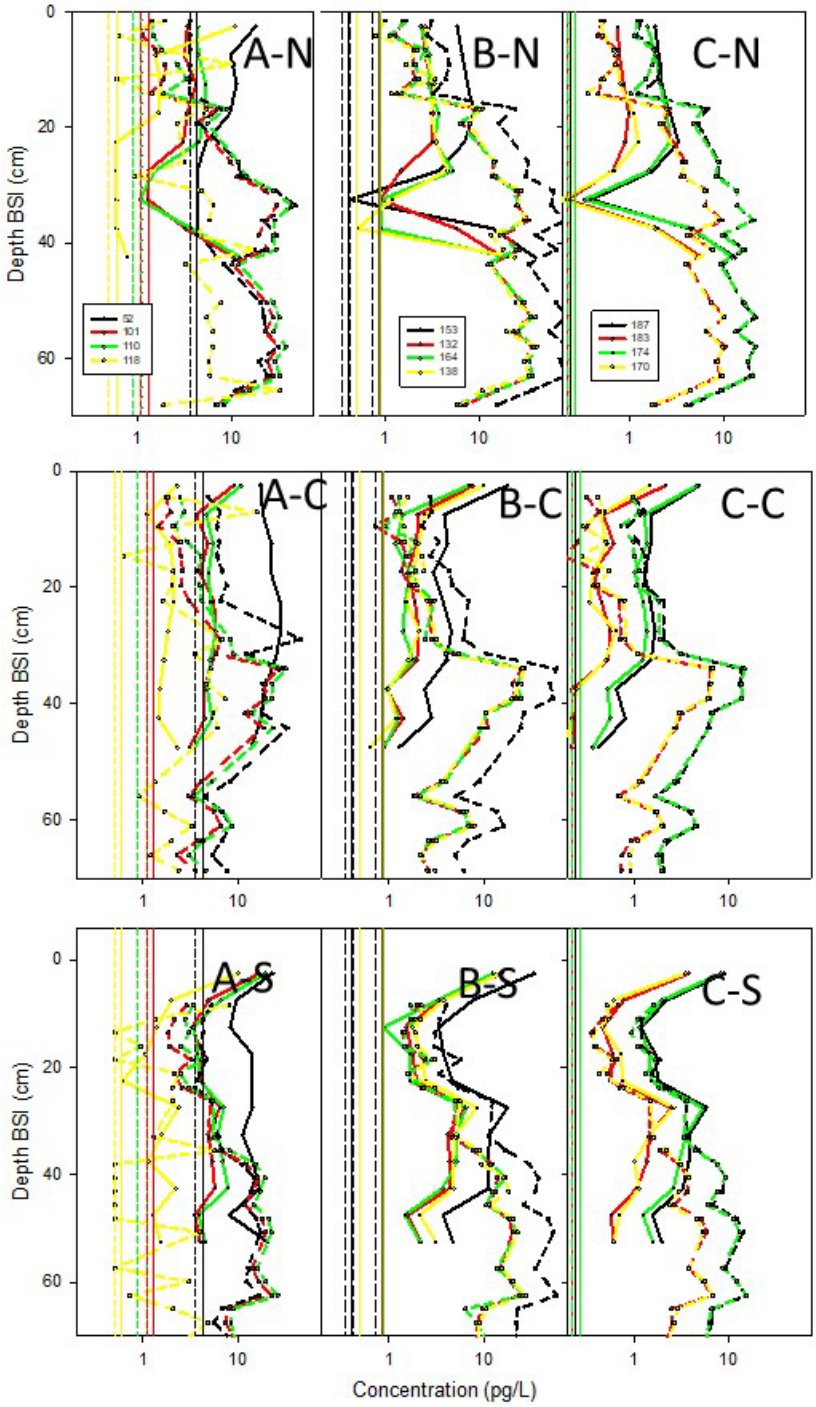


Figure 5.33. PCB Concentration Distribution with Depth for the Bioaugmentation+Sedimite North, Central and South Sub-Locations

Figures A-N, C, S represent PCBs 52, 101, 110, and 118; figures B-N, C, S represent PCBS 153, 132, 164, and 138; and figures C-N, C, S represent PCBs 187, 183, 174, 170 with each individual PCB denoted by color in the legend of the topmost figure. Dashed lines represent the distribution produced by the sHRPP and solid lines represent the distribution produced by the T-Bar samplers.

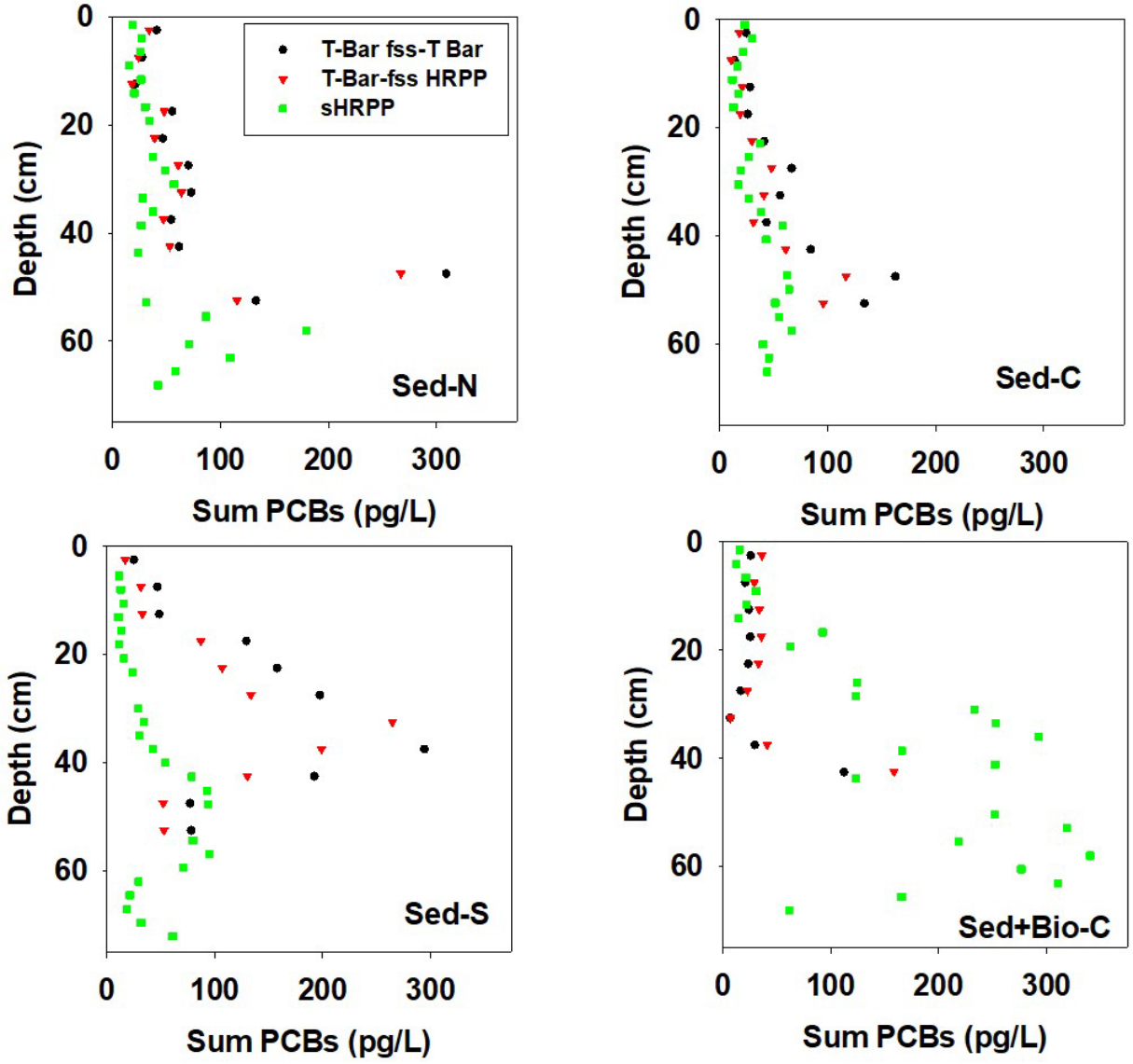


Figure 5.34. Depth Distribution of the Sum of PCBs (excluding 52 and 118) for T-Bar Samplers

Depth Distribution of the Sum of PCBs (excluding 52 and 118) for T-Bar samplers with concentrations corrected for steady state using the fss values for the T-Bar sampler from that location (black symbol), the fss value from all sHRPP (red symbol), or the concentrations from sHRPP (green symbol).

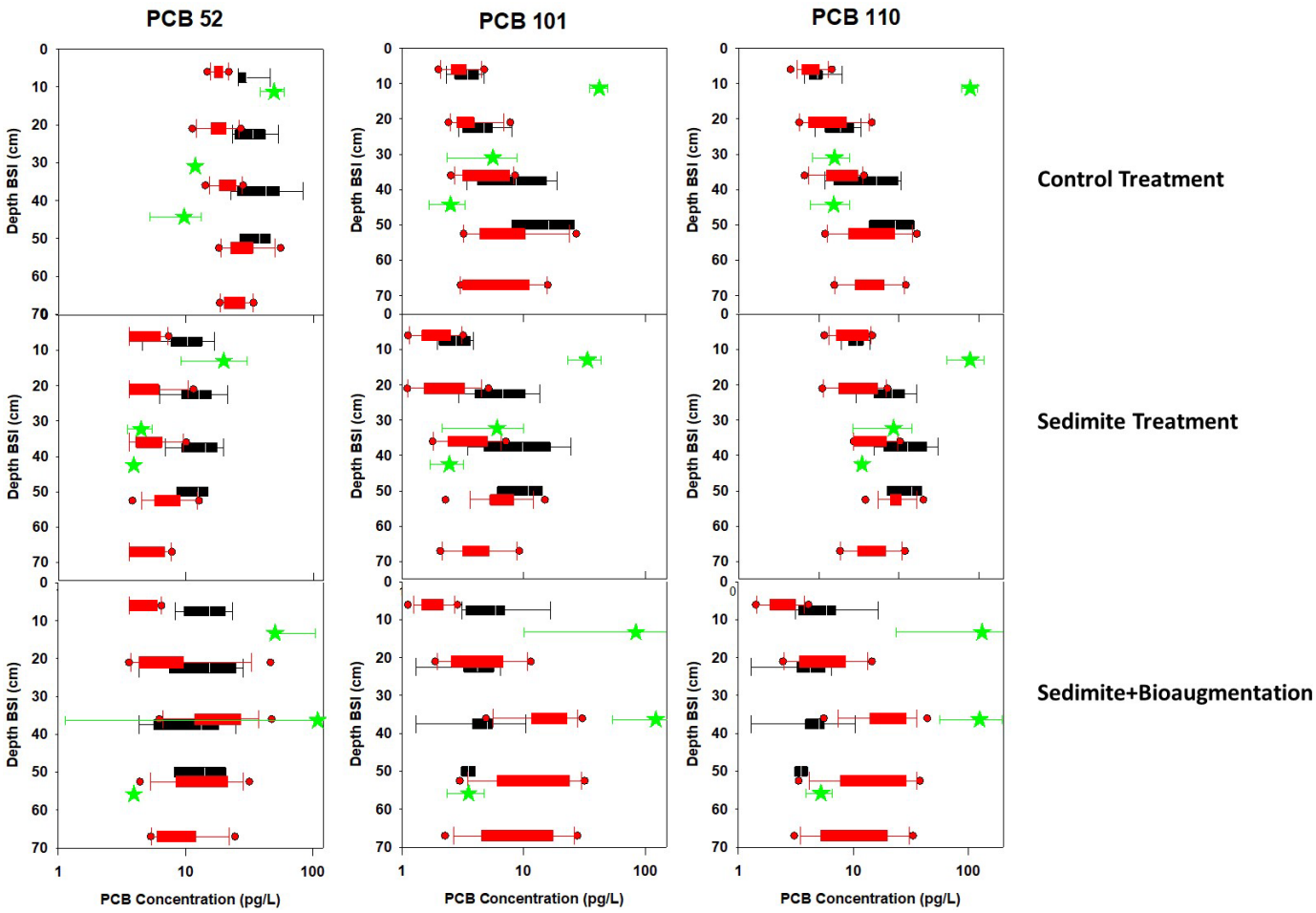


Figure 5.35. PCBs (52, 101, 110) Concentration Distributions with Depth over Defined Depth Intervals

The top, middle, and lower rows of figures represent the Control, Sedimite, and Sedimite+Bioaugmentation treatments. In each figure the red box plots represent the PCB concentrations based on sHRPP, the black box plots represent the PCB distribution based on T-Bar samplers, and the green star ex situ measurements. Box plots represent all concentrations within the depth range for all replicate locations within the given treatment. Depth ranges for sHRPP and T-Bar samplers were 0-15, 15-30, 30-45, 45-60, and >60 cm BSI. Ex situ measurements represent more variable depth intervals (8 to 20cm) but are plotted at the mid-point of the sampled interval.

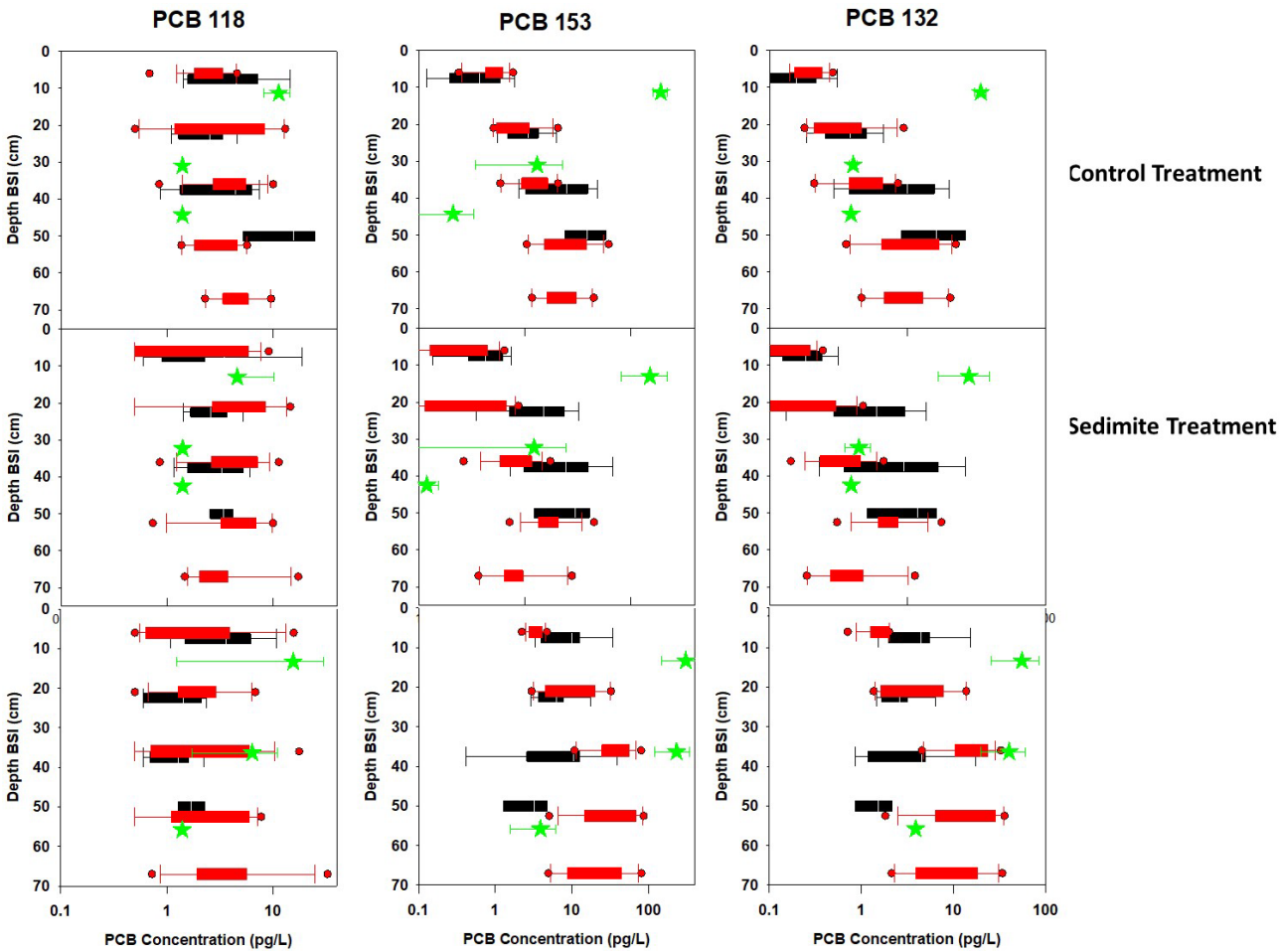


Figure 5.36. PCBs (118, 153, 132) Concentration Distributions with Depth over Defined Depth Intervals

The top, middle, and lower rows of figures represent the Control, Sedimite, and Sedimite+Bioaugmentation treatments. In each figure the red box plots represent the PCB concentrations based on sHRPP, the black box plots represent the PCB distribution based on T-Bar samplers, and the green star ex situ measurements. Box plots represent all concentrations within the depth range for all replicate locations within the given treatment. Depth ranges for sHRPP and T-Bar samplers were 0-15, 15-30, 30-45, 45-60, and >60 cm BSI. Ex situ measurements represent more variable depth intervals (8 to 20cm) but are plotted at the mid-point of the sampled interval.

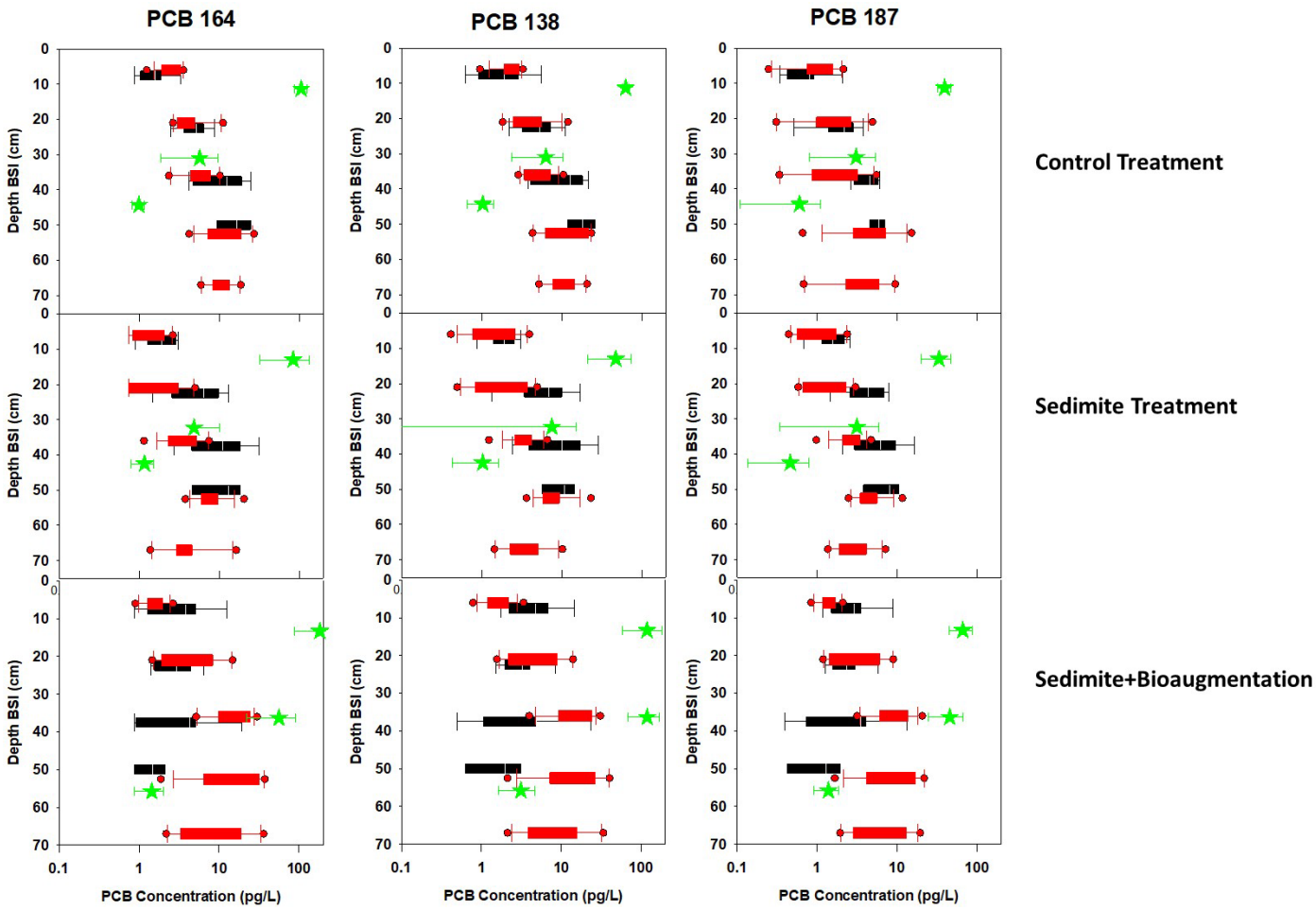


Figure 5.37. PCBs (164, 138, 187) Concentration Distributions with Depth over Defined Depth Intervals

The top, middle, and lower rows of figures represent the Control, Sedimite, and Sedimite+Bioaugmentation treatments. In each figure the red box plots represent the PCB concentrations based on sHRPP, the black box plots represent the PCB distribution based on T-Bar samplers, and the green star ex situ measurements. Box plots represent all concentrations within the depth range for all replicate locations within the given treatment. Depth ranges for sHRPP and T-Bar samplers were 0-15, 15-30, 30-45, 45-60, and >60 cm BSI. Ex situ measurements represent more variable depth intervals (8 to 20cm) but are plotted at the mid-point of the sampled interval.

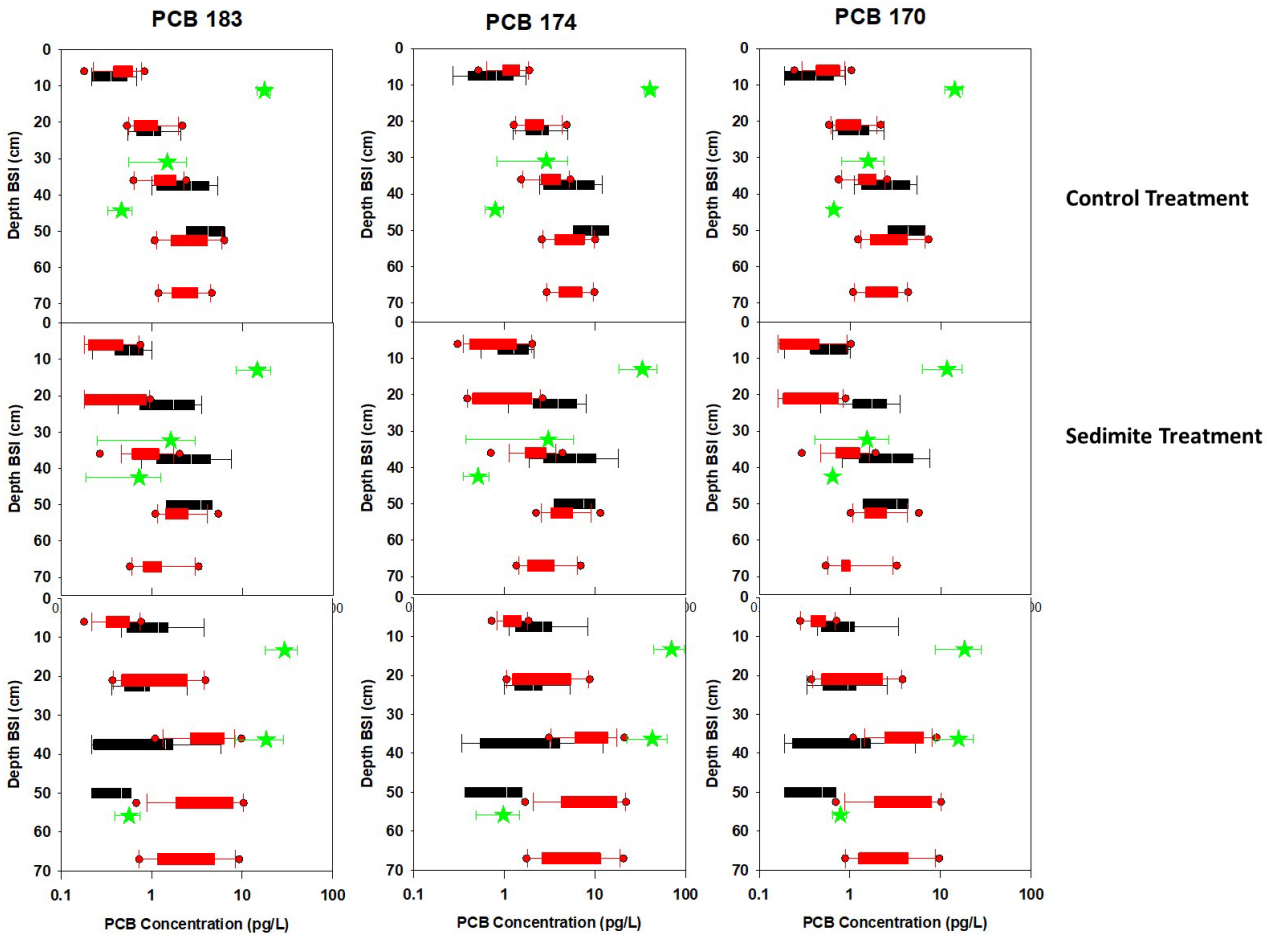


Figure 5.38. PCBs (183, 174, 170) Concentration Distributions with Depth over Defined Depth Intervals

The top, middle, and lower rows of figures represent the Control, Sedimite, and Sedimite+Bioaugmentation treatments. In each figure the red box plots represent the PCB concentrations based on sHRPP, the black box plots represent the PCB distribution based on T-Bar samplers, and the green star ex situ measurements. Box plots represent all concentrations within the depth range for all replicate locations within the given treatment. Depth ranges for sHRPP and T-Bar samplers were 0-15, 15-30, 30-45, 45-60, and >60 cm BSI. Ex situ measurements represent more variable depth intervals (8 to 20cm) but are plotted at the mid-point of the sampled interval.

PCB concentration depth distributions produced by sHRPP are qualitatively similar for all locations and PCBs, except 52 and 118. Concentrations are lowest near the surface (0-20 cm BSI) and increase ~10X to maximum concentrations at depths 40-60 cm BSI, with small decreases below 60cm. This is somewhat in contrast to T-Bar sample results for which the PCB distribution was qualitatively similar for the Control and Sedimite treatments but different for the Sedimite+Bioaugmentation treatment. For the control and Sedimite treatments, the T-Bar PCB distribution was very similar to the sHRPP not only qualitatively but in magnitude as well, with concentration range substantially overlapping (Figure 5.39). The only consistent exception to this observation, was for the 15-30 cm depth range for the sedimite plot, where the T-Bar concentration range was consistently higher than the sHRPP. The T-Bar concentration distribution in the Sedimite+Bioaugmentation treatment was unique. Concentrations decreased with depth contrary to all other locations. PCB concentrations down to 30 cm were very similar between samplers, but below 30 cm the T-Bar concentrations were substantially lower.

Ex situ PCB porewater concentration profiles did not match in situ profiles mainly due to the high concentrations of PCBs in the near surface. Ex situ concentrations were all highest in the shallowest increment. For the Control and Sedimite treatments concentrations consistently decreased with depth. For the Sedimite+Bioaugmentation treatment, concentrations were generally similar for the upper two increments (0-20 cm and 20-40 cm) but decreased by an order of magnitude at the lowest depth increment (50-60 cm). Ex situ concentrations for the two lower depth increments were generally similar to in situ estimates but ex situ concentrations in the shallowest interval were 1-2 orders of magnitude higher than in situ estimates. This is most likely due to the impact of PCB loss to the bulk water in situ which maintains low concentrations. This impact is heightened by bioturbation which can produce low porewater concentrations in the upper 5-15 cm. Ex situ measurements do not incorporate any loss to the bulk water.

5.3.6.4 Site Interpretation Using Passive Samplers

Site evaluation of Abraham's Creek using the sHRPP indicates varying peak PCB concentrations at depths of 45 to 65 cm with rapidly decreasing concentrations at shallower and deeper depths. Between 0 and 20 cm concentrations were lowest and largely unvarying. To illustrate this, all covarying PCBs (excludes 52 and 118) were summed at each depth and all three replicate locations for each treatment displayed (Figure 5.39).

Using the T-Bar sampler, observations are somewhat similar with the exception of the Sedimite+Bioaugmentation plot which has no clear peak at depth and anomalously high concentrations at the surface. One of the objectives of the deployment at Abraham's Creek was to evaluate the impact of two treatments (Sedimite and Sedimite+ Bioaugmentation) previously applied. We compared the concentration of total PCBs in the top 15 cm of each treatment. PCB concentrations were marginally lower in the Sedimite and Sedimite+Bioaugmentation treatments compared to the control but substantially overlap (Figure 5.40). Average concentrations were ~18 pg/L in both the Sedimite and Sedimite+Bioaugmentation treatments and 25 pg/L in the control. Given the spatial variation there does not appear to be any practical impact of the Sedimite treatments. There also does not appear to be any remaining impact of the bioaugmentation conducted based on the similar microbial abundances in each treatment.

As part of our objective was to compare the difference in treatments using each sampling technique, we also performed a statistical analysis. Using a one-way Anova, the sHRPP data passed the normalcy test and there was a statistical difference between treatments (P=0.002). The control treatment was statistically lower in concentration compared to both the Sedimite (P=0.004) and Sedimite+Bioaugmentation (P=0.011) treatments but there was no difference between plots with Sedimite (P=0.782). The T-Bar data from the Sedimite+Bioaugmentation plot had a much larger range of values. As such, the normalcy test failed. Using a Kruskall-Wallis one-way analysis of variance by ranks, there was no difference in means (P=0.068) between treatments. In order to better compare the statistical power of each data set (sHRPP and T-Bar), only the Control and Sedimite treatment were compared using a T-test. Both the sHRPP and T-Bar data for those two treatments pass the normalcy test. Using the sHRPP data the concentrations of PCBs in the control plot were higher (P=0.001) than in the Sedimite plot, while using the T-Bar data set there was no statistical difference (P=0.803). It should be noted as both T-Bar and sHRPP use the same SPME technique. However, the sHRPP produces more samples per depth and more spatial integration per depth, reducing spatial variation.

The sHRPP provides additional advantages over the traditional in situ method. The resolution provided is 2x greater using the sHRPP. In addition, the sediment interface is much more clearly defined. Other advantages of the sHRPP include the evaluation of biogeochemistry which suggests the redox conditions are appropriate for dechlorination. The SHRPP also provides microbial abundances of PCB dechlorinating organisms which are present throughout the profile in all treatments. Finally, based on pore water velocity and Cl^- profiles there does not appear to be any substantial advective flux, limiting transport to diffusion and bioturbation alone.

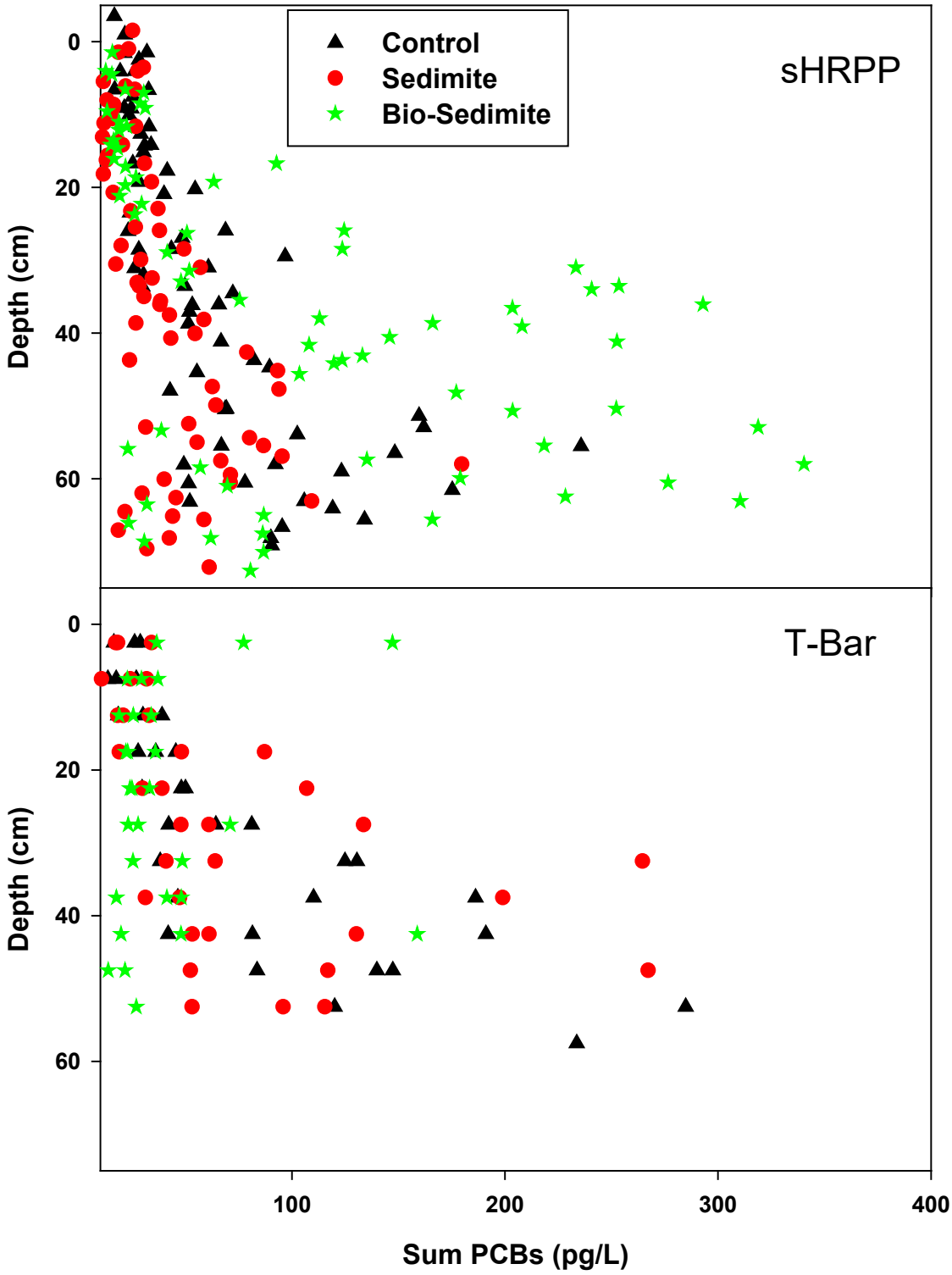


Figure 5.39. Sum of Covarying PCBs (excluding 52 and 118) at each Depth and All Three Replicate Locations for Each Treatment

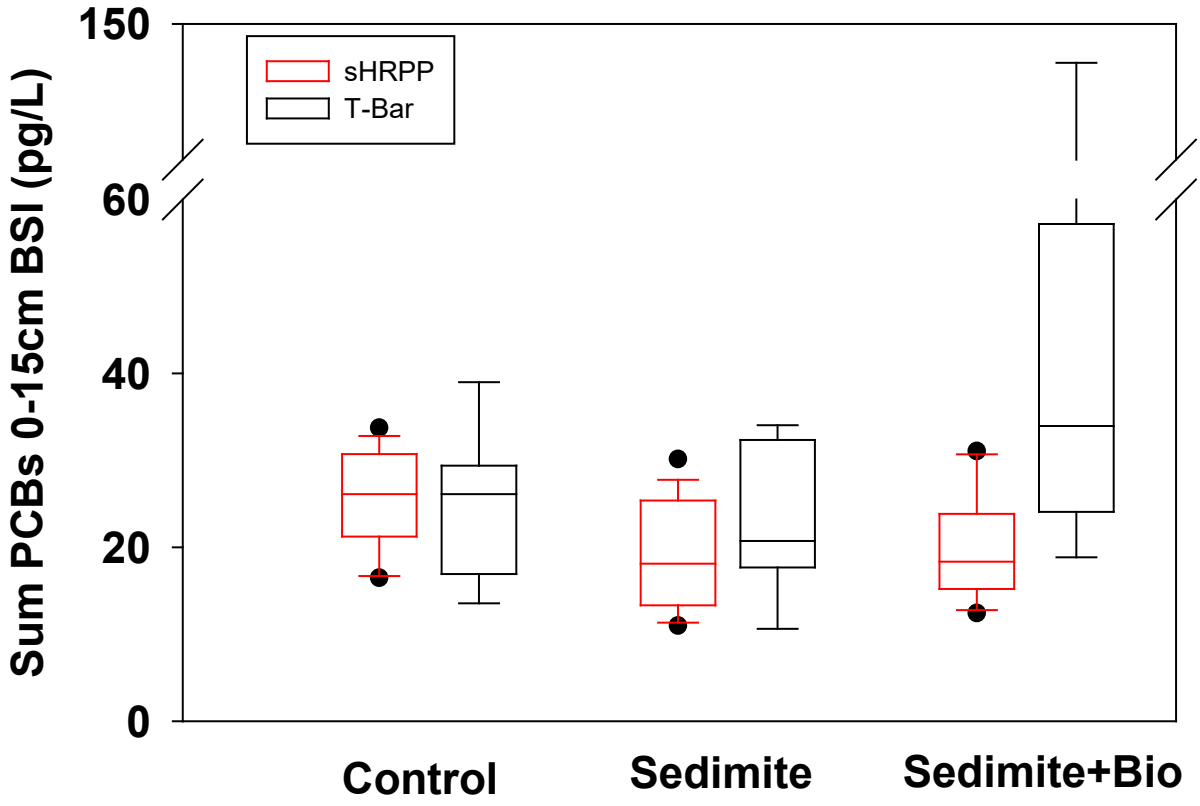


Figure 5.40. Total PCB Concentrations in the Top 15 cm of each Treatment

5.4 QUANTICO EMBAYMENT SITE TESTING

5.4.1 Conceptual Experimental Design

The Quantico Embayment (Site 99) was primarily chosen due to the presence of a thin layer cap below which lies sediment contaminated with DDX. The site is subject to tidal variations making it an ideal location to demonstrate the utility of the sHRPP for monitoring cap performance and producing data of sufficient quality and resolution for modeling of long-term cap behavior and performance of thin layer capping/Enhanced Natural Monitored Recovery. There is also sufficient pre-capping and post capping data to serve as baselines. For this site our implementation goals were:

1. To demonstrate that the sHRPP can produce high resolution spatial concentration profiles of DDX with depth including evaluating recontamination of capped areas by surface deposition of contaminated sediments from uncapped areas.
2. To demonstrate that the sHRPP can measure the impact of dynamic daily bidirectional pore velocities caused by tidal fluctuations and/or their impact on cap breakthrough and groundwater/surface water fluxes and interaction.

3. To demonstrate the differences in cost and effort between traditional pore water sampling methods and the sHRPP, as well as the increased resolution, quality and reliability of sHRPP produced data.
4. To evaluate the increase in model resolution and confidence for the overall transport of DDX through thin layer caps to surface receptors using the sHRPP data compared to traditional methods.

The successful completion of these goals would demonstrate the ability of the sHRPP to provide data of sufficient resolution and breadth to predict cap performance including the exposure, risk, and attenuation of DDX over prolonged periods. Microbial community analysis was not included in this deployment.

5.4.2 Baseline Characterization

As the demonstrated technology is a site characterization tool, typical baseline characterization activities do not apply. However, as mentioned and discussed in the following subsections, there is sufficient pre-capping and post capping data to serve as baselines and an accepted traditional method of sediment characterization (in-situ passive sampling with SPME) was performed as part of the demonstration for comparison purposes.

5.4.3 Design and Layout of Technology Components

The demonstration at the Quantico Embayment was designed to compare pore water concentrations of DDX produced by analysis of the SPME fibers within the sHRPP with an accepted passive sampling method, ex-situ SPME analysis. We also used the sHRPP equilibrium cells to measure anions and general geochemical indicators (Cl^-, dissolved organic carbon (DOC), NO^{2-}, NO^{3-}, FeT, Fe^{+2}, SO_4^{-2}, and S^{-2}). As diffusion-based samplers are the accepted method for these species, we did not measure them by an alternate method.

We deployed twelve sHRPPs, four locations (9ft, 50ft, 100ft, and 140ft from shore), each with three sHRPPs, across the capped area along a transect from near shore to the edge of the cap (see Figure 5.41). For this site, we expected below cap sediment concentrations to vary based on previous sampling efforts. We chose to deploy the samplers over a transect to capture varying sediment concentrations and resulting pore water concentration profiles, deployment in varying water depths, impact of varying sand cap depths, and finally impact of tidal fluctuations. It should be noted that sediment concentrations and cap thickness can vary substantially even over small distances (<1 m). At each location where a sHRPP was deployed, we also obtained a 5 cm diameter direct push core within 0.3 m of the sHRPP. The cores were collected upon sHRPP retrieval to minimize disruption of the cap in the vicinity of the samplers. The cores were used to evaluate the depth of the depth of cap material and used for ex-situ SPME analysis.

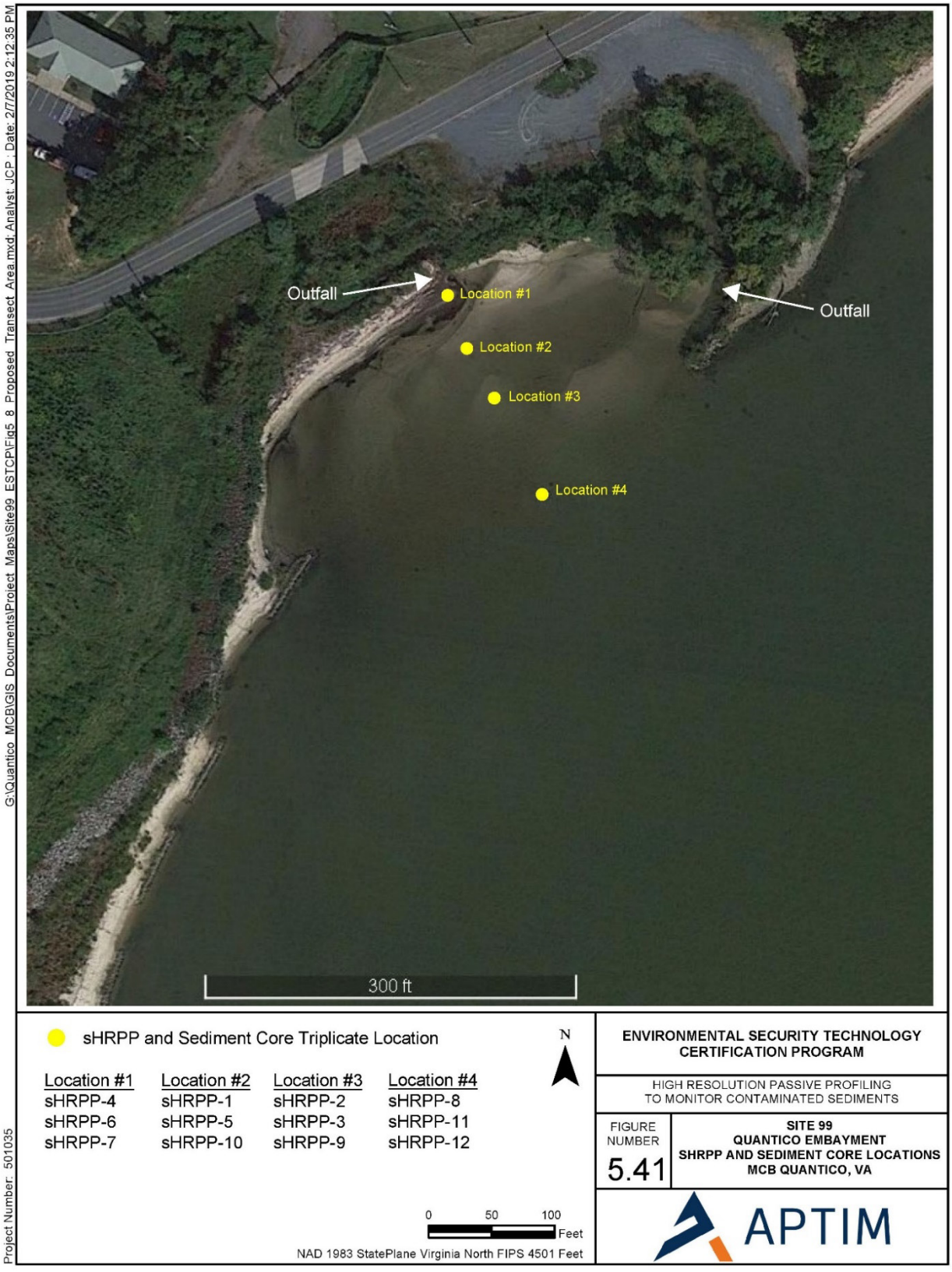


Figure 5.41. Quantico Embayment Demonstration Area

For this site, we anticipated this data set will allow us to do the following:

1. Generate data to compare the cost and time required for each method.
2. Compare each technique's ability to acquire depth dependent non-altered data sets.
3. Allow direct comparisons of spatial profiles of DDX for each method and associated variance in concentration with depth.
4. Generate high spatial resolution geochemical indicator profiles (see above).
5. Measure fluxes and average pore velocities produced by tidal fluctuations.
6. Compare model resolution and confidence for each method.

The transect location we chose (see Figure 5.41) starts near the shore (within 9ft) close to the Site 32 Pesticide Control Building and historical maximum sediment concentrations and extends southeast approximately 140 feet towards the cap perimeter and overall lower historic sediment concentrations. Figure 5.42 presents historic DDX concentrations in sediment, with the approximate location of the transect outlined in blue.

The samplers were driven into the cap and underlying sediments using a slide hammer. The samplers were deployed by wading from the shore and using a removable extension and were fitted with buoys to aid in retrieval. The top cells were positioned to remain in the bulk surface water 3-10 cm above the sediment surface to obtain time averaged bulk water concentrations.

5.4.4 Field Testing

As mentioned previously, field-testing the sHRPPs consisted of two mobilizations; the first to prepare and deploy the sHRPPs, and the second to retrieve and sample the sHRPPs, as well as advance/collect the sediment cores. All field activities were conducted in accordance with a site-specific APP/SSHP, to ensure a safe work environment during the demonstration. Prior to mobilization to the Site, APTIM worked with our POCs at MCB Quantico (Ms. Lyndsay Kelsey and Mr. Rodney Aguirre) to procure all required base work permits including a NAVFAC work request and base excavation permit. A utility mark-out dig ticket request was also made through Miss Utility VA811 prior to initiating intrusive activities at the site.

The sHRPP were prepared on shore and carried to the site for installation. The sHRPPs were prepared by submerging in distilled water spiked with NaBr (200 mg/l-Br). The nylon membrane (0.2µm pore size), stainless steel mesh (10µm pore size), and coarse mesh were secured with the cover plates and the sampler stored (~up to 12 hours) submerged until deployment. SPME fibers (~10cm) pre-equilibrated with PRCs are placed over select equilibration cells sandwiched between the stainless fin and coarse mesh and secured using a trace of silicone at the ends of each fiber. Water and additional SMPE fibers from the sHRPP preparation were subsampled to evaluate any pre-deployment contamination (see SOP in Appendix C). See Appendix E3 for photographs of pre-deployment sHRPP preparation (Photos 1-3).

As shown in Section 5.1, each of the samplers is designed to assess pore water over an approximately 1.0 m vertical interval. Table 5.7 presents the total number and types of samples that were collected within the transect of locations. One sHRPP was used as a control and was not deployed at the site.

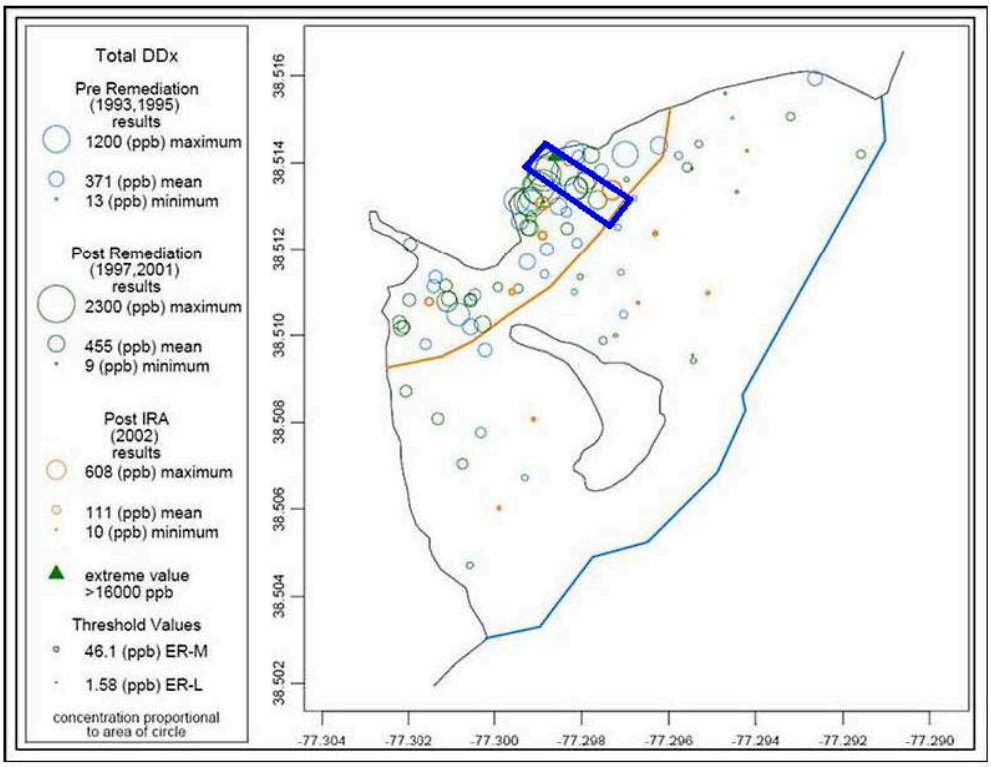


Figure 5.42. DDX Concentrations in Quantico Embayment Sediment

(NAVFAC, 2013) The orange line represents the boundary between the inner Quantico Embayment and the outer Quantico Embayment. The blue rectangle represents the location of the sampler transect.

Table 5.7. Total Number and Types of Samples Collected (Quantico Embayment)

Matrix	Number of sHRPPs / Samples per sHRPP	Total Number of Samples	Analyte	Location
Transect				
sHRPP SPME Fiber	6 / 48	288	DDX	sHRPP#1 through sHRPP#4, sHRPP#6, and sHRPP#7
sHRPP Pore Water	6 / 48	288	Anions	
	6 / 48	288	DOC	
	6 / 12	72	Pore Water Velocity	
in-situ SPME Sampling (T Bar)	6 / 12	72	DDX	
Control				
sHRPP SPME Fiber	1 / 6	6	DDX	Control sHRPP#5 (not deployed at site)
sHRPP Prep Water	1 / 6	6	Anions	
	1 / 6	6	DOC	
in-situ SPME Sampling (T Bar)	1 / 6	6	DDX	

To deploy the samplers, a rope was first attached to the hole machined into the top of the sampler. An extension rod was then positioned over the top of the sampler (not connected to the sampler), and the unit was driven into the cap/underlying sediment to the proper depth (as discussed in Section 5.4.3). The extension rod was then removed, and a marker buoy was attached to the tag end of the rope to assist in locating the sampler during retrieval. The samplers remained in the cap/sediment for approximately four weeks. See Appendix E3 for photographs of sHRPP deployment activities (Photos 4-9).

5.4.5 Sampling Methods

5.4.5.1 sHRPP Retrieval and Sampling

After approximately four weeks of equilibration, the samplers were removed by hand pulling and a breaker bar for leverage. The samplers were transported by small boat to shore where a large, high-roof cargo van was outfitted with tables to aid in the sampling process (See Appendix E3 for photographs of sHRPP retrieval and sampling activities (Photos 10-18)). The equilibration cells and velocity cells were sampled first. A pre-cleaned glass syringe with 18-gauge needle was inserted through the membrane and water removed by suction. A second needle was placed through the membrane to relieve any vacuum and prevent any outside water from being pulled through the membrane. Water from each cell was placed in an appropriate container, as summarized in Table 5.8, for analysis of anions (Cl^-, NO_2^-, NO_3^-, SO_4^{-2}), and DOC. The remaining solution (in equilibrium cells) was used for on-site testing (Fe^{+2}, FeT, total sulfide) using field test kits (Hach Methods).

After the equilibration cells were sampled, the velocity cells were sampled in a similar manner with the total volume of each cell placed in a separate glass vial for Br- analysis. SPME fibers were retrieved by removing the top cover plate and pulling off the protective nylon mesh while retrieving the fibers with tweezers as each cell is uncovered. The SPME fibers were gently rinsed in DI water and placed in vials prefilled with solvent, which was then used for DDX analysis.

Table 5.8. Sample Analytical Methods, Volume, Preservation, and Containers

Analyte	Method/ Laboratory	Sample Volume	Preservative	Bottle
DDX	EPA 8081A Texas Tech	SPME	4°C	5 mL glass vial w/ hexane (x1)
DOC	EPA 415.3 Texas Tech	9 mL	4°C with H_2SO_4	5 mL glass vial (x1)
Anions (Br^-, NO_2^-, NO_3^-, SO_4^{-2})	EPA 300.0 Texas Tech	2 mL	4°C	5 mL glass vial (x1)
On-Site Testing (Fe^{+2}, FeT, total sulfide)	Hach 8133 and 8146 Field Test Kits	3 mL	On Site Only	5 mL glass vial (x1) or direct analysis

5.4.5.2 Sediment Core Collection

During sampler retrieval, we also collected soil cores using a 5-cm diameter direct push-coring device (Multi-Stage Sludge/Sediment Sampler, manufactured by AMS, Inc.). The cores were advanced by hand or driven into the sediment using a slide hammer to a depth of approximately 0.8 m.

The soil sampler's "valved core tip" fills the sampler without losing the sample upon retrieval. The sampler uses a disposable plastic soil catcher that fits on the end of a 5 x 30 cm plastic liner. The core tip allows the plastic soil core catcher and liner to fit snuggly over the lip of the core tip. Once the soil core catcher and liner are placed on the core tip, they are loaded into a stainless steel multi-stage base section and screwed together. During deployment, the flap cap opens and allows excess air and water to escape through the top of the sampler, eliminating pressure buildup. The sediment enters and fills the liner. When the sampler is lifted, the flap closes and creates suction to assist the soil core catcher in retaining the sample. The top of the core is then capped and sealed, and the core removed from the multi-stage base section. The bottom of the core is then capped and sealed.

Three 30-cm base sections were threaded together and used to try to acquire a 0.9 m long soil core at each sHRPP location, spaced (~ 0.3 m) from the sHRPP. Each sealed core was shipped on ice in a cooler to Texas Tech, where the cores were carefully opened, visually inspected, photographed, and logged. The logging focused on identifying the type and thickness of sediment above the cap, the characteristics and thickness of the cap, and the type and thickness of the sediment below the cap. Cores were sectioned either into 3 sections, (top, middle, and bottom) or based on texture analysis. Homogenized subsamples were used to evaluate TOC and perform ex-situ DDX evaluation.

5.4.6 Sampling Results

Results are presented for each HRPP location within the transect shown on Figure 5.41, followed by an overall site evaluation. Laboratory analytical results are tabulated in Appendix F3.

5.4.6.1 Location #1 (9 ft from shore)

5.4.6.1.1 Transport Indicators

The 9ft location is located adjacent to shore and adjacent to an outfall presumed to be from the wastewater treatment plant. During high tide the water level covered the top HRPP cells, but at low tide the water level was below the sediment surface (Figure 5.43). It should also be noted that at the 9ft location, sediment appeared to be stable over the 28 day deployment, but the outfall had a substantial change in course over the 28 days, cutting through a sand bar and impacting the 50ft site, as discussed in Section 5.4.6.2.

HRPP equilibrium cells were completely equilibrated (~95%) for the central and north locations. For the south locations cells above 45cm BSI were >95% equilibrated with those below >85% (Figure 5.44). The high equilibrium values are consistent with pore velocities. Pore velocities varied between replicate locations and with depth. For the south and central locations, velocities decreased from >100 cm/d above the sediment interface to ~ 15 to 20 cm/d down to 45cm BSI. Below 45cm, the central location velocity remained high, and the south location decreased to <5cm/d. The north location was variable with low velocities at upper depths and higher at the lowest depth. Some variation in velocities may be due to the variation in sediment type between the replicate locations. Based on core data, the sediment for the central location with uniformly elevated velocities, was primarily coarse sand with some organic matter in the upper and lower sections. Pictures of sediment core material are presented in Figure 5.45. The south and north cores had more fine-grained composition (silty sand and silty clay) at lower depths. However, due to the poor core recovery (<60%), depths are difficult to corelate to HRPP depths.

Overall, the pore velocities are consistent with the large tidal fluctuations which would cause bank drainage in the upper sediment and proximity to the outfall potentially allowing for subsurface flow.

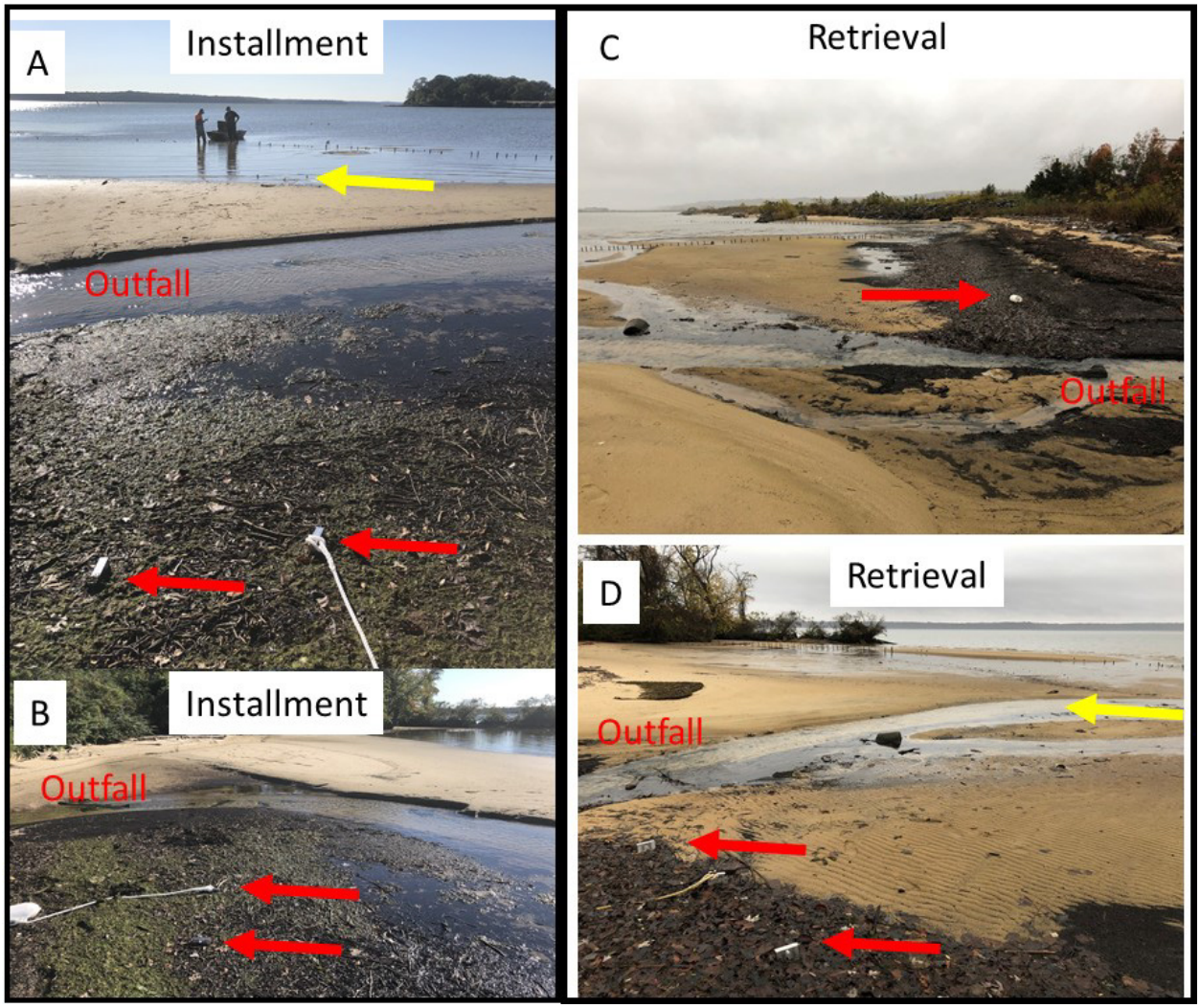


Figure 5.43. Location #1 (9 ft location) Photos

A) and B) are pictures of the 9ft location (Location #1) during installation at high tide and C) and D) are pictures after 28days of deployment at low tide. Red arrows denote location of HRPP (not all shown). Yellow arrows show the location of the 50ft location (Location #2).

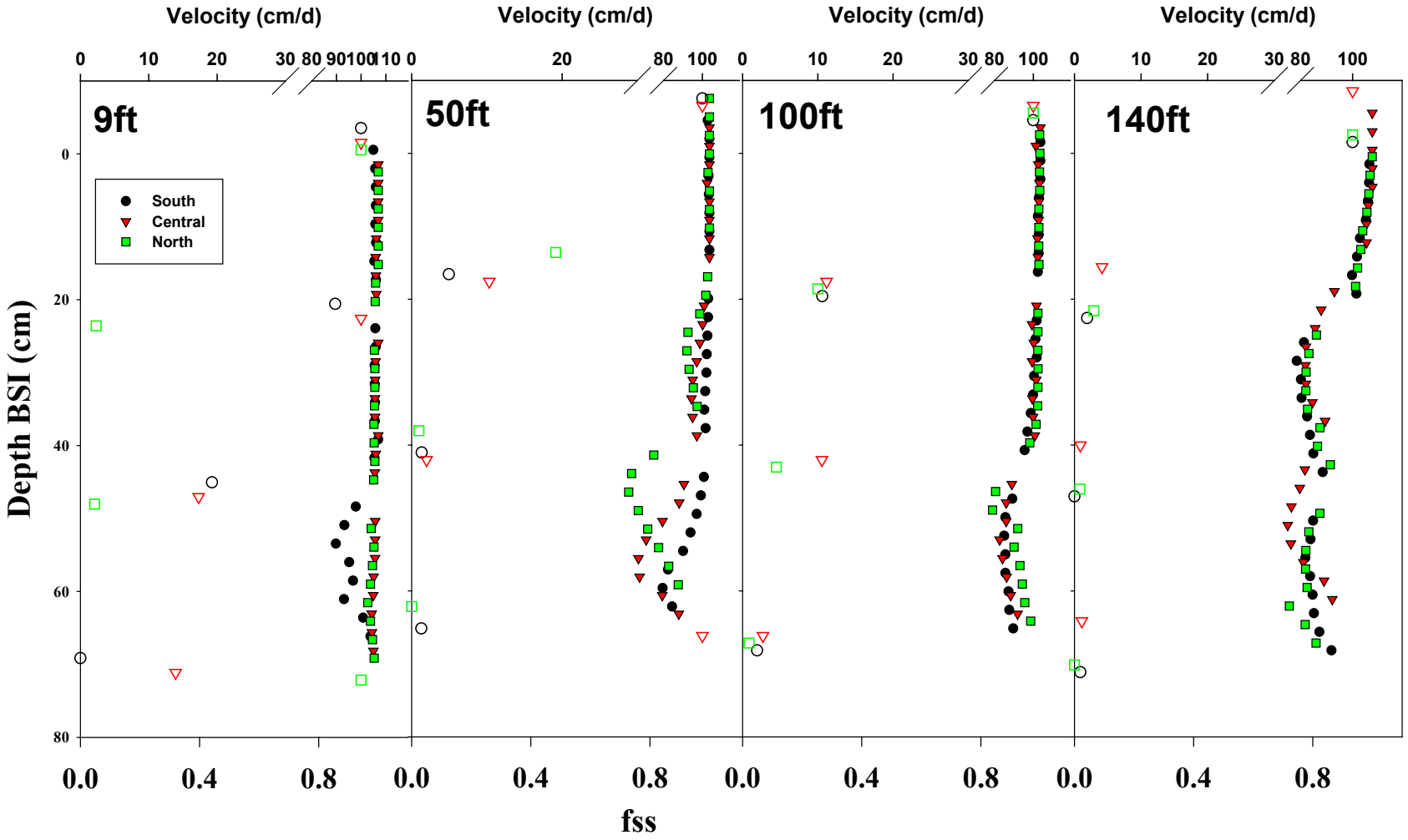


Figure 5.44. Estimated Pore Velocities and Equilibrium Cell Fraction of Steady State

Estimated pore velocities (open symbols) and equilibrium cell fraction of steady state (closed symbols) for each transect sample location.

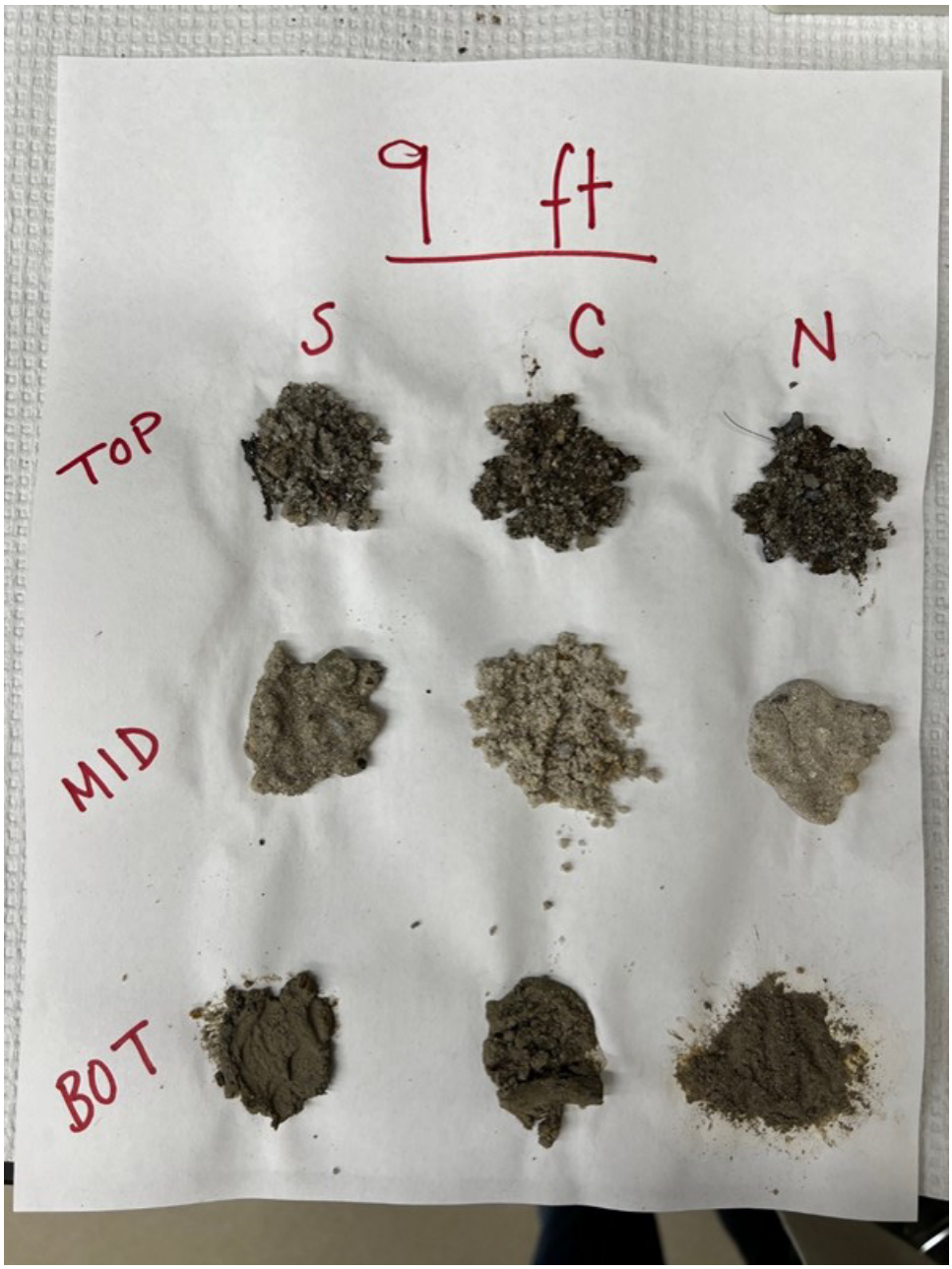


Figure 5.45. Photos of Sediment from 9ft location (Location #1)

Chloride profiles are consistent between the 3 replicate locations (see Figure 5.46). Chloride concentrations in surface water and sediment (~70 mg/l) increase to concentrations of 300-400 mg/l at a depth of ~30- 35 cm and then decrease to 70-100 mg/l at the lowest depths. These profiles suggest that a separate source(s) of water impacts the middle depths. One possibility is that the middle depths are impacted by the outfall due to subsurface flow. Higher chloride concentrations would be consistent with wastewater effluent.

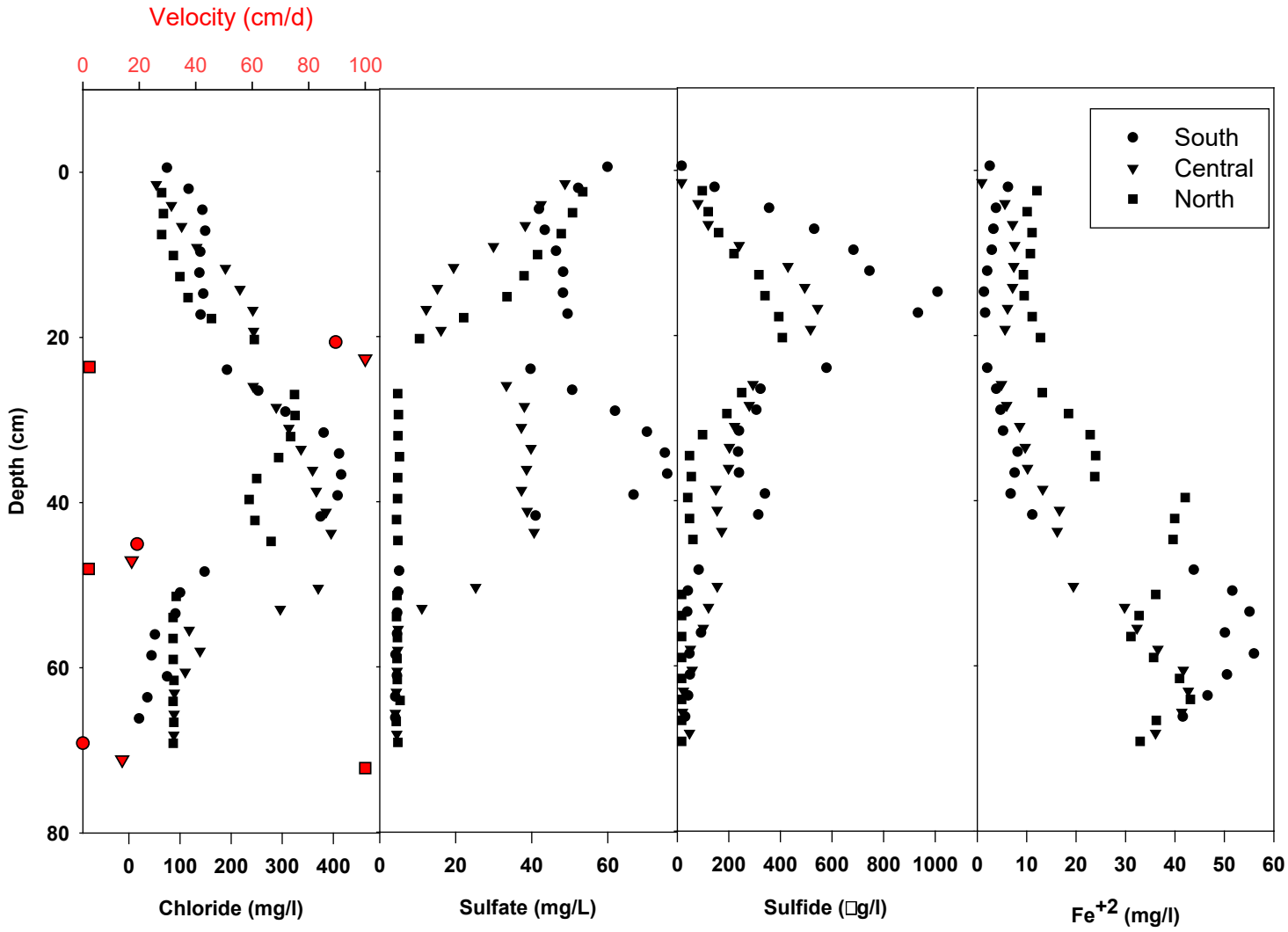


Figure 5.46. Concentration Depth Profiles at 9ft Location (Location #1)

Concentration depth profiles of chloride, sulfate, sulfide, and iron (II) and pore velocity with depth at 9 ft location for the south, central and north HRPP.

5.4.6.1.2 Geochemical Indicators

Sulfate concentrations decrease and sulfide concentrations increase from the surface to ~20cm BSI (Figure 5.46). From 20 cm to 50 cm sulfate concentrations in the central and south locations increase, similar to chloride and then decrease to <2.5 mg/l at lower depths. The north location sulfate concentrations do not increase below 20cm. This could be consistent with the very low velocities measured at this location, which would reduce sulfate supply and promote sulfate reduction. Sulfide concentrations at depths below 20 cm decrease likely due to the rapid increase of Fe^{+2} concentrations (up to 60 mg/l) at depths below 20 cm, which would complex with free sulfide. Overall, the sediments appear to rapidly transition to reducing conditions below the sediment water interface with iron and sulfate reducing conditions dominating.

5.4.6.2 Location #2 (50 ft from shore)

5.4.6.2.1 Transport Indicators

The 50ft location is located ~50 ft from the shoreline. At installation during high tide the water level covered the top HRPP cells but at low tide the water level was below the sediment surface (Figure 5.47). The HRPP when installed were in a sand bar located between the wastewater outfall and stormwater outfall (Figure Site 9ft and Figure 5.8). During the deployment, the wastewater outfall flow cut through the sand bar resulting in the removal of 4-8cm of sand/sediment and exposed the top 2-3 equilibrium cells at low tide.

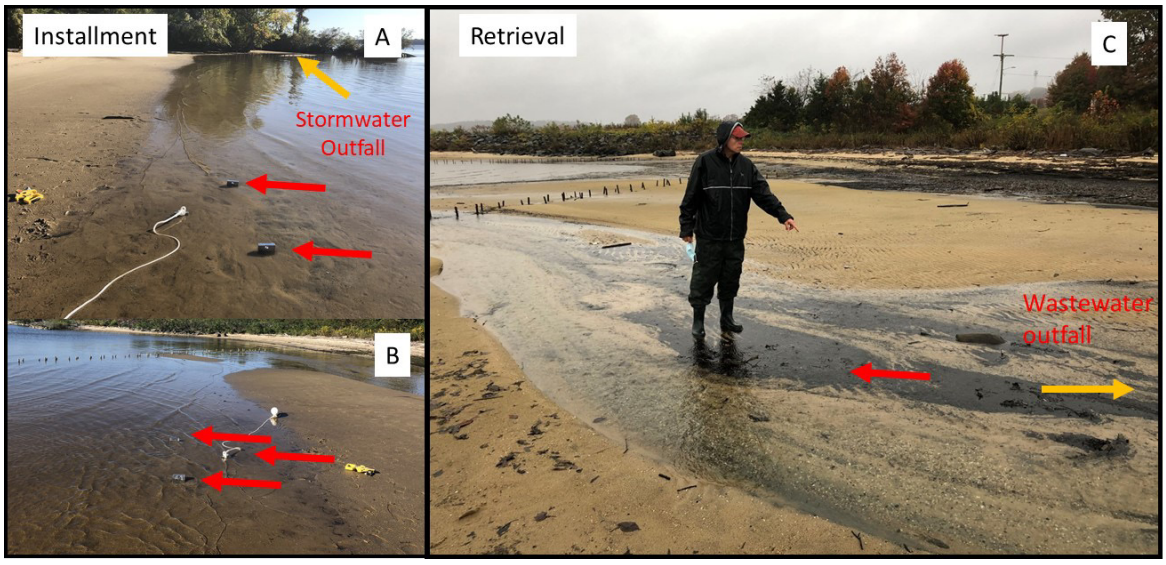


Figure 5.47. Location #2 (50 ft location) Photos

A) and B) are pictures of the 50ft location (Location #2) during installation at mid tide and C) is a picture after 28days of deployment at low tide. Red arrows denote location of HRPP. Orange arrows show location of stormwater outfall and wastewater outfall. Flowing water is the wastewater outfall.

HRPP equilibrium cells were completely equilibrated (95%) to a depth of 40 cm BSI (Figure 5.44). Below this equilibrium ranged from 70 to 100%. The high equilibrium values in the upper depths are consistent with pore velocities. Pore velocities decreased from >100 cm/d above the sediment interface to ~ 5 to 20 cm/d at 18 cm BSI. Below 18 cm, the velocity decreased to <5 cm/d.

Based on core data, all locations were dominated by coarse sand above ~ 40 cm, with increasing finer grained material, (silt and clay) below that depth. Pictures of sediment material are presented in Figure 5.48. Due to the poor core recovery (<60%), depths are difficult to corelate to HRPP depths. Overall, the pore velocities are consistent with the large tidal fluctuations which would cause bank drainage in the upper sediment and proximity to the outfall potentially allowing for subsurface flow. Lower velocities at the deepest depths are also consistent with fine grained material.

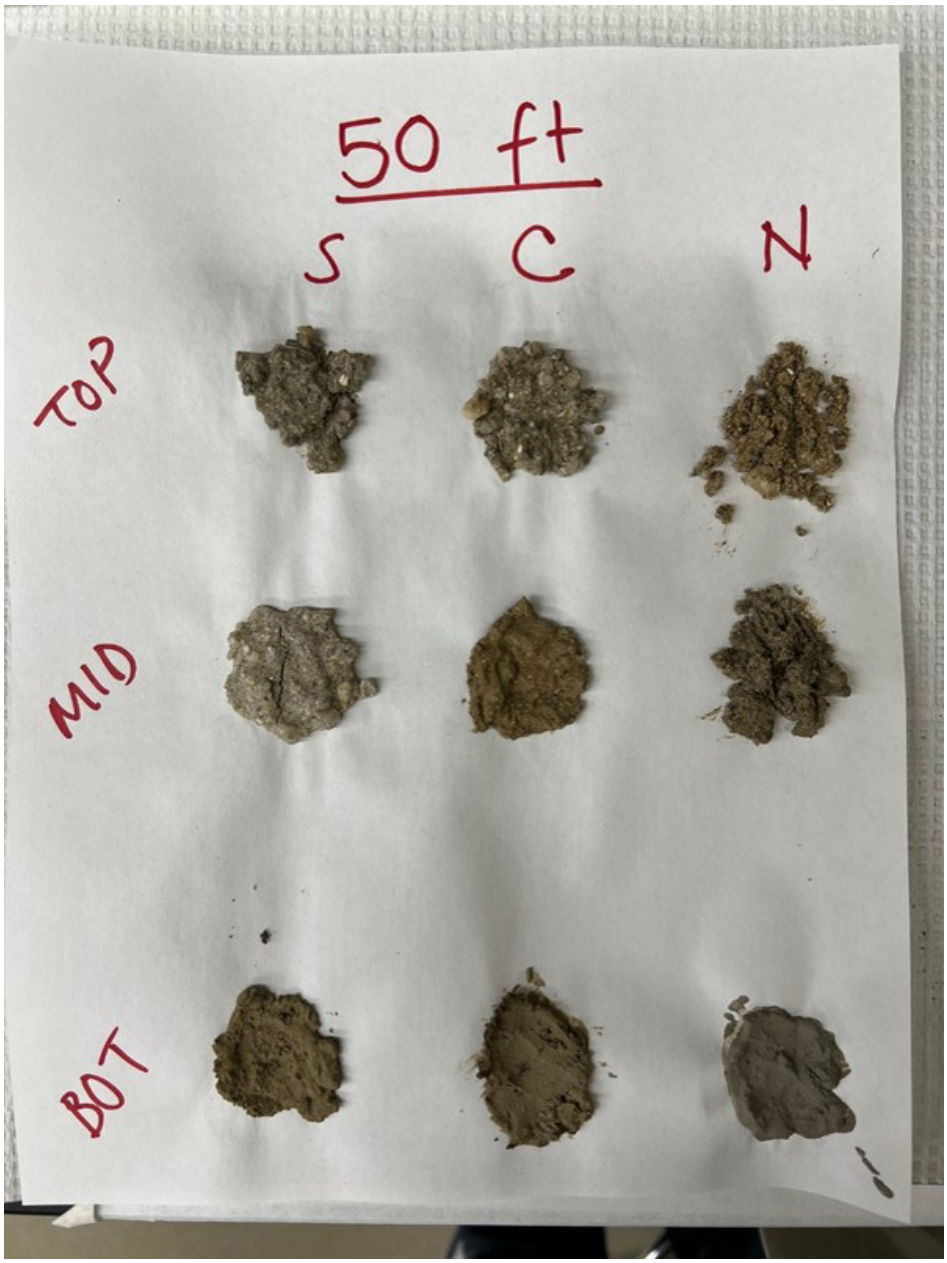


Figure 5.48. Photos of Sediment from 50ft location (Location #2)

Chloride profiles are consistent between the 3 replicate locations. Chloride concentrations in surface water and sediment (~70 mg/l) slightly decrease below the sediment interface and then steadily increase to between 110 and 120 mg/L at the deepest sampled depths (Figure 5.49).

The surface water and deepest porewater concentrations are similar to site 9ft but there is no chloride peak at mid-depths. The washout event and position between two outfalls may have resulted in flushing of the sediment with lower chloride concentration water from stormwater.

5.4.6.2.2 Geochemical Indicators

Sulfate concentrations increase below the sediment surface to a peak concentration at ~10 cm and then rapidly decrease with depth (Figure 5.49). Sulfide concentrations were below detection throughout the sampled depths. Iron (II) concentrations were below detection to a depth of 8 cm, (supporting the oxic environment) and then consistently increased at lower depths. The lack of reduced iron, increase in sulfate, and absence of sulfide to a depth of ~8-10 cm BSI, could suggest that the upper sediment was recently oxidized with increased sulfate due to either oxidation of solid iron sulfide or preservation of sulfate from source water. Given the known loss of surface sediment due to scouring, it appears that the upper sediment has been highly impacted by a flushing event.

5.4.6.3 Location #3 (100 ft from shore)

5.4.6.3.1 Transport Indicators

The 100ft location is located ~100 ft from the shoreline. During high tide the water level covered the top HRPP cells but at low tide the water level was just below the top equilibrium cell for the central location and above it for the North and South locations (Figure 5.50). The HRPP were installed in a sand bar located on the bay side of the stormwater outfall. Sediment at this location appeared stable over the 28 day deployment with no visual signs of scour or burial.

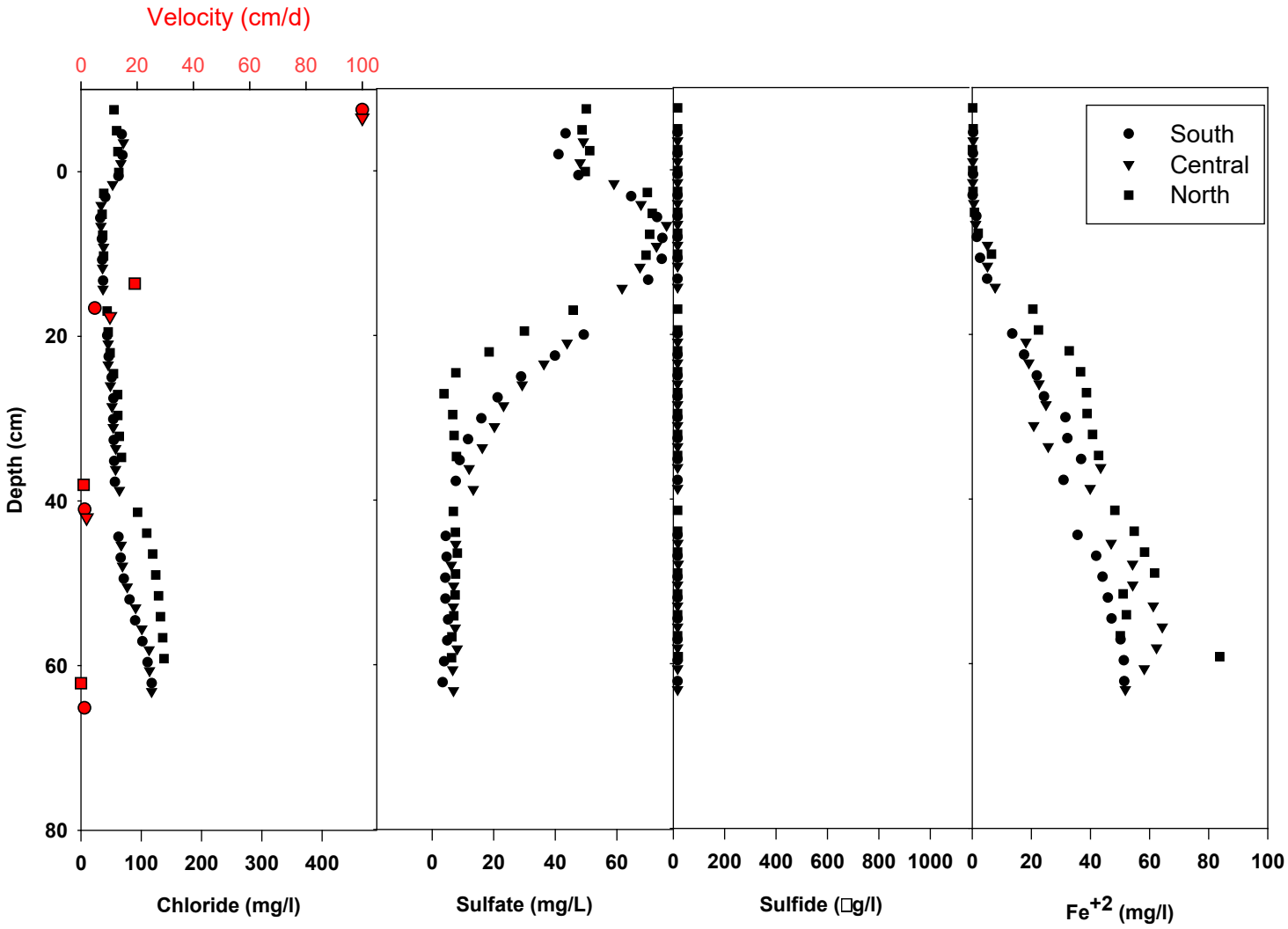


Figure 5.49. Concentration Depth Profiles at 50ft Location (Location #2)

Concentration depth profiles of chloride, sulfate, sulfide, and iron (II) and pore velocity with depth at location 50ft for the south, central, and north HRPP.

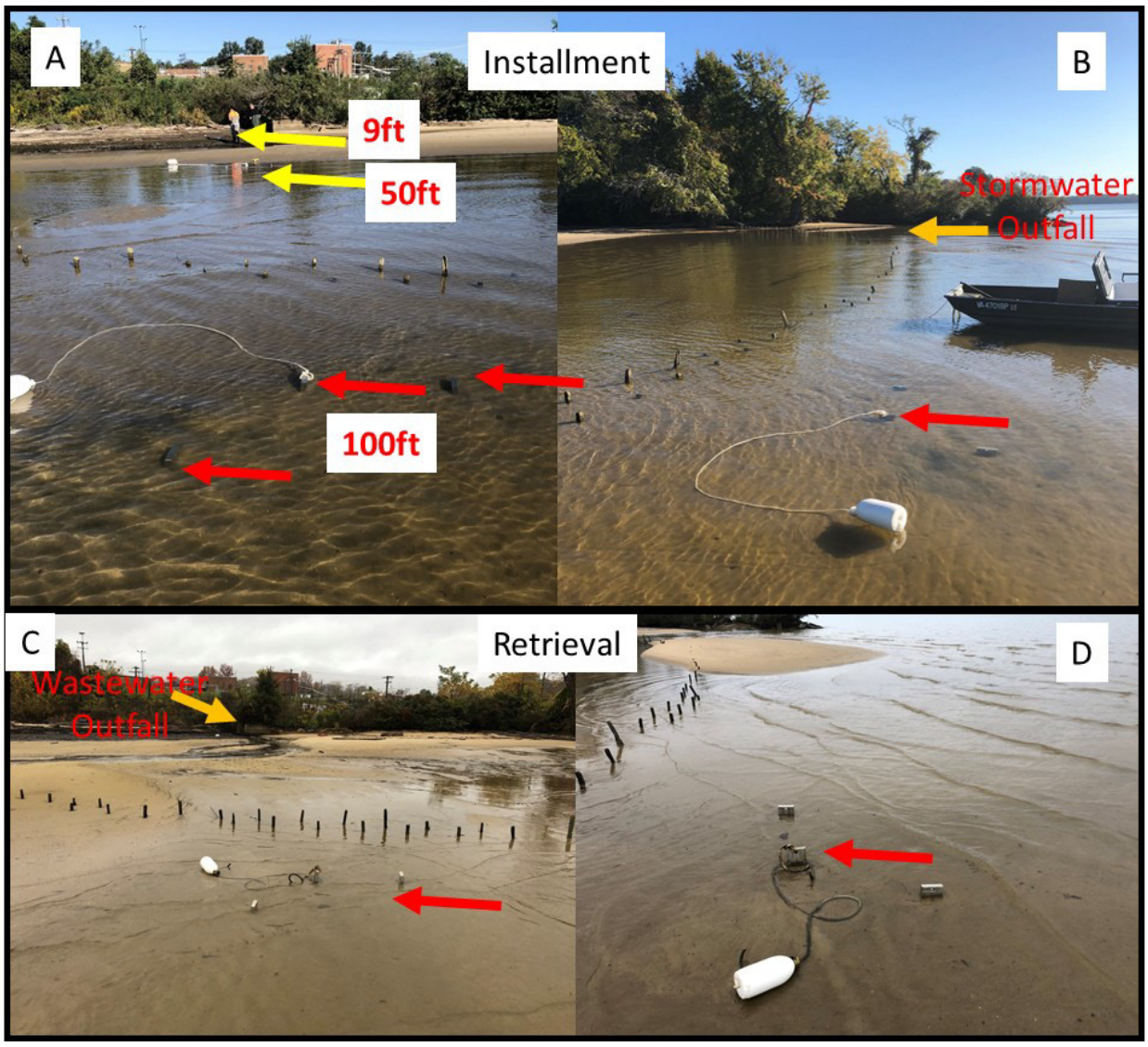


Figure 5.50. Location #3 (100 ft location) Photos

A) and B) are pictures of site 100ft during installation at mid tide and C) and D) are pictures after 28 days of deployment at low tide. Red arrows denote location of HRPP. Orange arrows show location of stormwater outfall and wastewater outfall. The 9ft and 50ft location are shown in panel A for reference.

HRPP equilibrium cells were completely equilibrated (95%) to a depth of 40 cm BSI. Below this, equilibrium ranged from 80 to 100% (Figure 5.44). The high equilibrium values in the upper depths are consistent with pore velocities. Pore velocities decreased from >100 cm/d above the sediment interface to ~ 5 to 10 cm/d at 20 cm BSI where it remained relatively constant to a depth of 40 cm BSI. At lower depths, the pore velocity decreased to 1-5 cm/d. Based on core data, all locations were dominated by coarse sand above ~ 40 cm, with an increase in finer grained material, (fine sand and silt) below that depth. Pictures of sediment material are presented in Figure 5.51. Due to the poor core recovery (<60%), depths are difficult to corelate to HRPP depths. The relatively high pore velocities down to 40 cm BSI suggest that there may be lateral flow occurring as vertical flow would not decrease with depth.

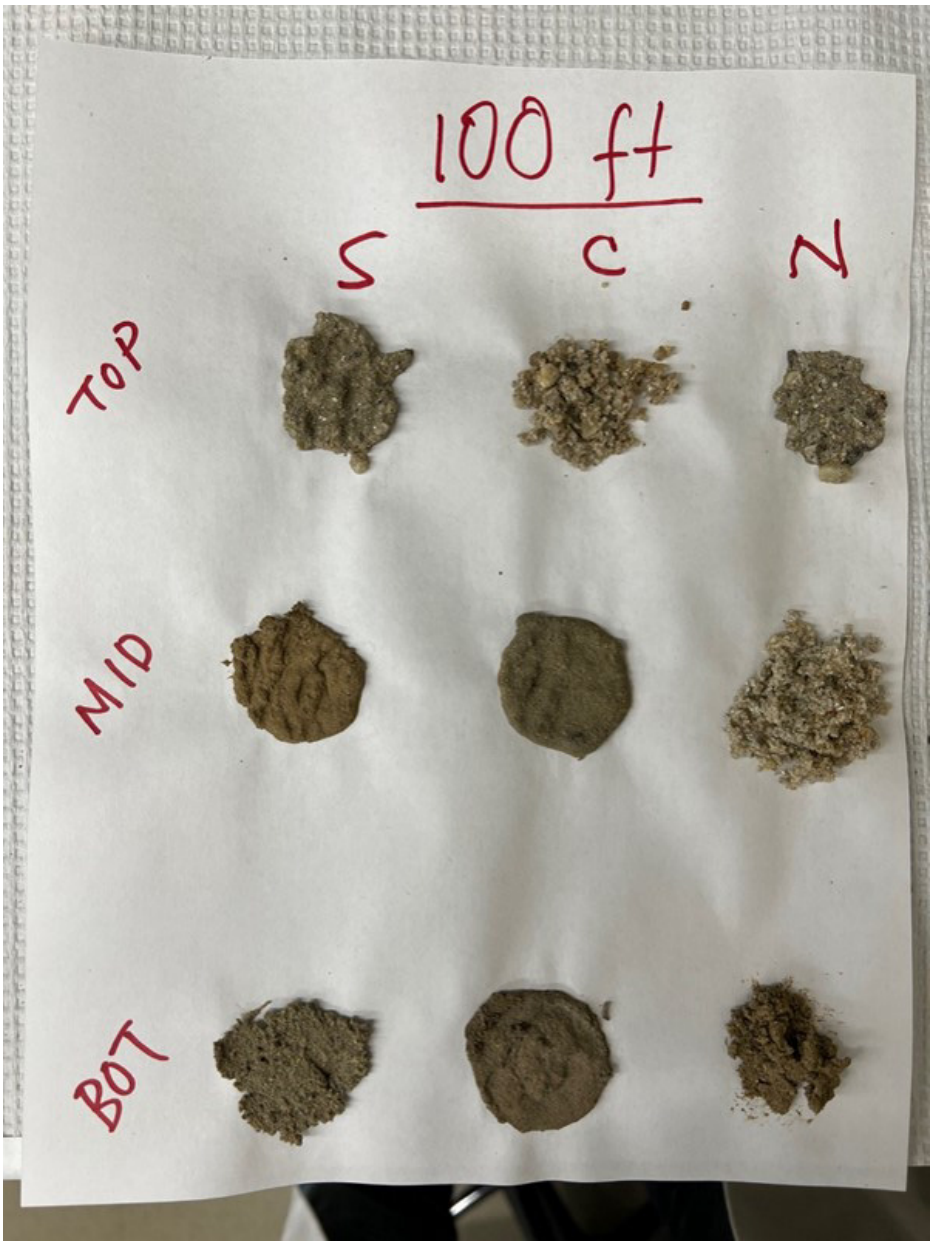


Figure 5.51. Photos of Sediment from 100ft Location (Location #3)

Chloride profiles are consistent between the 3 replicate locations except at the deepest depths. Chloride concentrations in surface water and sediment (~70 mg/l) increase to between 250 and 400 mg/L at 35 cm BSI (Figure 5.52). Below this depth they decrease to ~ 200mg/l at 50 cm. The north and central location then increase (250 to 400 mg/l), while the north location decreases to ~ 100 mg/l. The surface water concentrations are similar to the 9ft and 50ft locations. The north location concentrations at the deepest depth are similar to the concentrations at the deepest depths at the 50ft and 9ft locations. The peak in chloride concentrations at 35 cm is similar to that at 9ft in both depth and magnitude. The peak of chloride concentration similar to site 9ft would be consistent with lateral bank drainage. Regardless of the cause, some active process must maintain the profile as diffusion alone would rapidly attenuate it.

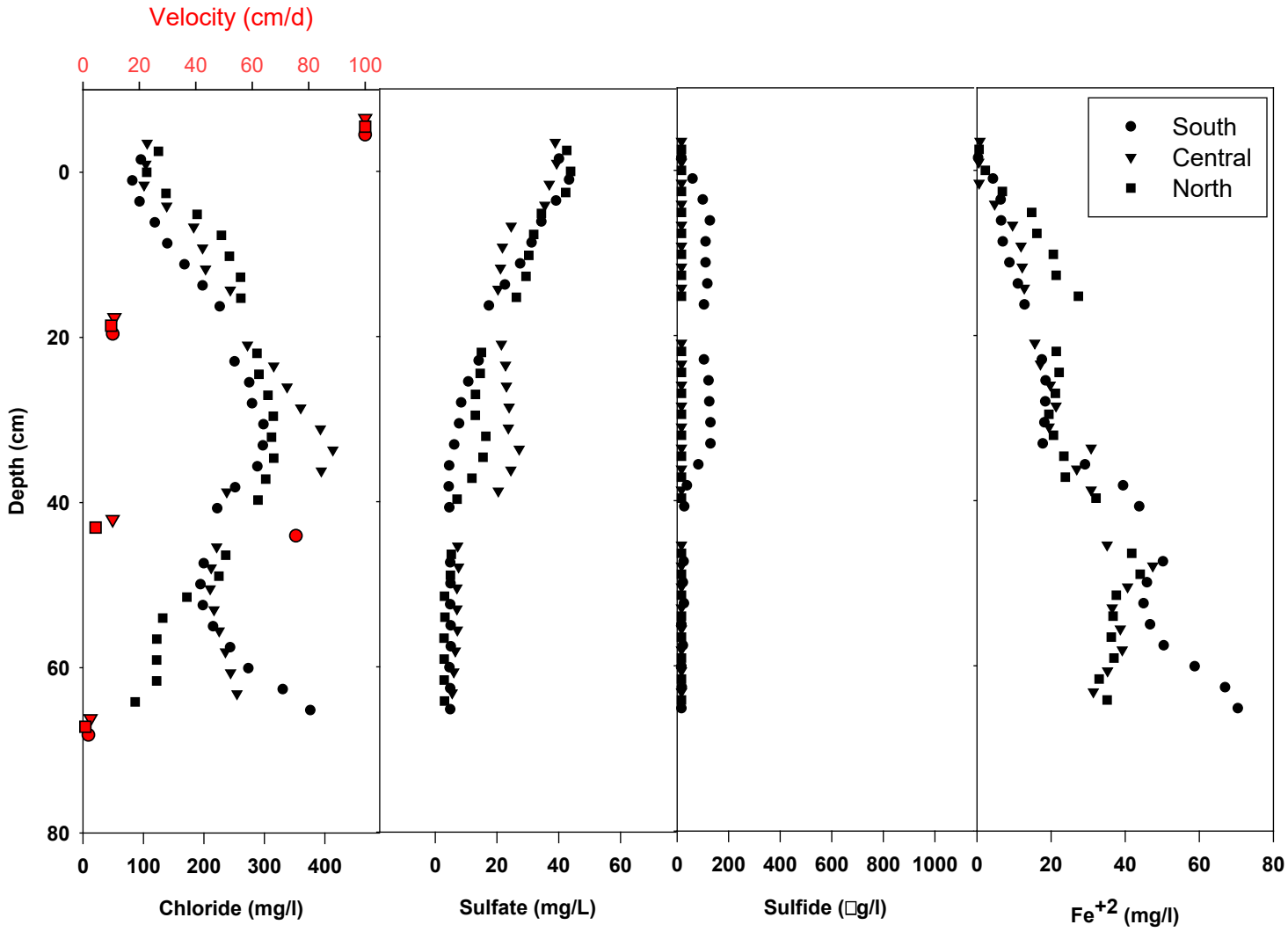


Figure 5.52. Concentration Depth Profiles at 100ft Location (Location #3)

Concentration depth profiles of chloride, sulfate, sulfide, and iron (II) and pore velocity with depth at location 100ft for the south, central, and north HRPP.

5.4.6.3.2 Geochemical Indicators

Surface sulfate concentrations were similar to the 9ft and 50ft locations. Sulfate concentrations decrease with depth from the surface to 40 cm BSI, below which they are constant and near the detection limit (Figure 5.52). Sulfide concentrations were below detection throughout the sampled depths for the central and north locations and low <200 µg/l for the south. Iron (II) concentrations were below detection at the sediment water interface and then increased to a depth of 50 cm below which they remained constant or continued to increase. Based on reduction in sulfate and increases in Fe (II), the sediments appear to be very reducing.

5.4.6.4 Location #4 (140 ft from shore)

5.4.6.4.1 Transport Indicators

The 140ft location is located ~140 ft from the shoreline on the bay side of all outfalls. During both low and high tide, the water level covered the HRPP (Figure 5.53).

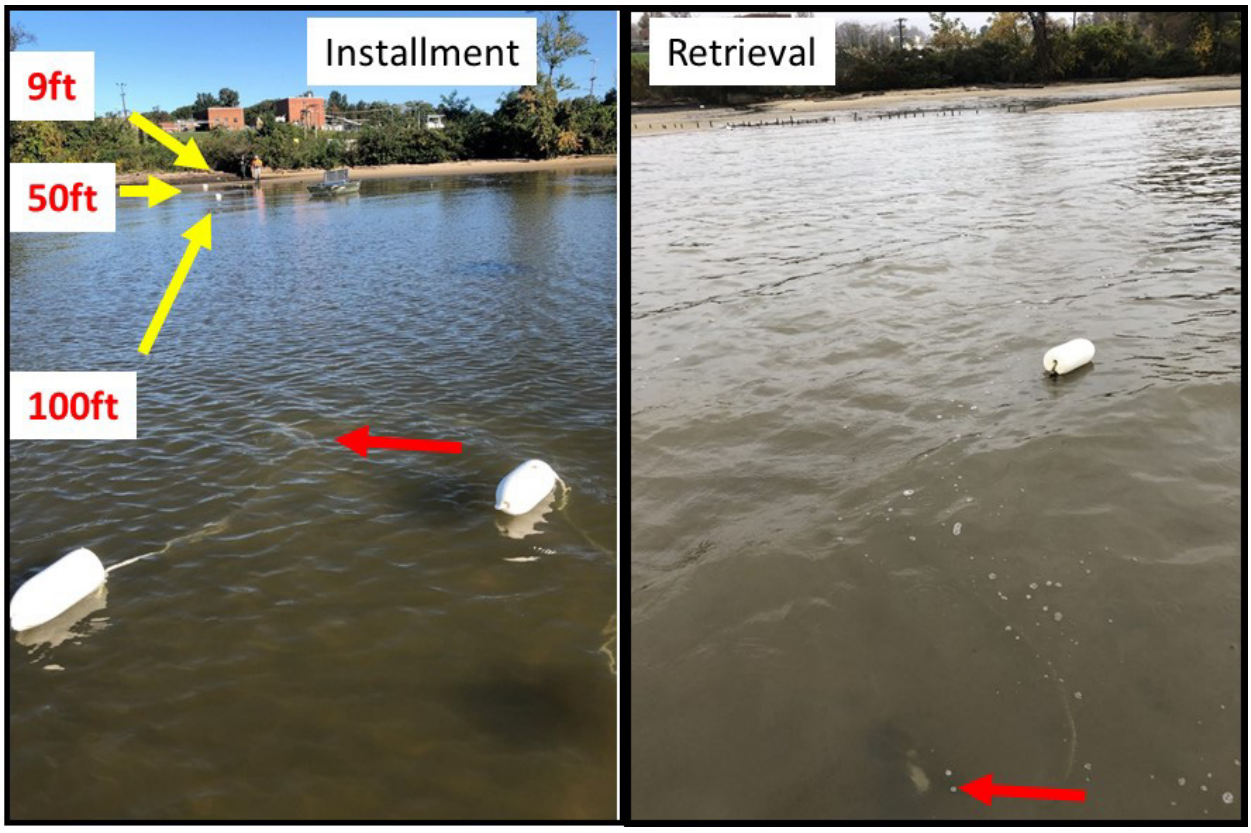


Figure 5.53. Location #4 (140 ft location) Photos

A) and B) are pictures of the 100ft location during installation at mid tide and C) is a picture after 28 days of deployment at low tide. Red arrows denote location of HRPP. Orange arrows show location of stormwater outfall and wastewater outfall. Flowing water is the wastewater outfall.

HRPP equilibrium cells were completely equilibrated (>95%) to a depth of 20 cm BSI (Figure 5.44). Below this equilibrium ranged from 70 to 90%. The high equilibrium values in the upper depths are consistent with pore velocities. Pore velocities decreased from >100 cm/d above the sediment interface to ~ 2 to 5 cm/d at 20 cm BSI. Below 20 cm, the velocity decreased to < 0 to 2 cm/d. Based on core data, all locations were dominated by sand above ~ 40cm, with increasing finer grained material, (silt) below that depth. Pictures of sediment material are presented in Figure 5.54. Due to the poor core recovery (<60%), depths are difficult to corelate to HRPP depths. Relatively low pore velocities below 20 cm suggest little lateral or vertical flow.

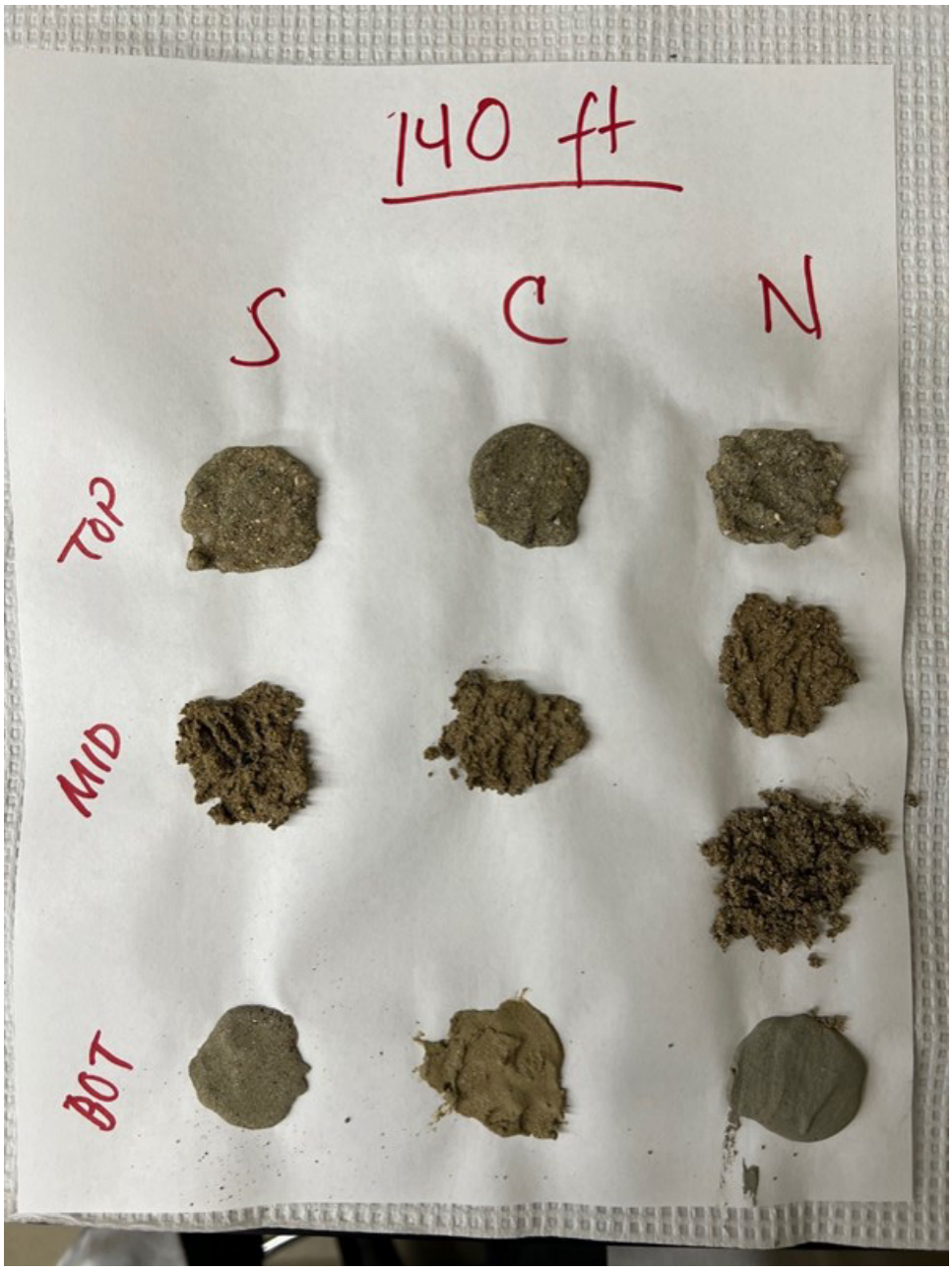


Figure 5.54. Photos of Sediment from 140ft location (Location #4)

Chloride profiles are consistent between the 3 replicate locations. Chloride concentrations in surface water and sediment (~70 mg/l) increase to ~ 400 mg/L at 15cm BSI (Figure 5.55). Below this depth they decrease to ~ 200mg/l at ~30cm BSI. The central and North location then increase (400 mg/l), while the south location remains relatively stable ~ 200-250 mg/l. The surface water concentrations are similar to all other sites. The double peak in chloride concentrations is similar to the 100ft location except the peak concentrations occur at depths closer to the surface, likely due to the decrease in sediment surface elevation. The double peak could be consistent with a stratified lateral flow with two sources of water, a higher concentration and lower concentration perhaps due to variation in hydraulic conductivity with depth due to changes in sediment. Regardless of the cause, some active process must maintain the profile as diffusion alone would rapidly attenuate it.

5.4.6.4.2 Geochemical Indicators

Sulfate, sulfide and iron concentration profiles were similar to the 100ft location, with small variations. Sulfate reduction occurred more rapidly (mainly over the top 20 cm BSI), sulfide concentrations were generally higher but relatively low except for one location (North) at the lowest depths, and iron (II) generally increased with depth but to a smaller extent than at the 100ft location.

5.4.6.5 DDX Concentration Distribution with Depth

5.4.6.5.1 PRC Performance

SPME fibers were equilibrated with both DDX and PCB PRCs. ^{13}C p,p-DDE, ^{13}C p,p-DDD, and ^{13}C p,p-DDT were used to evaluate DDX equilibrium, while PCB PRCs were only used as a reference for DDX PRC behavior. The PRC ^{13}C p,p-DDE fss was highly variable within a profile, between replicates at a location, and between locations (Figure 5.56). There was generally no consistent relationship between depth and fss. The cause of the high degree of variability is not completely understood, nor why there was little impact of depth as the shallow sediments (upper 20 cm) were characterized by high rates of porewater exchange based on pore velocities (as described in previous sections).

In stark contrast to the ^{13}C p,p-DDE fss profiles, the profiles of ^{13}C p,p-DDD were very similar between replicate locations and locations and there was a strong dependence on depth (Figure 5.57). The ^{13}C p,p-DDD fss values were ~ 1 near the surface and decreased with depth to ~ 15 to 30 cm BSI, below which they remained constant (~0.5 to 0.8). The depth at which fss values stopped decreasing and became constant was deeper near shore and became shallower (closer to sediment interface) with distance from the shore. The high fss values near the surface would be consistent with higher velocities measured in the near surface. The increasing depths at which ^{13}C p,p-DDE fss values became constant with respect to distance from shore are consistent with higher pore water velocities at deeper depths near shore and higher fss values of Br^- at depth with locations near shore.

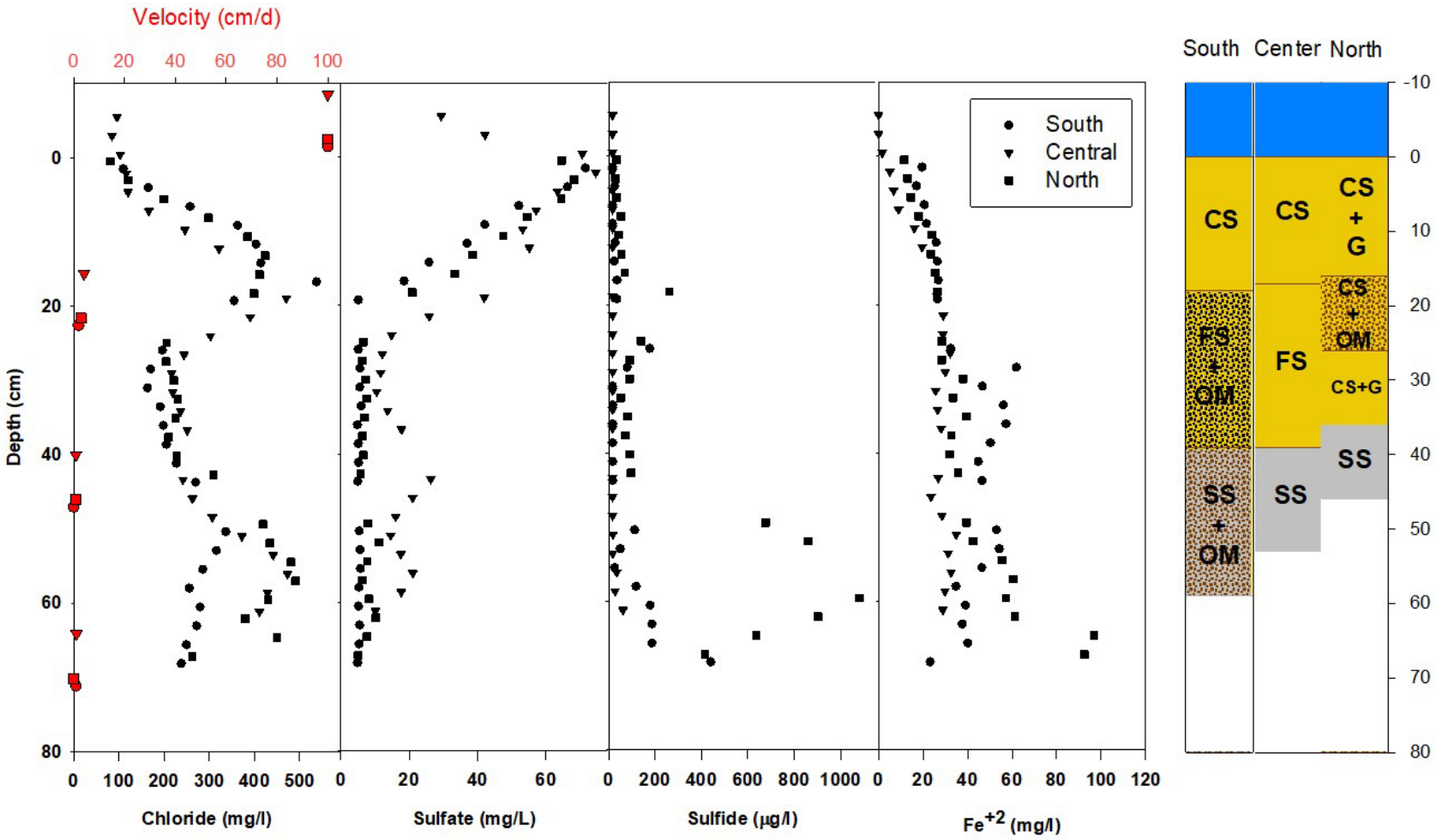


Figure 5.55. Concentration Depth Profiles at 140ft Location (Location #4)

Concentration depth profiles of chloride, sulfate, sulfide, and iron (II) and pore velocity with depth at location 140ft for the south, central, and north HRPP.

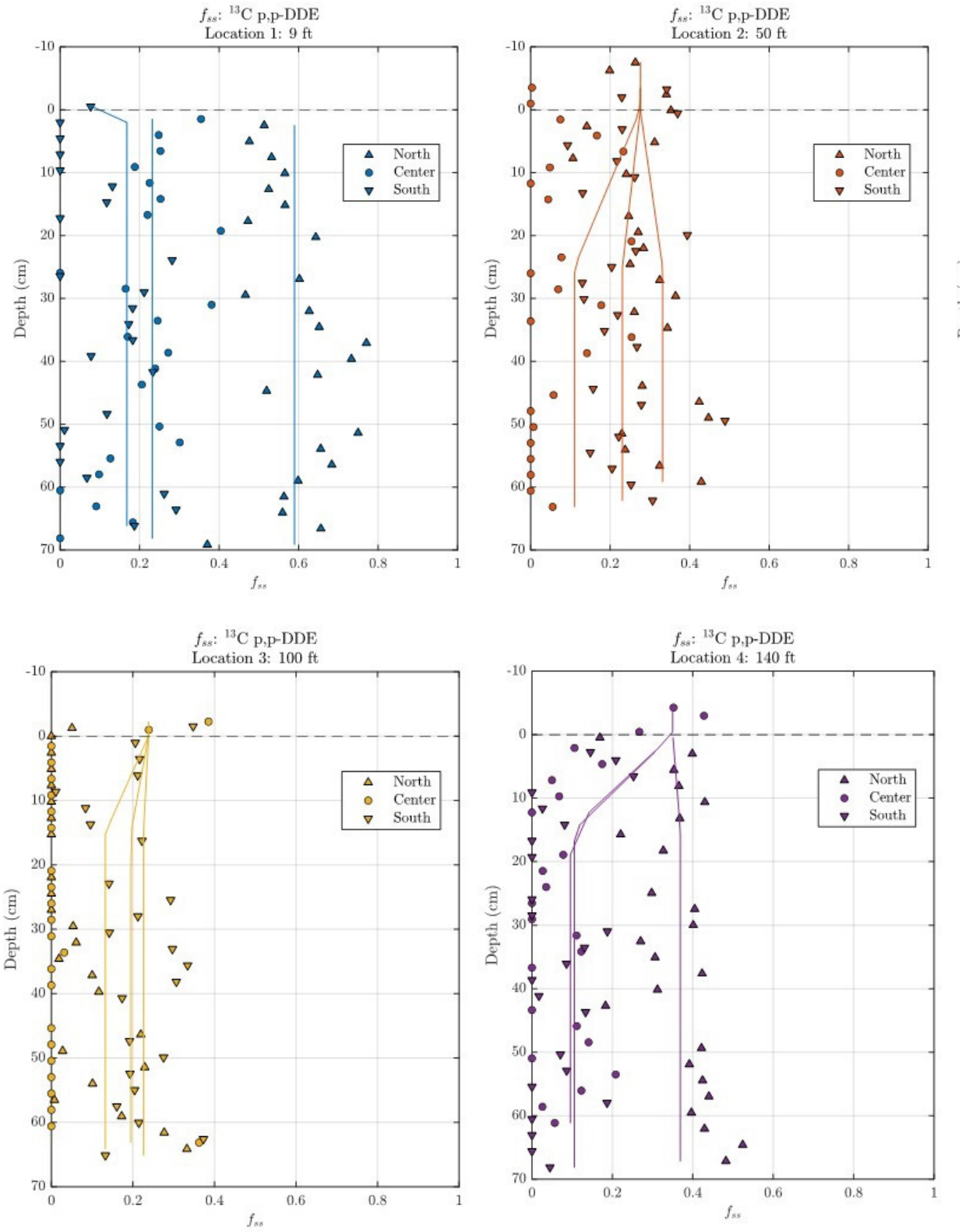


Figure 5.56. ^{13}C-p,p-DDE PRC fss Values with Depth at Each Sample Location

Solid lines represent trends in fss and were used as fss values to reduce variability.

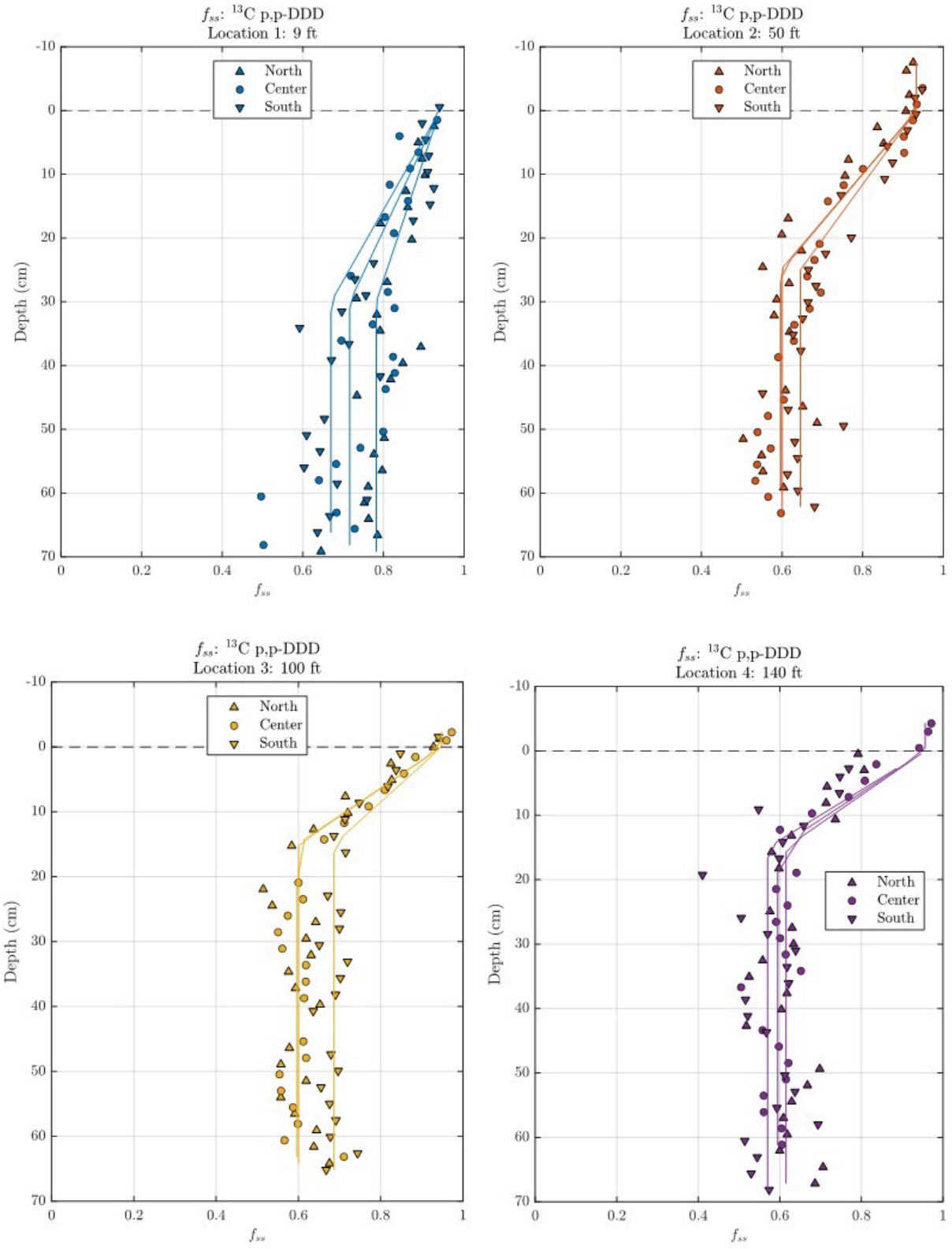


Figure 5.57. ^{13}C-p,p-DDD PRC fss Values with Depth at Each Sample Location

Solid lines represent trends in fss and were used as fss values to reduce variability

The fss depth profiles of ^{13}C p,p-DDT were the reverse of those for ^{13}C p,p-DDD but were generally consistent between replicates and locations (Figure 5.58). The fss values were lower (0.2-0.6) at the sediment interface and increased with depth (15-30cm BSI) at which point they stabilized generally near to values (0.7 to 0.9). The depth at which they stabilized was similar to ^{13}C p,p-DDD and followed the same trend with lower depths near shore and increasing depths away from shore. It should also be noted that in cases where SPME fibers were located above the sediment water interface the fss values were similar (~0.5) regardless of whether the fss values at the sediment interface were lower or higher, perhaps suggesting a separate control mechanism. The lower DDT fss values near the surface are the opposite of what would be expected due to pore flushing based on porewater velocities. Organic carbon content could impact fss values if it varied significantly with depth. However, in this case, fss values of all three PRCs would show the same trend with DDE being the most impacted. However, as all three PRCs showed separate trends, it seems most likely that degradation of ^{13}C p,p-DDT occurred as discussed below.

DDX PRC fss values were weakly related to reported log Kow DDX values (Figure 5.59). PCB PRCs were highly related to log Kow values with ex situ ~ 0.1 units higher than in situ. The behavior of the PCB PRCs suggests that an additional process impacted DDX PRCSs. Reported DDX log Kow values are highly variable ± 1 log unit. Ex situ fss values of DDX PRCs were similar but greater for DDT and DDD, while DDE ex situ fss values (~ 0.4) were greater than in situ (~ 0.2). The combined observations are that 1) at lower depths DDT was almost completely equilibrated and fss values were greater than predicted based on log Kow values, and 2) DDD was almost completely equilibrated in the near surface but fss values at depth were constant and lower. In deeper anaerobic sediments, DDT could degrade to DDD which would increase fss values of DDT and decrease fss values of DDD at depth. At shallow aerobic depths degradation would be inhibited and fss would be dominated by transport. DDT which has a higher Kow than DDD, and so DDT would be less impacted by transport processes. Degradation of DDX PRCs has been previously observed (Tcaciuc et al., 2018). As discussed below the dominance of DDD compared to DDT at the site supports the potential for degradation to impact DDT and DDD PRCs.

5.4.6.5.2 DDX distribution with Depth

<u>9ft Location (Location #1)</u>

Sediment concentrations of p,p DDT were higher (1-100 µg/kg) than o,p DDT (0.1-1 µg/kg) at all depths (Figure 5.60). While concentrations of p,p DDT were highest at deeper depths (>30cm), concentrations of o,p DDT were generally similar with depth. Concentrations of both o,p and p,p were generally similar between replicate locations. Concentrations of DDD (0.1 to 10,000 µg/kg) were much higher than DDT and p,p DDD concentrations were much higher than o,p DDD (1 to 100 µg/kg). Concentrations of DDD were higher at depths > 30cm and were similar between replicate locations. Concentrations of p,p DDE (1-100 µg/kg) were much higher than o,p DDE (0.1-10 µg/kg). Concentrations of p,p DDE were generally constant with depth, while deeper depths were highest for o,p DDE. Organic carbon content was ~1 order of magnitude greater at depths below 40cm, potentially accounting for the higher concentrations of DDT with depth (Figure 5.61).

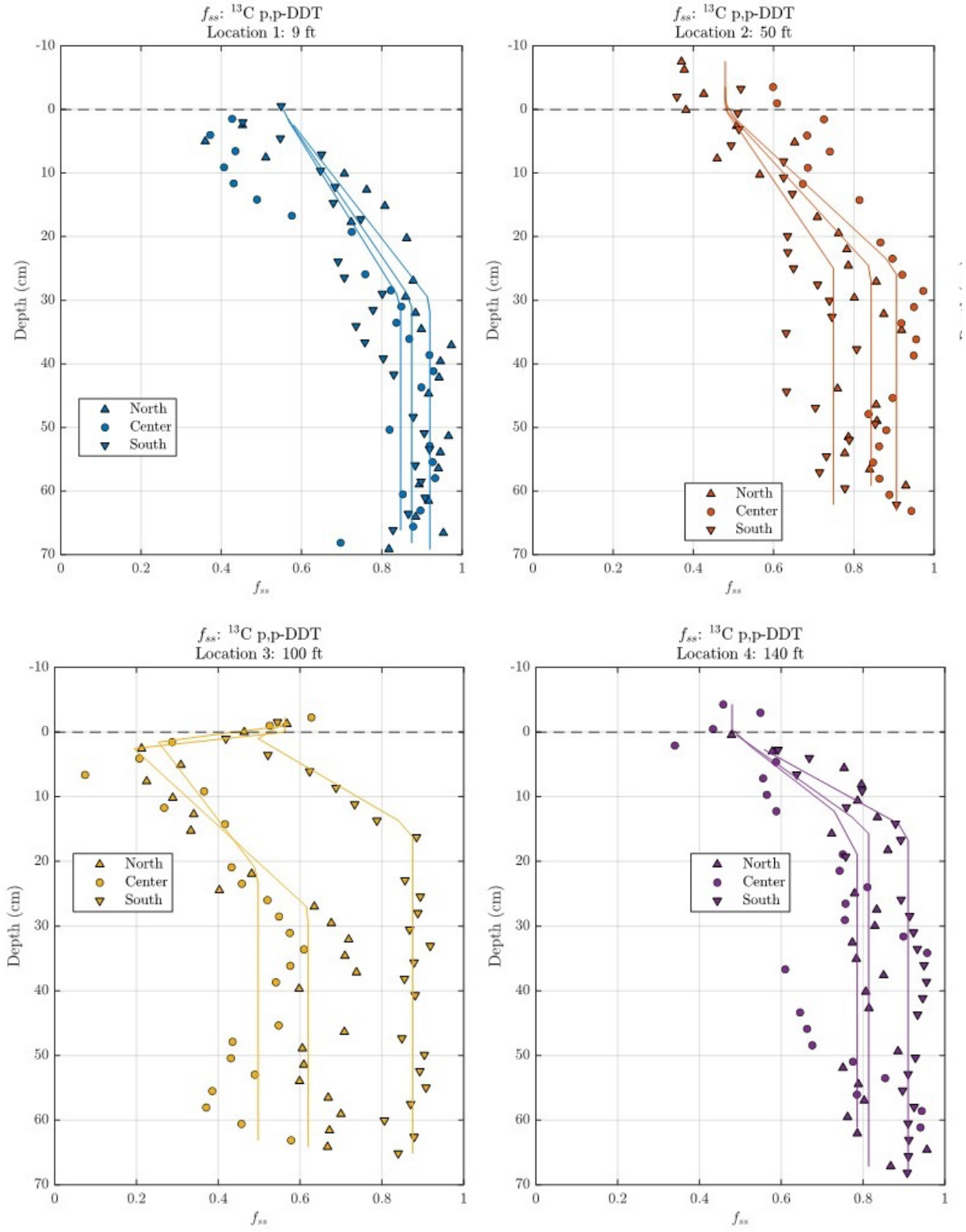


Figure 5.58. ^{13}C-p,p-DDT PRC fss Values with Depth at Each Sample Location

Solid lines represent trends in fss and were used as fss values to reduce variability.

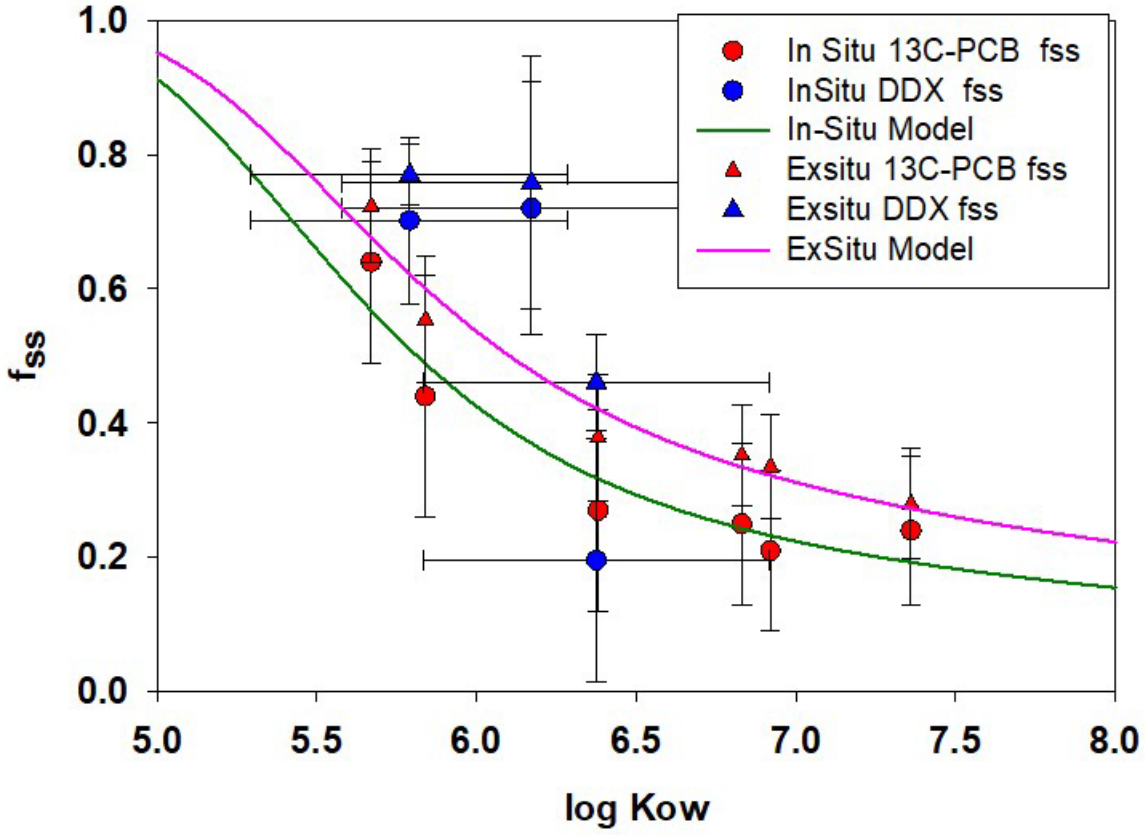


Figure 5.59. The fss Values of DDX and PCB PRCs with Respect to log Kow Values

In situ porewater concentrations of DDX were generally constant with depth (Figure 5.60). Concentrations of p,p DDD (1-10 ng/L) were ~1 order of magnitude greater than p,p DDT (0.1-1 ng/L) with a similar relationship between o,p DDT and o,p DDD but reduced in concentrations by a factor of 10. No o,p DDE was detected in in-situ porewater above the PQL, while p,p DDE concentrations (0.1 to 1 ng/L) were 1 order of magnitude lower than p,p DDD. Concentrations with depth and between replicate locations were similar for each DDX species.

Ex situ porewater concentrations of DDT (o,p and p,p) were generally lower than insitu concentrations and varied little with depth (Figure 5.60). Ex situ porewater concentrations of p,p DDD varied with depth. Near surface (0-10cm BSI) concentrations (10-100 ng/l) were very similar to in situ. At lower depths (>20cm BSI), ex situ concentrations increased and were higher (10-100 ng/l) than in situ. Increases in p,p DDE generally coincided with increases in sediment concentrations at lower depths. Similar observations were observed for o,p DDD, although overall changes in concentrations were smaller and in situ and ex situ concentrations were more similar. Ex situ porewater concentrations of p,p DDE were similar to in situ with no increase with depth. Ex situ concentrations of o,p DDE were generally very low and similar to in situ at or below the PQL.

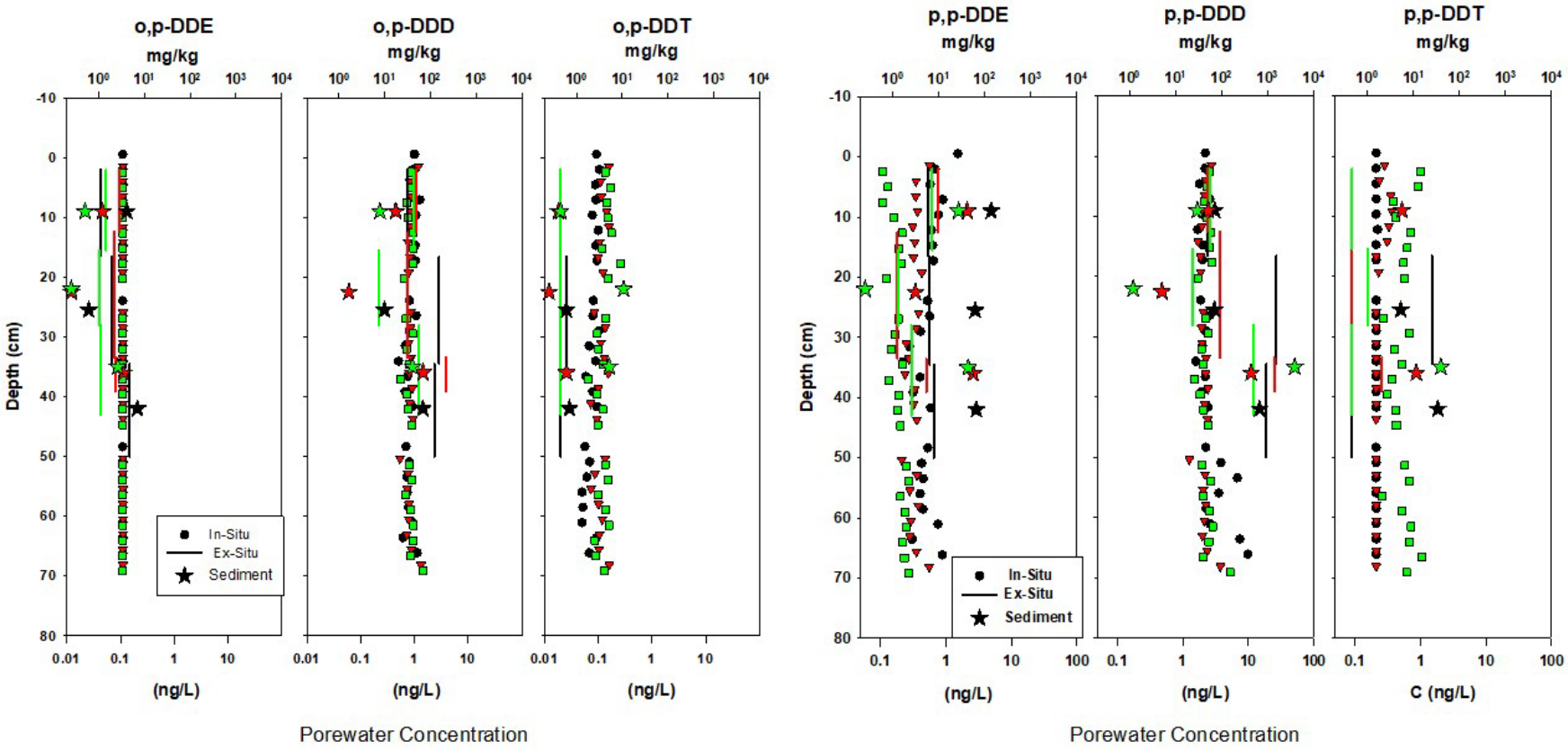


Figure 5.60. 9ft Location (Location #1) Concentrations of DDX with Depth in Porewater Measured by In Situ SPME and Ex Situ SPME As Well As Sediment Concentrations

Ex situ porewater concentrations were measured on core sediments which were also used to measure sediment concentrations. Symbol colors denote replicate location with black, red, and green representing the South, Central, and North replicate location respectively.

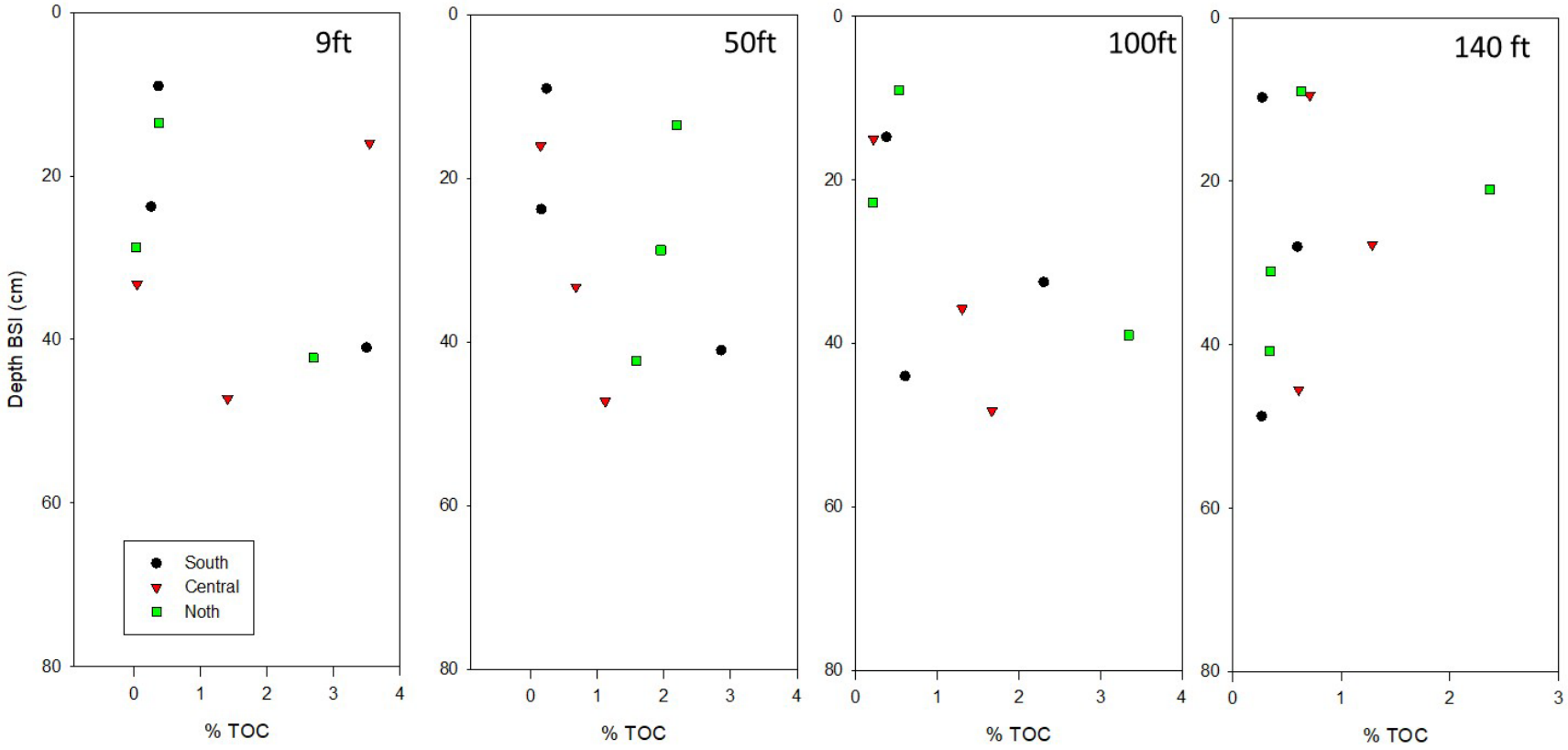


Figure 5.61. TOC Concentrations with Depth at Each Sampled Location

Colors represent replicate location with black, red and green representing the South, Central, and North locations respectively.

50ft Location (Location #2)

Sediment p,p DDT concentrations were similar to those at the site closest to shore (9ft location) (Figure 5.62). Concentrations were generally low (< 1 µg/kg) except between 30-45cm over which concentrations increased (10-100 µg/kg) and below which they declined (<1 µg/kg). Concentrations of o,p DDT were lower than p,p DDT and only weakly varied with depth, although highest concentrations were observed over the same depth interval as p,p DDT. Concentrations of p,p DDD were higher than p,p DDT but followed the same trend with respect to depth, with high concentrations (100-1000 µg/kg) between 30-40cm BSI and lower concentrations (0.1 to 10 mg/kg) at shallower and deeper depths. Concentrations of p,p DDD were lower than those closer to shore (9ft). Concentrations of o,p DDD were lower but very similar to p,p DDD and followed the same trend with depth. Concentrations of p,p DDE were lower but similar to p,p DDD and followed the same depth trend as p,p DD and DDT. Concentrations of o,p DDE were very low (0.1-1 µg/kg) except for peak concentrations ~ 10 mg/kg that occurred at the same depths as other DDX species. Concentrations of sediment organic carbon increased with depth from 0.2-0.4% to 1-3% for the south and central locations, while for the north location TOC was higher at shallower depths (~2%) and declined to ~1.5% at depth (Figure 5.61). Elevated TOC at depths near 40cm corresponded to higher sediment DDX concentrations but not in shallower depths for the north replicate.

In situ concentrations of p,p DDT were below the PQL except for the north replicate which varied from 10 to 100 ng/l with peak concentrations near the surface (Figure 5.62), even though sediment TOC was high at these depths and sediment DDT concentrations low. In situ concentrations of o,p DDT were ~ 1ng/L and varied little with depth. In situ concentrations of p,p DDD varied with depth and were very similar between replicate locations. Concentrations were highest (10 ng/L) at the sediment interface and declined to ~10 cm BSI, below which they were generally constant (~1 ng/L). In situ concentrations of o,p DDD were similar to p,p DDD and followed the same trend with respect to depth. In situ concentrations of p,p DDE were low and only above the PQL (~0.08 ng/L) for depths near the surface interface except for the central replicate which increased with depth (~1 ng/L). In situ concentrations of o,p DDE were all below the PQL (0.11 ng/L).

Ex situ concentrations of p,p DDT were at or near the PQL (0.09 ng/L) for all depths as were o,p DDT concentrations (PQL = 0.02 ng/L). Ex situ concentrations of p,p DDD were higher but similar to in situ concentrations at depths above 20 cm and below 50 cm, but were much higher than insitu concentrations at depths of 20 to 50cm BSI. The same depths at which sediment concentrations peaked. Similar observations can be made for ex situ concentrations of o,p DDD and the relationship to in situ porewater concentrations. Ex situ concentrations of p,p DDE followed the same trend with depth and were generally similar to in situ. Ex situ porewater concentrations of o,p DDE were low and generally near the PQL. Overall ex situ porewater concentrations were only higher for depths with higher sediment concentrations of p,p DDD, p,p DDE, and o,p DDD.

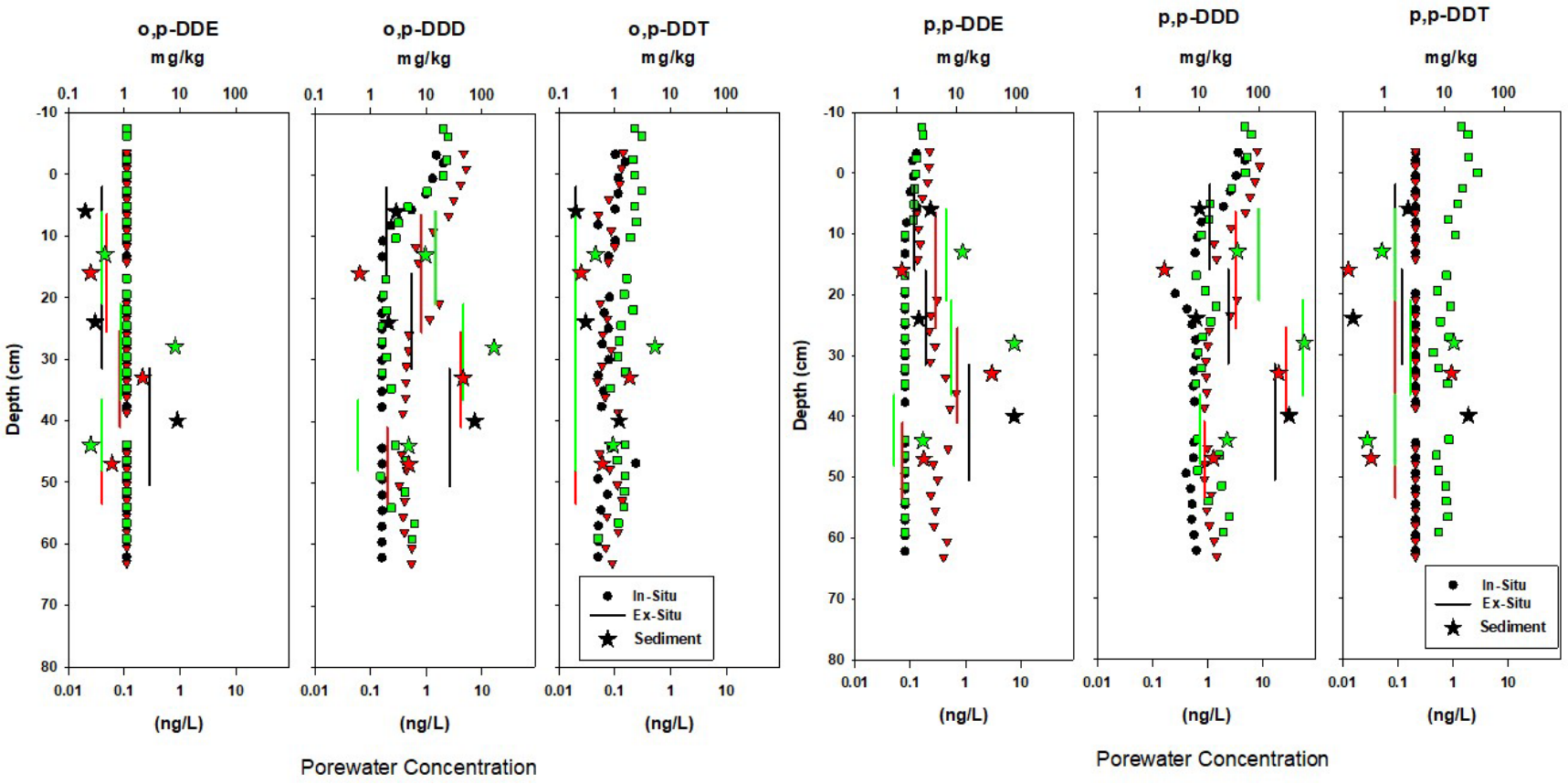


Figure 5.62. 50ft Location (Location #2) Concentrations of DDX with Depth in Porewater Measured by In Situ SPME and Ex Situ SPME As Well As Sediment Concentrations

Ex situ porewater concentrations were measured on core sediments which were also used to measure sediment concentrations. Symbol colors denote replicate location with black, red, and green representing the South, Central, and North replicate location respectively.

100ft Location (Location #3)

Sediment concentrations of p,p DDT were similar to site 50ft with sporadically elevated concentrations at 30-50 cm BSI for the south and central but not north replicate location (Figure 5.63). Concentrations of o,p DDT were generally near 1 µg/kg with no relationship with depth. Sediment concentrations of p,p DDD and o,p DDD were consistently elevated at depths > 30cm BSI. Concentrations of p,p DDD were higher (100-500 mg/kg) than o,p DDD (30-100 µg/kg), similar to location 50ft but DDD concentrations were lower less than location 9ft. Sediment concentrations of p,p DDE and o,p DDE were also consistently elevated for all replicate locations at depths > 30cm BSI. Concentrations of p,p DDE (10-100 µg/kg) were ~ 10X higher than o,p DDE (0.1 to 10 µg/kg). TOC concentrations were higher at depths 30 to 50 cm BSI similar to depths at which DDX peaked but very variable (Figure 5.61).

In situ porewater concentrations of p,p DDT were similar to site 50ft (Figure 5.63). Concentrations were below or near the PQL for the south and central locations but higher (1-10 ng/L) for the north location. In addition, similar to Site 50ft concentrations peaked at the sediment interface and declined with depth. In situ concentrations of o,p DDT were extremely similar to p,p DDT. In situ concentrations of p,p DDD were higher (~2 ng/L) at the sediment interface and at ~40cm BSI and lower (~0.5 ng/L) at other depths. In situ concentrations of o,p DDD were similar to p,p DDE at depths near the surface but lower at deeper depths. In situ concentrations of p,p DDE were highest (1-2 ng/L) at the deepest depths compared to upper depths (< 0.5 mg/L). Concentrations of o,p DDE were all less than the PQL.

Ex situ concentrations of p,p DDT and o,p DDT were almost all near the PQL with no consistent relationship to depth, similar to in situ concentrations (Figure 5.63). Concentrations of p,p DDD and o,p DDD were similar to in situ at depths above 30cm BSI, but much higher (~30 ng/L) than in situ at depths below 30cm where sediment concentrations peaked. Ex situ concentrations of p,p DDE were also similar to in situ at depths > 30cm BSI and generally higher than in situ at lower depths except for the north replicate. Ex situ concentrations of o,p DDE were low (near PQL = 0.04 ng/L) for depths > 30cm with a slight increase (0.1 ng/L) at lower depths.

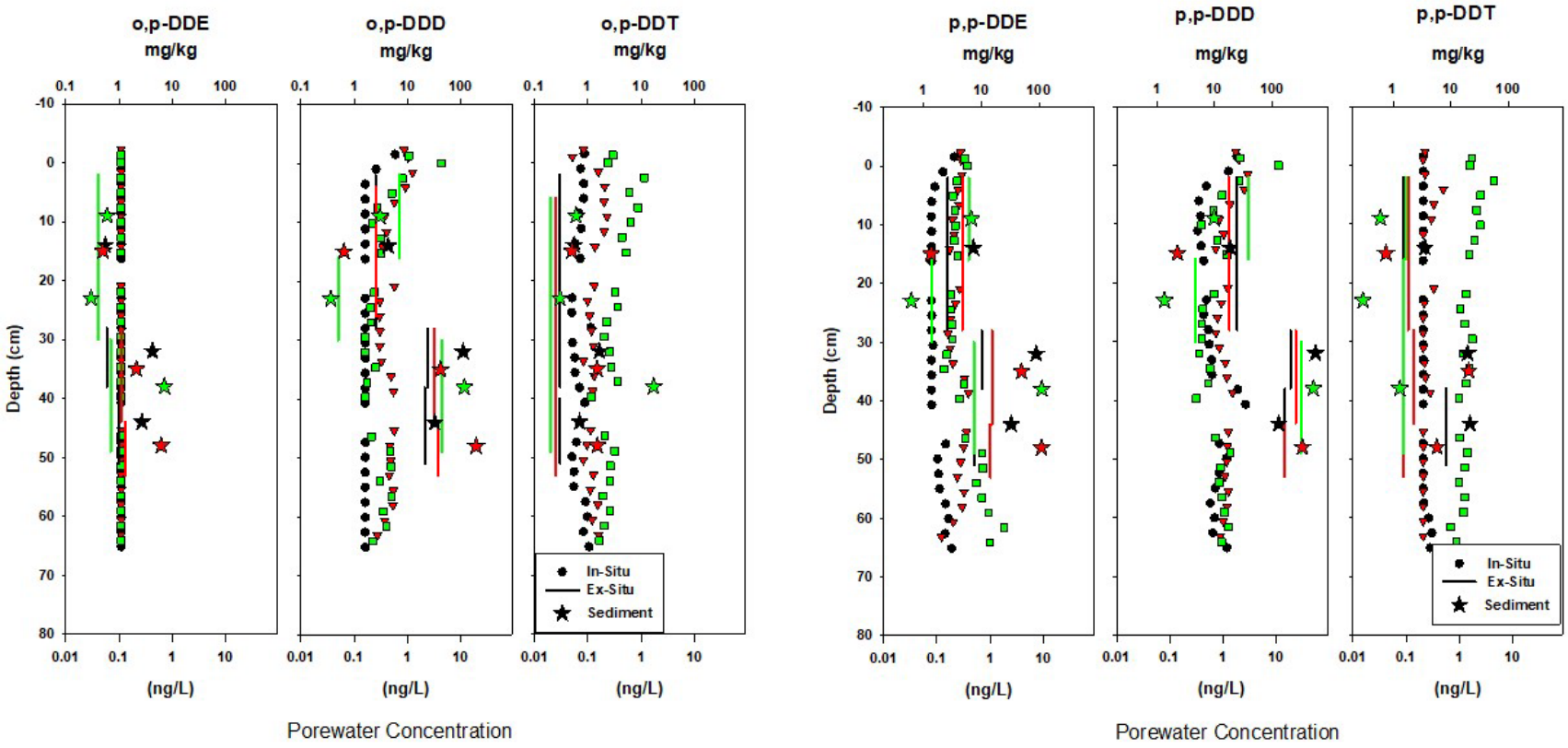


Figure 5.63. 100ft Location (Location #3) Concentrations of DDX with Depth in Porewater Measured by In Situ SPME and Ex Situ SPME As Well As Sediment Concentrations

Ex situ porewater concentrations were measured on core sediments which were also used to measure sediment concentrations. Symbol colors denote replicate location with black, red, and green representing the South, Central, and North replicate location respectively.

140ft Location (Location #4)

Sediment concentrations (~20 µg/kg) of p,p DDT were largely constant with depth and similar to peak concentrations at site 100ft and 50ft but lower than concentrations at the 9 ft location (Figure 5.64). Sediment concentrations (~ 1 µg/kg) of o,p DDT were also constant with depth. Sediment concentrations of p,p DDD were variable between replicate locations but generally higher than concentrations at sites 50 ft and 100 ft but lower than site 9 ft. Peak concentrations varied by replicate location and occurred at 10-30 cm BSI, shallower than at other sites. Sediment concentrations of o,p DDD were more consistent between replicate locations and like other sites were elevated at depths 20-30 cm BSI, with lower concentrations above and below that depth range. Sediment concentrations of p,p DDE were also consistent between replicates and highest at 20-30 cm BSI. Sediment concentrations of o,p DDE were lower than other DDX compounds but otherwise had similar trends with depth as p,p DDE. Sediment TOC was highest at depths 20-30 cm BSI congruent with the elevated DDX concentrations at this depth (Figure 5.61).

In situ porewater concentrations of p,p DDT and o,p DDT were constant with depth. In situ concentrations of p,p and o,p DDD were highest near the sediment interface and deepest depths (>60cm BSI). In situ concentrations of p,p DDE increased with depth for the south and central replicate and largely were < PQL for the north. As with other sites, in situ concentrations of o,p DDE were all less than the PQL.

Ex situ concentrations of DDT were all low (< PQL), and less than in situ. Ex situ concentrations of p,p DDD were generally much higher (100-1000 ng/L) than in situ (10-100 ng/L) and peaked between 20-40 cm although concentrations were variable with depth between sites. The relationship between ex situ porewater concentrations and sediment concentrations was weak for individual cores possibly due to TOC variations with depth. Similar trends were also observed for o,p DDD. Ex situ concentrations of p,p DDE were generally similar to in situ at lower depths but higher than in situ at upper depths although the difference was small. Highest ex situ concentrations did corelate to the highest sediment concentrations. Ex situ concentrations of o,p DDE were low and generally constant with depth and did not corelate with sediment concentrations.

5.4.6.6 Site Interpretation Using Passive Samplers

The embayment site is complex. Porewater fluxes appear to be dominated by lateral flow near shore and velocities generally decrease with distance from shore. There appears to be more than one source impacting the porewater possibly due to the presence of a wastewater outfall. The sediment surface (0-20cm) appears unstable near shore. The sediment is reduced at lower depths with complex redox conditions dependent on the resupply of SO4-2 from the surface and lateral flow. DDX is present across the transect with peak sediment concentrations ranging from 100 to 1000 ug/kg generally at depths 20-30 cm BSI with DDD (p,p and o,p) dominating the DDX distribution. There was no strong relationship between distance from shore and sediment DDX concentrations.

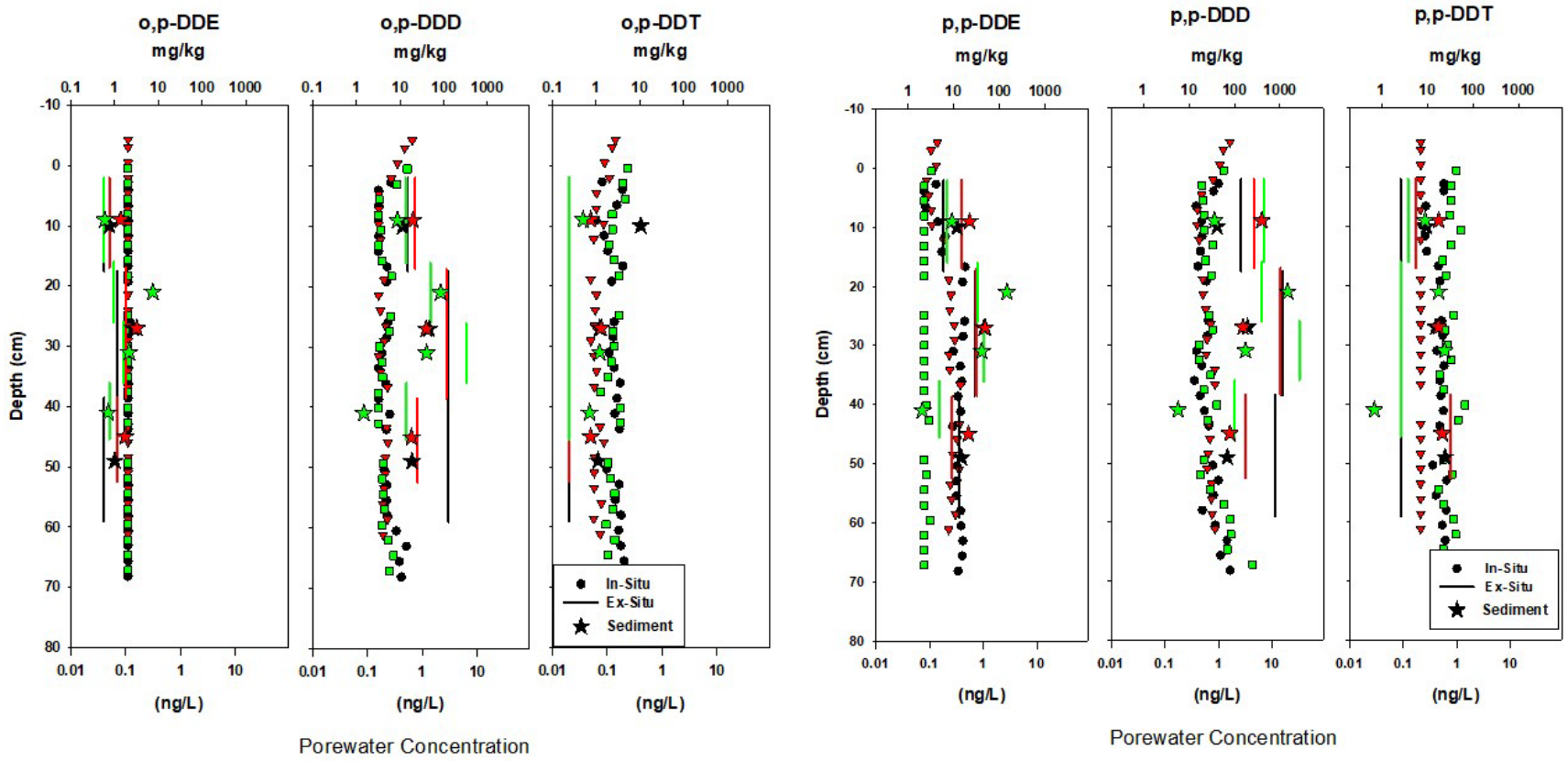


Figure 5.64. 140ft Location (Location #4) Concentrations of DDX with Depth in Porewater Measured by In Situ SPME and Ex Situ SPME As Well As Sediment Concentrations

Ex situ porewater concentrations were measured on core sediments which were also used to measure sediment concentrations. Symbol colors denote replicate location with black, red, and green representing the South, Central, and North replicate location respectively.

DDX profiles produced by sHRPP and ex situ SPME analysis were for the most part similar with some consistent exceptions. At shallow depths <20cm BSI, DDT concentrations measured by sHRPP were generally greater than those produced by ex situ analysis, while neither method was consistently higher or lower for DDD or DDE. At deeper depths ex situ measured concentrations of DDD were consistently higher than in situ. The lower concentrations measured using the in situ sHRPP method may be due to the way the SPME were deployed. If upper sediment is packed within the indention of the cover plate, it can reduce contact with the sediment at that depth. Assuming the upper sediment has lower concentrations of DDX, this would prevent DDX in sediment at the deployed depth from reaching the SPME fiber. This was not observed at Abrahams creek possibly due to the lack of change in concentrations with depth at that site. At shallow depths, this does not appear to be an issue likely due to the reduction in pressure forcing material to pack into the cell depression. This issue is explored further in the discussion of the Grand Cal deployment. Although the resolution of the ex situ method did not allow a comparison, at most sites there was not a clear indication of redeposition of contaminated sediment. At site 50ft, DDD concentrations were elevated near the surface and declined over the top 10cm consistently among replicates. This site was subject to extensive scour and the initial overlying sand was partially removed (~10cm) and so the increase likely reflects native sediment and not redeposition.

Although there appears to be an issue with deeper SPEM results of sHRPP bsed on the current design geometry, sHRPP SPME samples in the shallow zone <20cm appear to reflect concentrations produced by standard methods. Unlike other methods, the sHRPP also allow the impact of subsurface water flux to be considered and the potential role of biogeochemistry.

5.5 GREAT LAKES GRAND CALUMET RIVER AOC SITE TESTING

5.5.1 Conceptual Experimental Design

The Grand Calumet location was chosen due to the presence of PAHs, the past application of active and passive capping as well as the extensive past assessment and ongoing assessment with multiple sediment monitoring tools as part of the EPA monitoring activities. Our demonstration focused on two transects (East and West) across the Grand Calumet River (Figure 5.65). These transects have sampling stations where a variety of previous work has been conducted including pore water monitoring using SPME, coring, infauna, and PED sampling. Porewater from horizontal transect screens and vertical piezometers was also evaluated. Previous studies have also evaluated upwelling across the East Transect (ET) and West Transect (WT). The EPA resampled these locations in September of 2019, allowing the sHRPPs to be deployed during these sampling efforts, which provided a wealth of complimentary data to which to compare the performance of the sHRPPs. Due to these prior activities, the site was considered ideal to demonstrate the ability of the samplers to simultaneously evaluate numerous performance objectives. For this site our implementation goals were:

1. To demonstrate that the sHRPP can produce high resolution spatial concentration profiles of PAHs with depth including evaluating recontamination of capped areas by surface deposition of contaminated sediments from uncapped areas.

2. To demonstrate that the sHRPP can, simultaneously with goal 1, measure the geochemical sediment conditions that can be used to predict potential PAH degradation by measuring major redox transitions and conservative tracer transport at a scale which is less than the depth over which the transition takes place.
3. To demonstrate that the sHRPP can measure pore water velocity and upwelling in canal sediments.
4. To demonstrate the differences in cost and effort between traditional pore water sampling methods and the sHRPP, as well as the increased resolution, quality and reliability of sHRPP produced data.

The successful completion of these goals would demonstrate the ability of the sHRPP to provide data of sufficient resolution and breadth to predict cap performance including the exposure, risk, and attenuation of PAH over prolonged periods. Microbial community analysis was not included in this deployment.

Figure 5.65. Grand Calumet River Demonstration Area

5.5.2 Baseline Characterization

As the technology being demonstrated is a site characterization tool, typical baseline characterization activities do not apply. However, as mentioned and will be discussed in the following subsections, there was sufficient pre-capping and post capping data to serve as baselines. Further simultaneous testing by EPA using passive polyethylene device (PED) samplers, cores, and the co-deployment of *in-situ* SPME sampling with a T Bar sampler was performed as part of the demonstration for comparison purposes.

5.5.3 Design and Layout of Technology Components

We compared pore water concentrations of PAHs produced by analysis of the SPME fibers within the sHRPP with an accepted passive sampling method, *in-situ* SPME analysis. For *in-situ* measurements, we co-deployed T Bar samplers with the sHRPPs. These T Bar samplers contained a SPME fiber oriented along the sampler length and provided ~5cm resolution. They were directly pushed into the sediment. These samplers had been used to evaluate this site previously. We also used the sHRPP equilibrium cells to measure anions and general geochemical indicators (Cl^-, DOC, NO_2^-, NO_3^-, FeT, Fe^{+2}, SO_4^{-2}, and S^{-2}). As diffusion-based samplers are the accepted method for these species, we did not measure them by an alternate method.

We deployed 7 sHRPPs across two transects located across the river with predetermined sampling locations based on previous site evaluation and co-occurring re-evaluation by the EPA. We chose to deploy the samplers over a transect at set sampling locations to allow comparisons with data generated from these simultaneous sampling efforts by EPA. The transects also included known areas of historic pore water seepage. It should be noted that sediment concentrations and cap thickness can vary substantially over a meter. At each location where a sHRPP was deployed, EPA acquired sediment cores which were used to measure particle size, TOC, and PAHs. The cores were collected on sHRPP and T Bar retrieval to minimize disruption of the cap in the vicinity of the samplers. The cores were used to evaluate the depth of sediment above the cap material and the depth of cap material.

We anticipated that this data set would allow us to do the following:

1. Generate data to compare the cost and time required for each method.
2. Compare each technique's ability to acquire depth dependent non-altered data sets.
3. Allow direct comparisons of spatial profiles of PAH for each method and associated variance in concentration with depth.
4. Generate high spatial resolution geochemical indicator profiles (see above).
5. Measure fluxes and average pore velocities produced by seepage.
6. Compare model resolution and confidence for each method.

5.5.4 Field Testing

Field-testing the sHRPPs consisted of two mobilizations; the first to prepare and deploy the sHRPPs and T Bar samplers, and the second to retrieve and sample the sHRPPs and T Bar samplers.

All field activities were conducted in accordance with a site-specific APP/SSHP which was prepared by EPA as part of the overall site assessment activities, to ensure a safe work environment during the demonstration.

The sHRPPs and T Bar samplers were prepared on shore and carried to the site for installation. The sHRPPs were prepared by submerging in distilled water spiked with NaBr (100 mg/l-Br). The nylon membrane (0.2µm pore size) and nylon mesh (10µm pore size) were secured with the cover plates and the sampler stored (~up to 12 hours) submerged until deployment. SPME fibers (~8cm) pre-equilibrated with PRCs were placed over each equilibration cell, sandwiched between the nylon membrane and mesh, and secured using a trace of silicone. Water and additional SMPE fibers from the sHRPP preparation were subsampled to evaluate any pre-deployment contamination (see SOP Appendix C). See Appendix E4 for photographs of pre-deployment sHRPP preparation (Photos 1 and 2).

Each of the samplers was designed to assess pore water over an approximately 1.0 m vertical interval. Table 5.9 presents the total number and types of samples to be collected within the proposed test plots.

Table 5.9. Total Number and Types of Samples

Matrix	Number of sHRPPs / Samples per sHRPP	Total Number of Samples	Analyte	Location
Transect 1				
sHRPP SPME Fiber	4/ 30	120	PAHs	WT-01 to WT-04
sHRPP Pore Water	4 / 27 4/ 4	92 64	Anions Pore Water Velocity	
in-situ SPME Sampling (T Bar)	4/ 7	28	PAHs	
Transect 2				
sHRPP SPME Fiber	3/ 16	48	PAHs	ET-02 to ET -04
sHRPP Pore Water	3 / 24 3/ 4	72 12	Anions Pore Water Velocity	
in-situ SPME Sampling (T Bar)	3 / 7	21	PAHs	

To deploy the samplers, a rope was first attached to the hole machined into the top of the sampler. An extension rod was then positioned over the top of the sampler (not connected to the sampler), and the unit was pushed/driven into the cap/underlying sediment to the proper depth. The extension rod was then removed, and a marker buoy was attached to the tag end of the rope to assist in locating the sampler during retrieval. The samplers remained in the cap/sediment for approximately four weeks. See Appendix E4 for photographs of sHRPP deployment activities (Photos 3-8).

5.5.5 Sampling Methods

5.5.5.1 sHRPP and T Bar Retrieval and Sampling

After approximately four weeks of equilibration, the samplers were removed by hand pulling. The samplers were removed to a nearby enclosed area with tables to aid in the sampling process (See Appendix E4 for photographs of sHRPP retrieval and sampling activities (Photos 9-12)). The equilibration cells and velocity cells were sampled first. A pre-cleaned glass syringe with 18-gauge needle was inserted through the membrane and water removed by suction. A second needle was placed through the membrane to relieve any vacuum and prevent any outside water from being pulled through the membrane. Water from each cell was placed in an appropriate container, as summarized in Table 5.10, for analysis of anions (Cl^-, NO_2^-, NO_3^-, SO_4^{-2}), and DOC.

After the equilibration cells were sampled, the velocity cells were sampled in a similar manner with the total volume of each cell placed in a separate glass vial for Br^- analysis. SPME fibers were retrieved by removing the top cover plate and pulling off the protective nylon mesh while retrieving the fibers with tweezers as each cell was uncovered. The SPME fibers were gently rinsed in DI water and placed in vials prefilled with solvent, which was then used for PAH analysis. The SPME fiber from the T Bar sampler was sampled by removing the fiber from the vertical slot, gently rinsing with water and sectioning in ~2cm increments. Each 2cm increment was placed in hexane in the field and shipped on ice in a cooler under proper COC to Texas Tech.

Table 5.10. Sample Analytical Methods, Volume, Preservation, and Containers

Analyte	Method/ Laboratory	Sample Volume	Preservative	Bottle
PAHs	EPA 8310 or 8270 Texas Tech	SPME	4°C	5 mL glass vial w/ hexane (x1)
Anions (Br^-, NO_2^-, NO_3^-, SO_4^{-2})	EPA 300.0 Texas Tech	2 mL	4°C	5 mL glass vial (x1)

5.5.6 Sampling Results

Results are presented in the following subsections, followed by an overall site evaluation. Laboratory analytical results are tabulated in Appendix F4.

5.5.6.1 Transport Indicators

Chloride concentrations in surface water were different for the ET and WT. The WT Cl^- concentrations were ~20 mg/l higher probably due to the near-by wastewater effluent outfall (see Figure 5.66). Concentration profiles for both transects increased from the sediment interface to a depth of 20 cm (ET) or 30 cm BSI (WT) and then remained relatively constant (~100-120 mg/l) at deeper depths. The profiles are consistent with groundwater upwelling and a zone of mixing in the top ~20 cm. This is supported by transport modeling discussed later (Section 5.5.7). Based on core data the cap thickness is greater than 30 cm in both transects. One location ET-04 closest to the bank has a unique profile in which at depths below 20 cm, the Cl^- concentration decreased. This is most probably due to infiltration of precipitation from the bank into the shallow sediment due to bank drainage.

Pore velocity measurements show relatively uniform velocities (5-10 cm/d) for depths less than 20 cm (Figure 5.67). At shallower depths velocities are much higher but this is due to rapid pore exchange with surface water from other processes (e.g., bioturbation) and low sediment densities in the very near surface (fluff layer) or even open water. Overall, the velocities are comparable to those reported for these transects historically. The fraction of steady state reached in each compartment is compatible with the velocity measurements. The fss values ranged from near 1 to 0.7 in the ET and 1 to 0.6 in the WT.

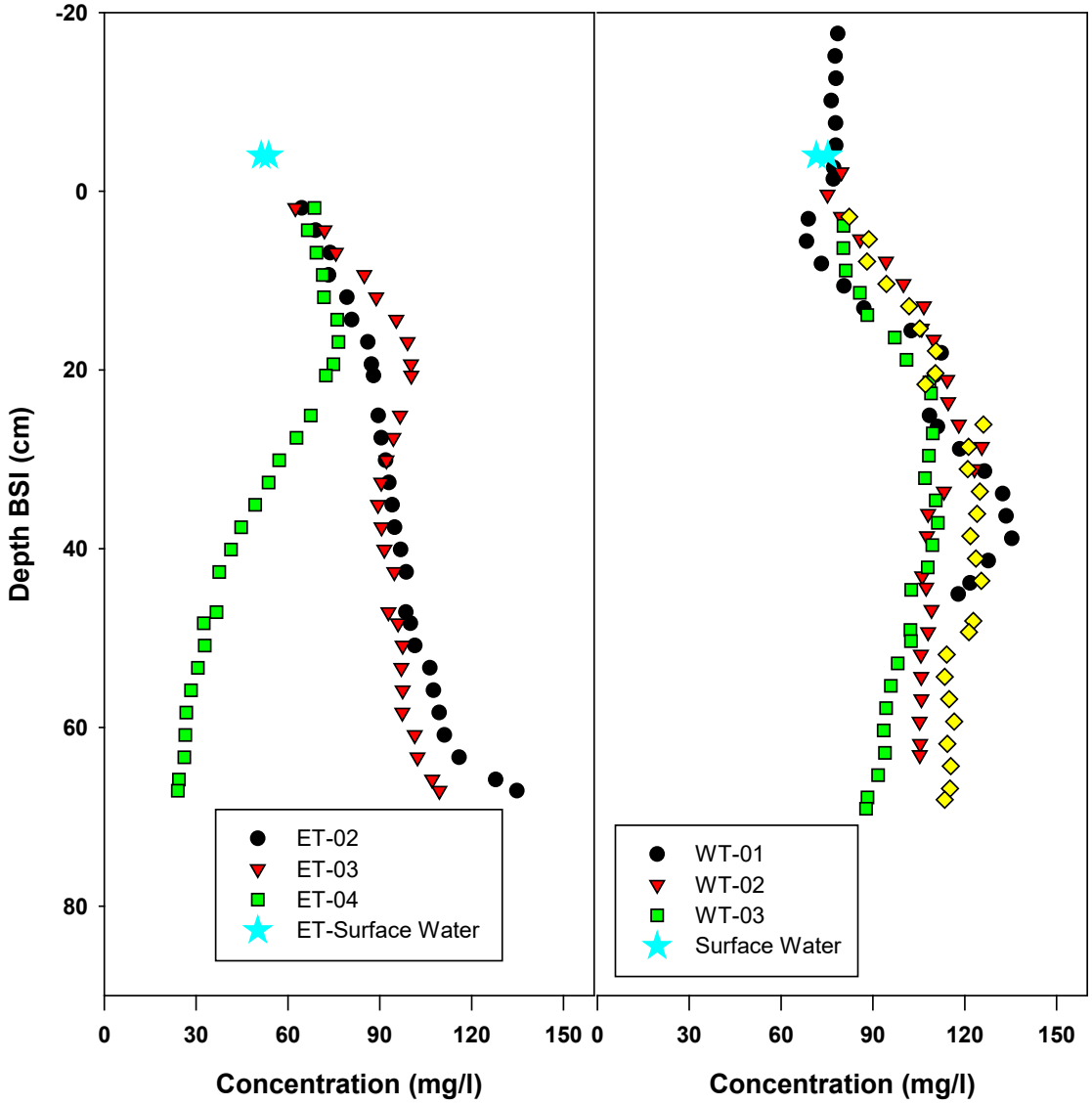


Figure 5.66. Chloride Concentration Profiles Across the ET and WT

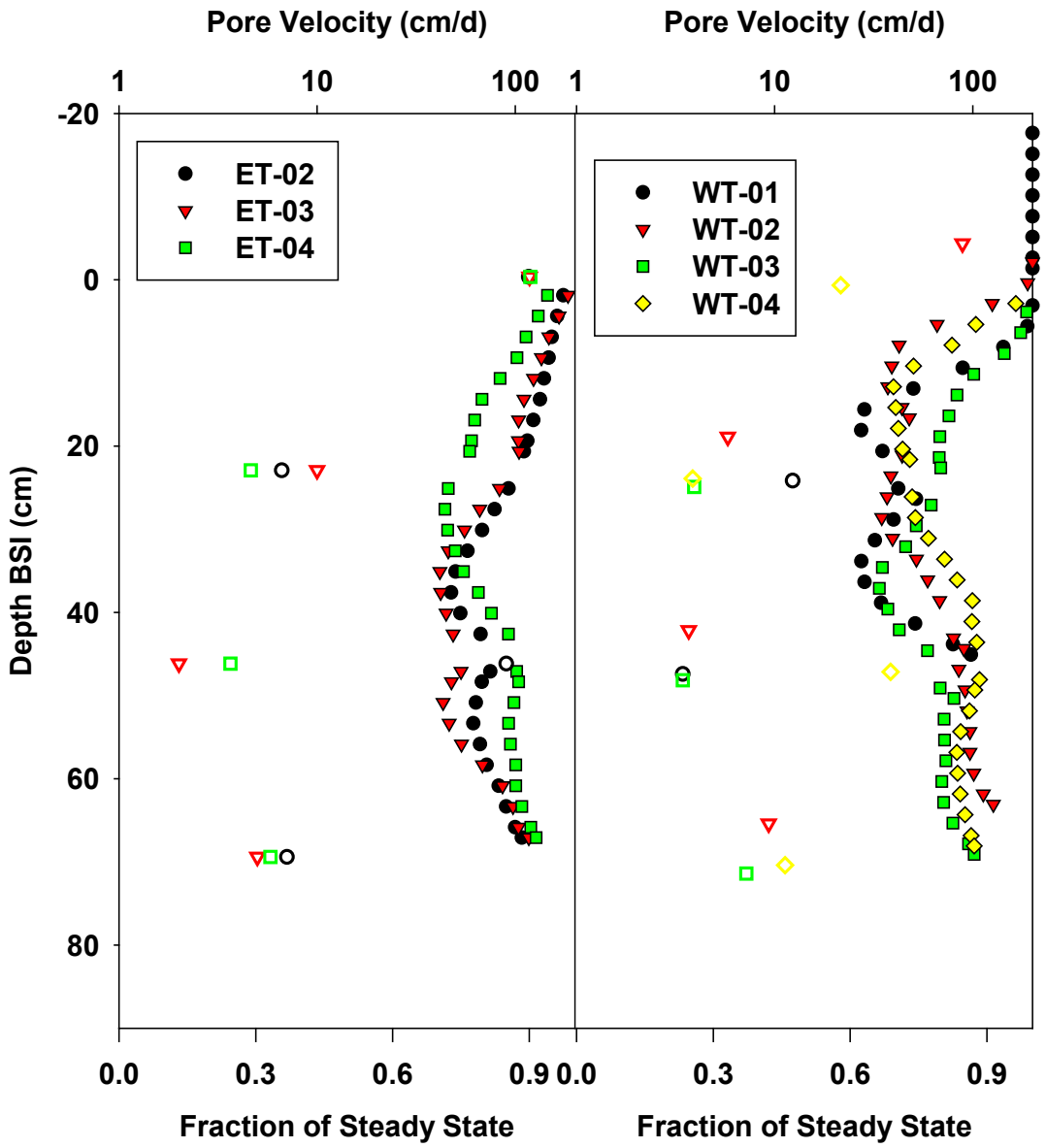


Figure 5.67. Porewater Velocities (Open Symbols) and fss Values (Filled Symbols) Across the ET and WT

5.5.6.2 Geochemical Indicators

Nitrate concentrations in surface water were ~2-3 mg/l as N. Concentrations in sediment were less than 0.5 mg/l (DL). Sulfate concentrations in the ET and WT surface water were 57 and 65 mg/l, respectively (Figure 5.68). Across the ET, sulfate concentrations were reduced to background within 2cm of the sediment surface interface. Across the WT sulfate concentrations were reduced to background within 10 cm of the sediment interface. Fe, S^{-2}, and methane were not measured at this site due to resource limitations but from the rapid loss of both nitrate and sulfate, it is clear that the sediments are highly reducing, and that sulfate reduction is active in the very near surface sediment while methanogenesis most probably dominates at lower depths.

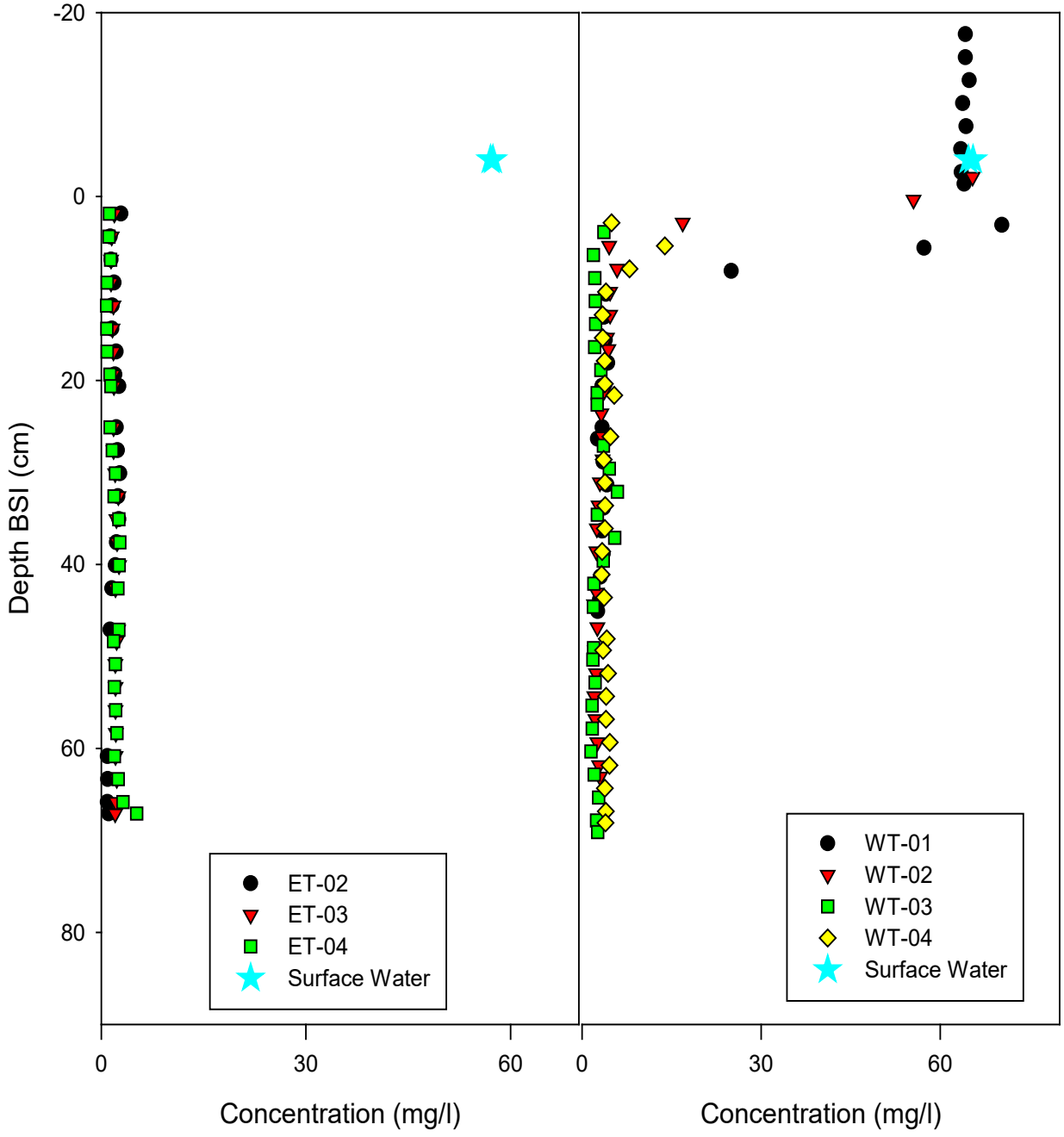


Figure 5.68. Distribution of Sulfate with Depth Across Each Transect

5.5.6.3 PAH Porewater Concentrations

PAH porewater concentrations were simultaneously evaluated with geochemical indicators and transport parameters using the sHRPP. In addition, porewater concentrations were also evaluated by co-located passive samplers including T-Bar samplers using SPME and PE sheet samplers. PE samplers were deployed by Battelle as part of an EPA study. In addition, the EPA study collected cores at each location at which sHRPP were deployed and the cores were sectioned and analyzed for sediment concentrations of each PAH as well as organic carbon content. Core data was used to estimate cap thickness and to calculate predicted porewater concentrations. The predicted porewater concentrations from each type of passive sampler are displayed for each individual PAH for the ET (Figures 5.69 through 5.79) and WT (Figures 5.80 through 5.90), separately. In addition to the PAH porewater concentrations, the estimated depth of the cap is shown at each location (red lines) based on the core interval in which contaminated sediment was identified. In addition, as core recovery was almost always less than the total core length, we also show the potential depth interval based on uncertainty due to core recovery (grey lines). Finally, we also present the sum of all PAH measured for each passive sampler with depth for the ET and WT, along with the sum of PAH measured as sediment concentrations (Figures 5.91 and 5.92, respectively). We first compare concentration distributions between each sampling method and then discuss the interpretation of the data. PE samplers had the lowest detection limits, followed by sHRPP and then T-Bar samplers.

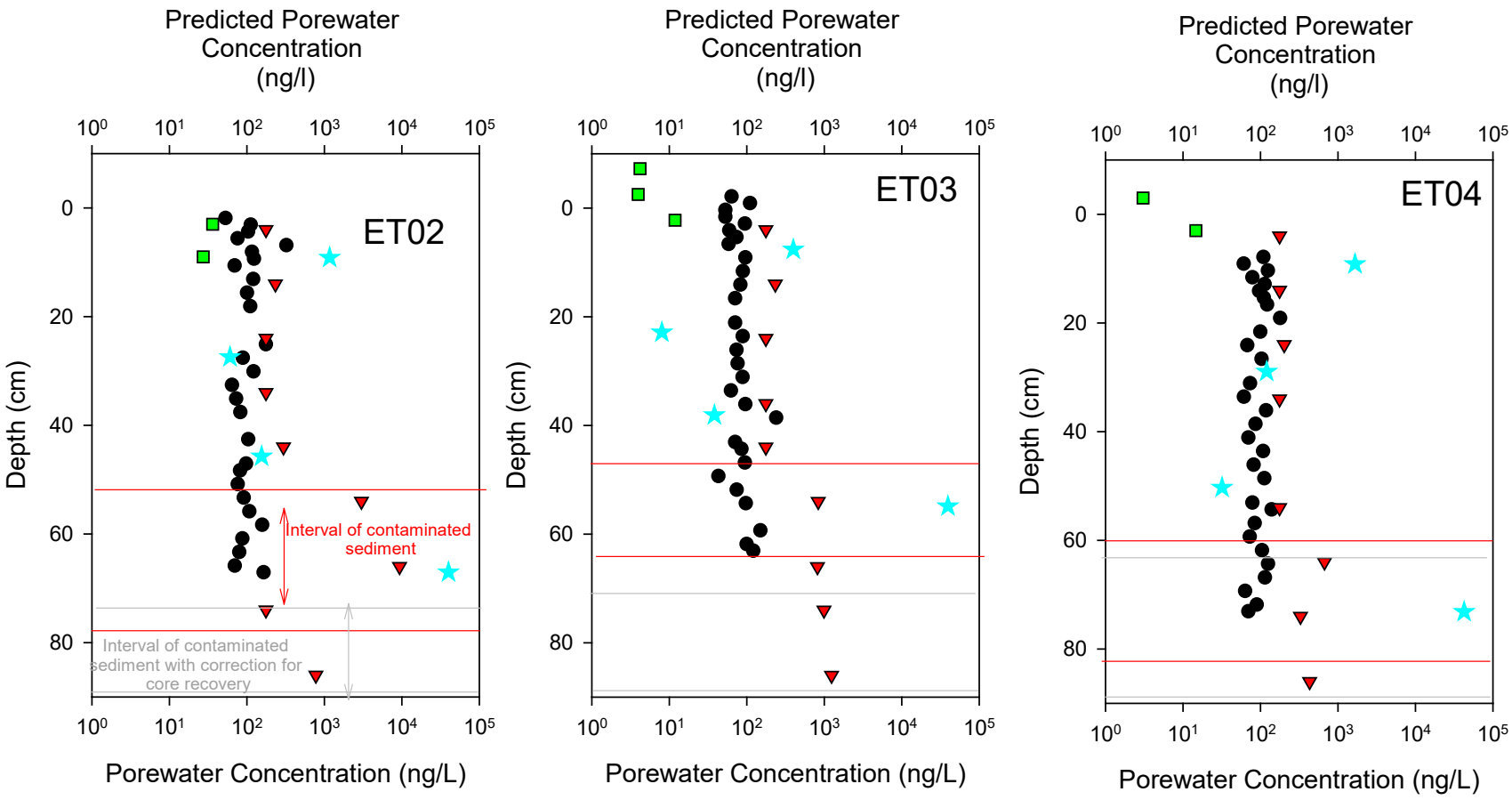


Figure 5.69. Fluorene Porewater Concentration Depth Distribution Across the East Transect

Fluorene porewater concentration depth distribution across the East Transect for sHRPP (black circles), T-Bar (red triangles), PE (green squares), and predicted porewater concentrations based on Koc and measured PAH and organic carbon concentration sediment concentration (blue stars). Red lines denote the core interval identified as including sediment below the cap. Grey lines denote the potential maximum depth interval identified as including sediment below the cap based on core recovery.

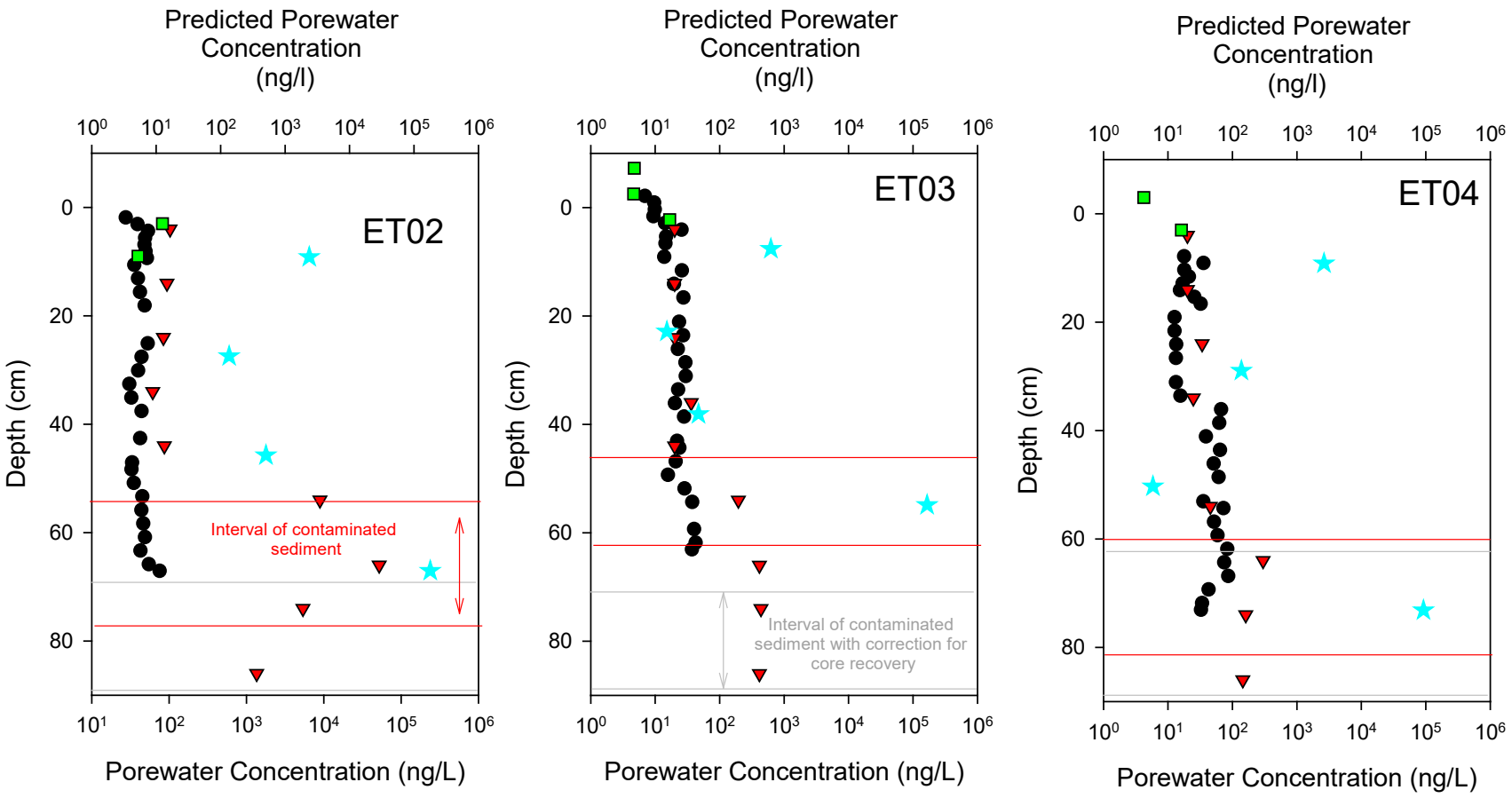


Figure 5.70. Phenanthrene Porewater Concentration Depth Distribution Across the East Transect

Phenanthrene porewater concentration depth distribution across the East Transect for sHRPP (black circles), T-Bar (red triangles), PE (green squares), and predicted porewater concentrations based on Koc and measured PAH and organic carbon concentration sediment concentration (blue stars). Red lines denote the core interval identified as including sediment below the cap. Grey lines denote the potential maximum depth interval identified as including sediment below the cap based on core recovery.

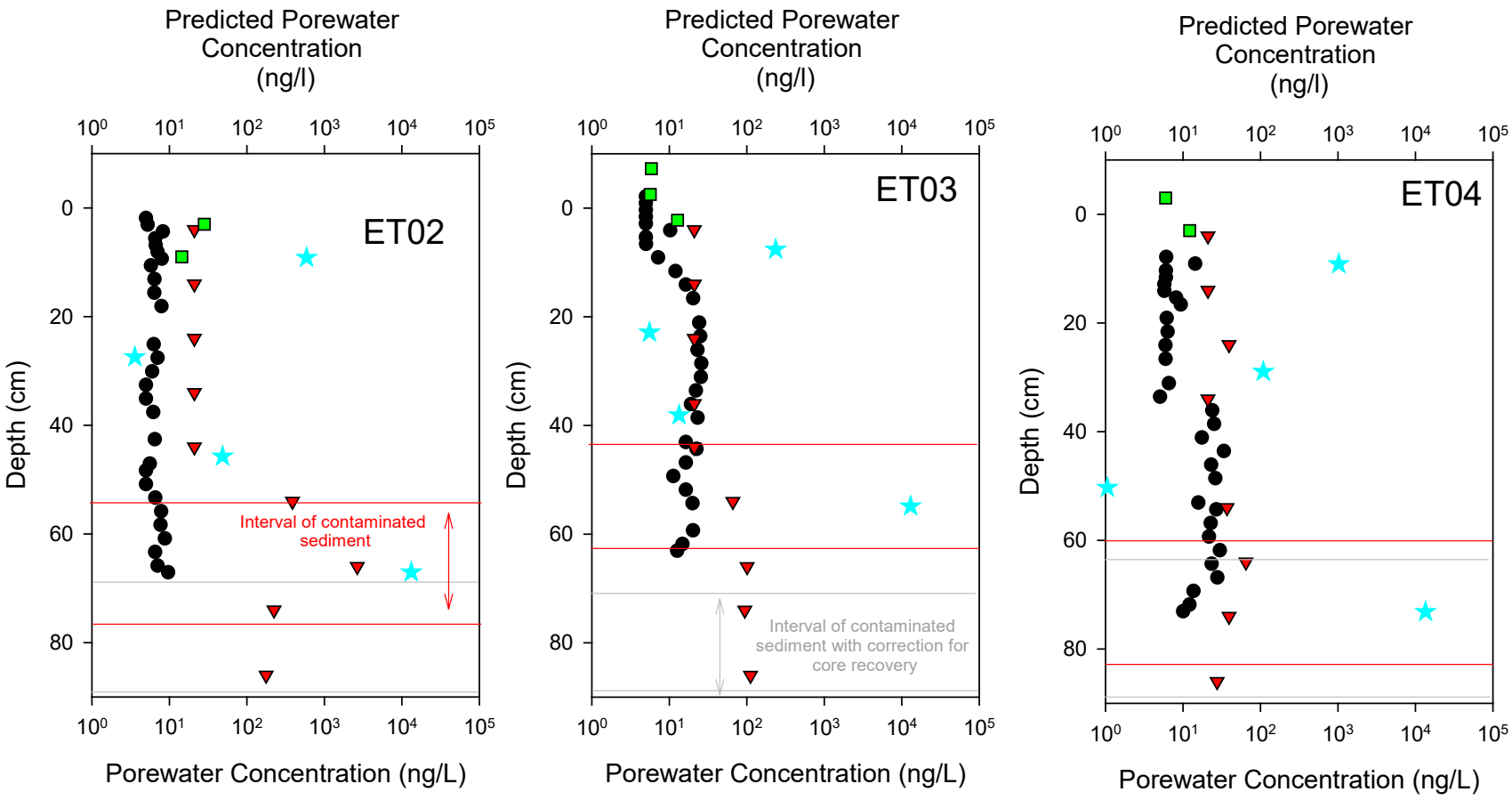


Figure 5.71. Anthracene Porewater Concentration Depth Distribution Across the East Transect

Anthracene porewater concentration depth distribution across the East Transect for sHRPP (black circles), T-Bar (red triangles), PE (green squares), and predicted porewater concentrations based on Koc and measured PAH and organic carbon concentration sediment concentration (blue stars). Red lines denote the core interval identified as including sediment below the cap. Grey lines denote the potential maximum depth interval identified as including sediment below the cap based on core recovery.

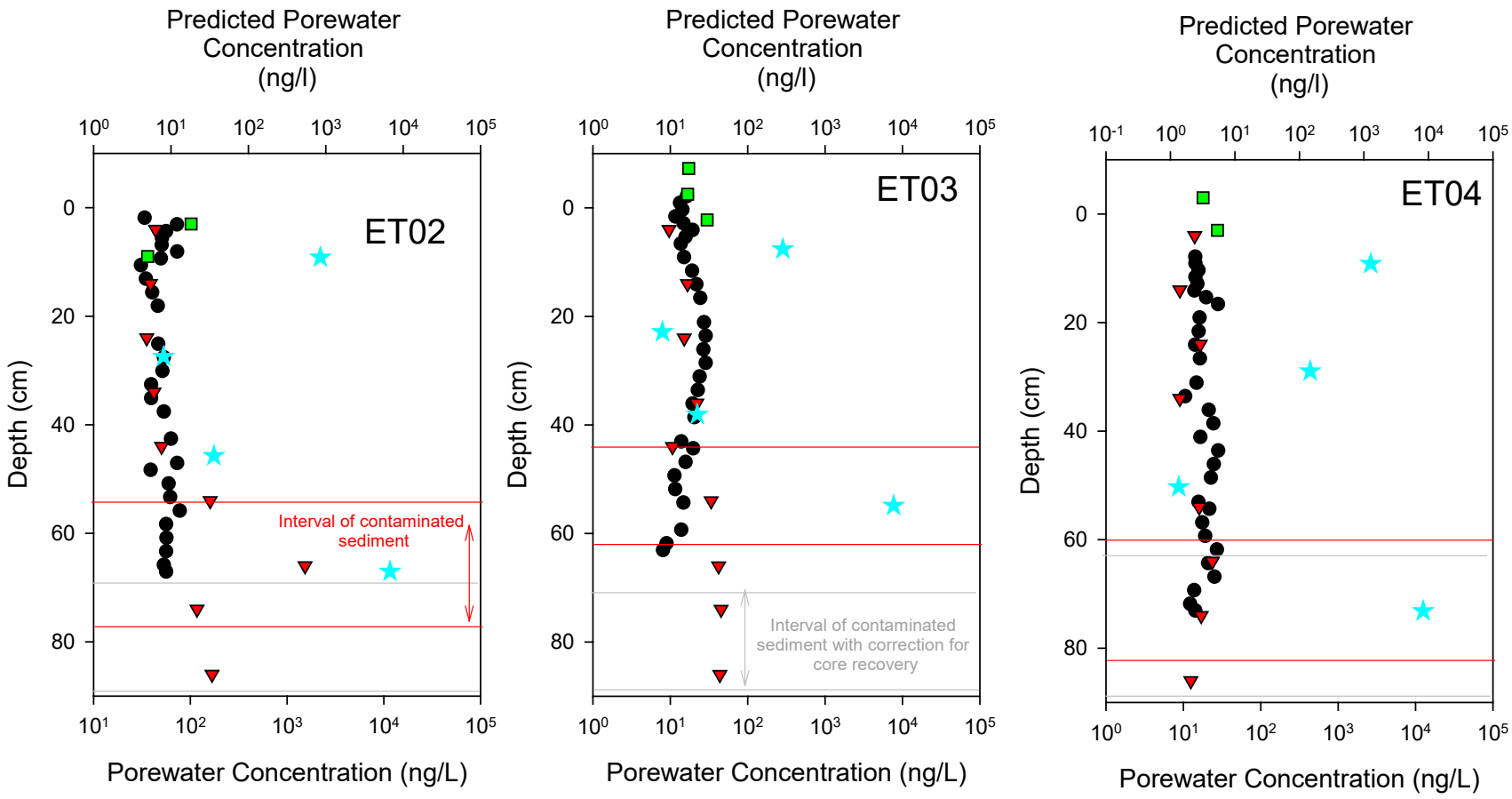


Figure 5.72. Fluoranthracene Porewater Concentration Depth Distribution Across the East Transect

Fluoranthracene porewater concentration depth distribution across the East Transect for sHRPP (black circles), T-Bar (red triangles), PE (green squares), and predicted porewater concentrations based on Koc and measured PAH and organic carbon concentration sediment concentration (blue stars). Red lines denote the core interval identified as including sediment below the cap. Grey lines denote the potential maximum depth interval identified as including sediment below the cap based on core recovery.

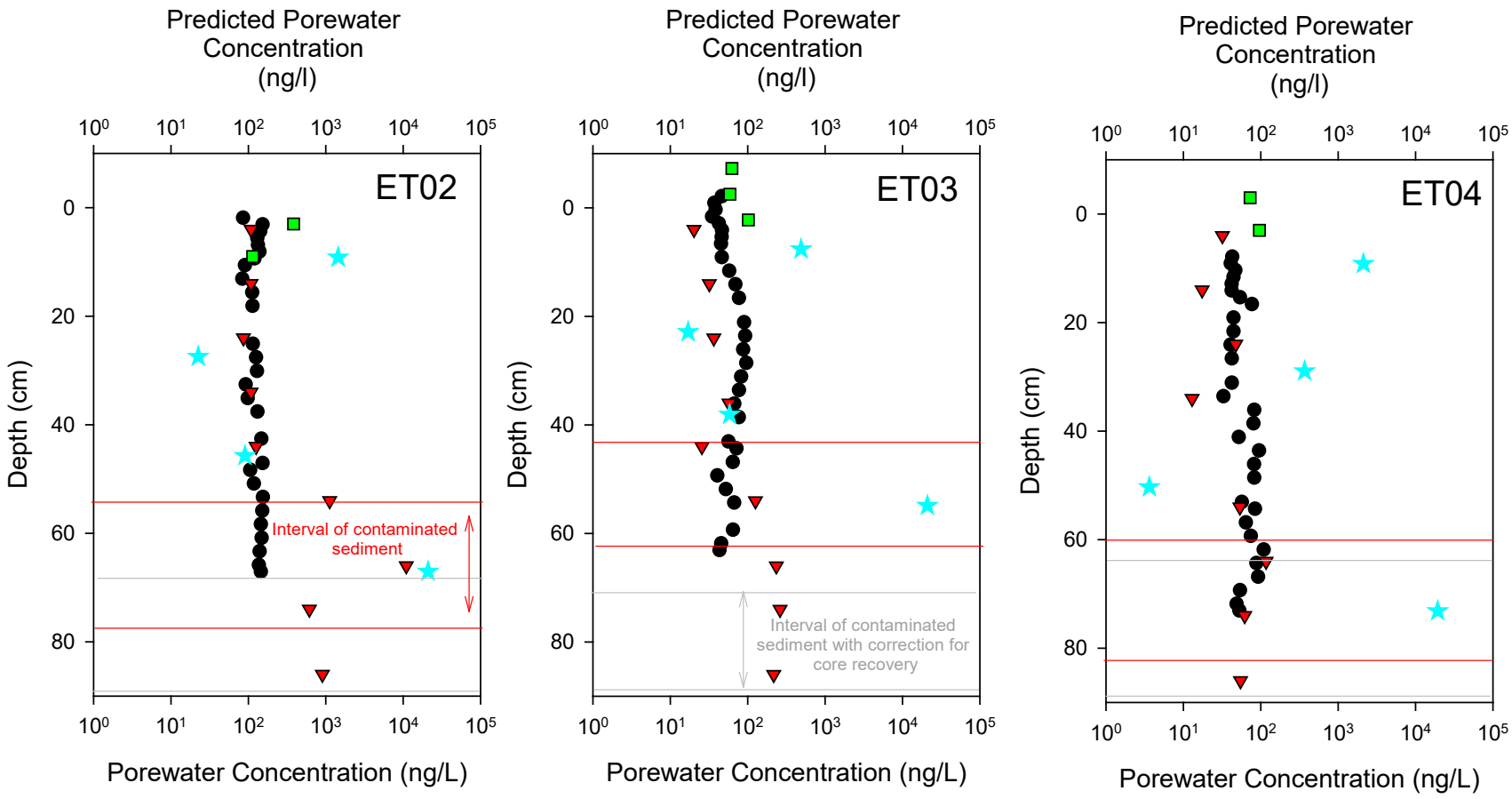


Figure 5.73. Pyrene Porewater Concentration Depth Distribution Across the East Transect

Pyrene porewater concentration depth distribution across the East Transect for sHRPP (black circles), T-Bar (red triangles), PE (green squares), and predicted porewater concentrations based on Koc and measured PAH and organic carbon concentration sediment concentration (blue stars). Red lines denote the core interval identified as including sediment below the cap. Grey lines denote the potential maximum depth interval identified as including sediment below the cap based on core recovery.

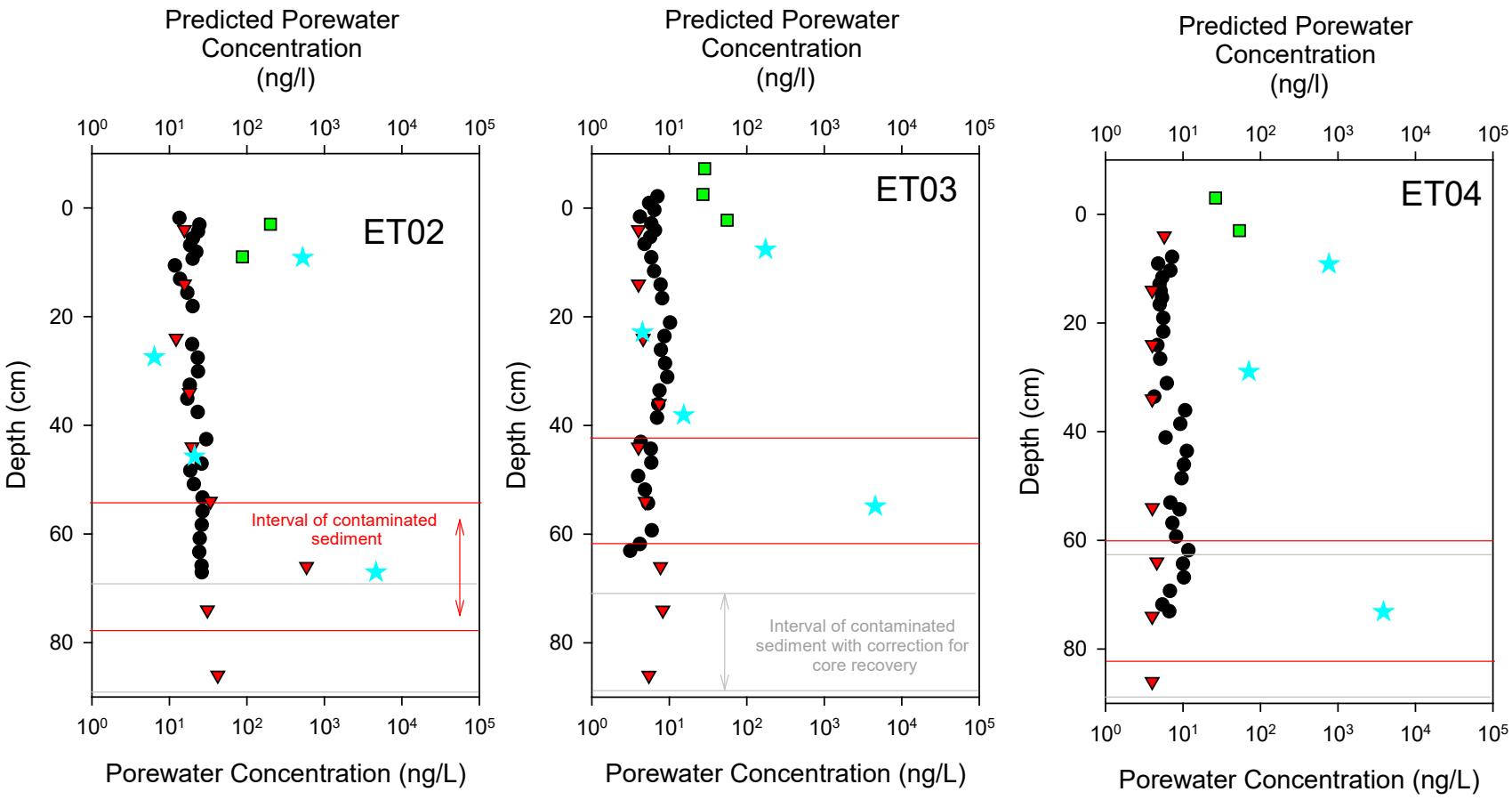


Figure 5.74. Chrysene Porewater Concentration Depth Distribution Across the East Transect

Chrysene porewater concentration depth distribution across the East Transect for sHRPP (black circles), T-Bar (red triangles), PE (green squares), and predicted porewater concentrations based on Koc and measured PAH and organic carbon concentration sediment concentration (blue stars). Red lines denote the core interval identified as including sediment below the cap. Grey lines denote the potential maximum depth interval identified as including sediment below the cap based on core recovery.

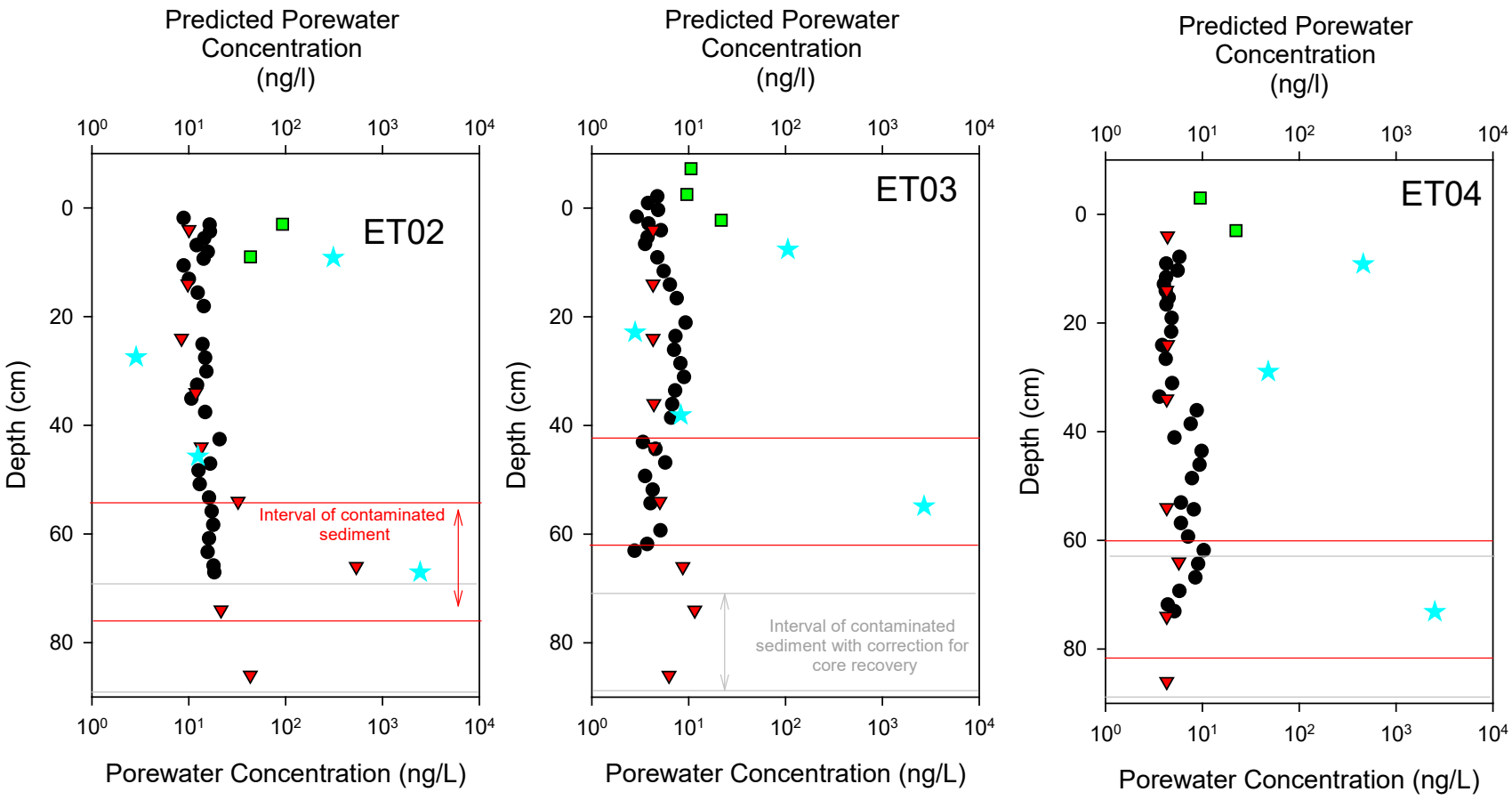


Figure 5.75. Benzo(a)anthracene Porewater Concentration Depth Distribution Across the East Transect

Benzo(a)anthracene porewater concentration depth distribution across the East Transect for sHRPP (black circles), T-Bar (red triangles), PE (green squares), and predicted porewater concentrations based on Koc and measured PAH and organic carbon concentration sediment concentration (blue stars). Red lines denote the core interval identified as including sediment below the cap. Grey lines denote the potential maximum depth interval identified as including sediment below the cap based on core recovery.

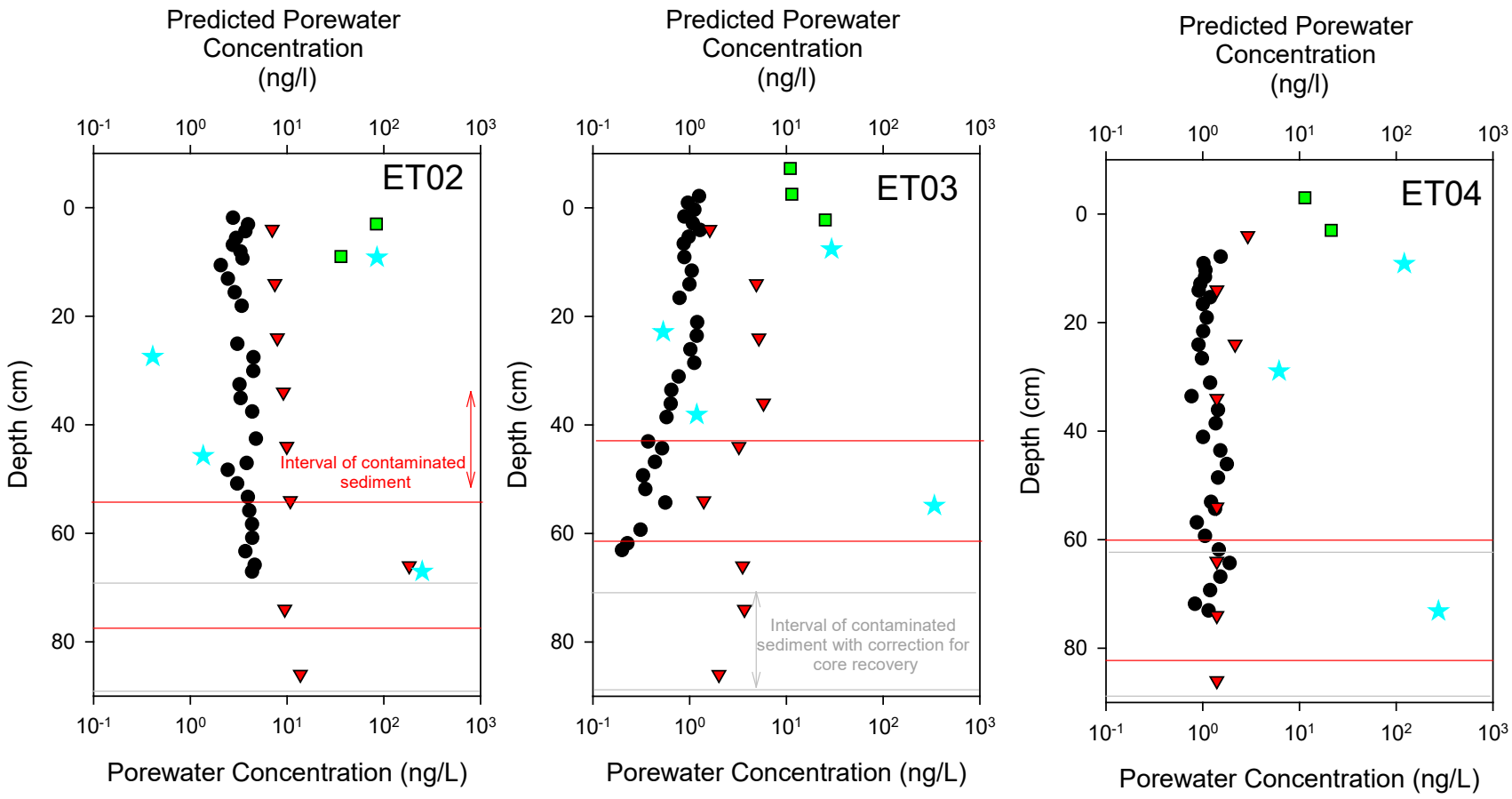


Figure 5.76. Benzo(b)fluoranthene Porewater Concentration Depth Distribution Across the East Transect

Benzo(b)fluoranthene porewater concentration depth distribution across the East Transect for sHRPP (black circles), T-Bar (red triangles), PE (green squares), and predicted porewater concentrations based on Koc and measured PAH and organic carbon concentration sediment concentration (blue stars). Red lines denote the core interval identified as including sediment below the cap. Grey lines denote the potential maximum depth interval identified as including sediment below the cap based on core recovery.

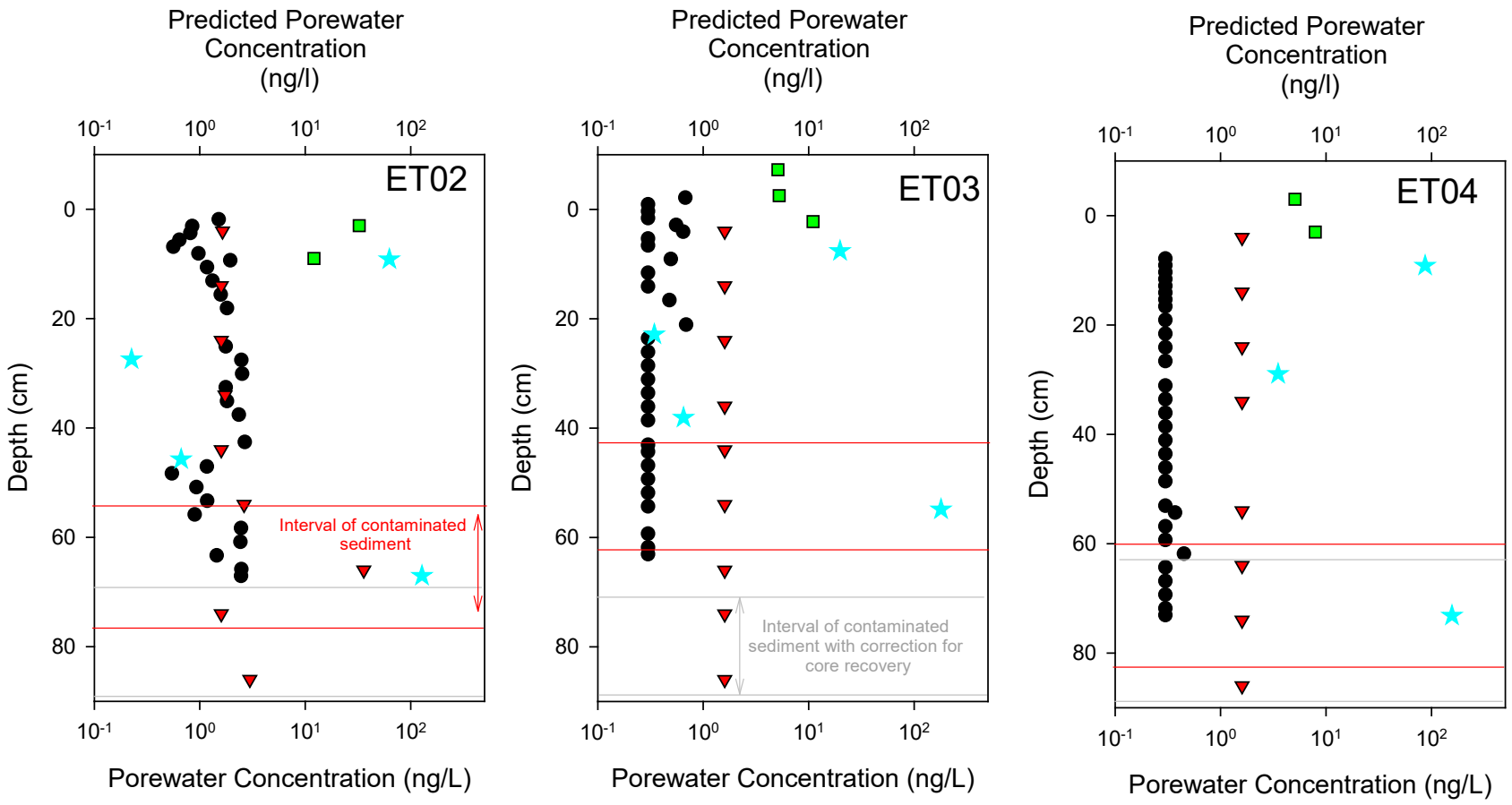


Figure 5.77. Benzo(k)fluoranthene Porewater Concentration Depth Distribution Across the East Transect

Benzo(k)fluoranthene porewater concentration depth distribution across the East Transect for sHRPP (black circles), T-Bar (red triangles), PE (green squares), and predicted porewater concentrations based on Koc and measured PAH and organic carbon concentration sediment concentration (blue stars). Red lines denote the core interval identified as including sediment below the cap. Grey lines denote the potential maximum depth interval identified as including sediment below the cap based on core recovery.

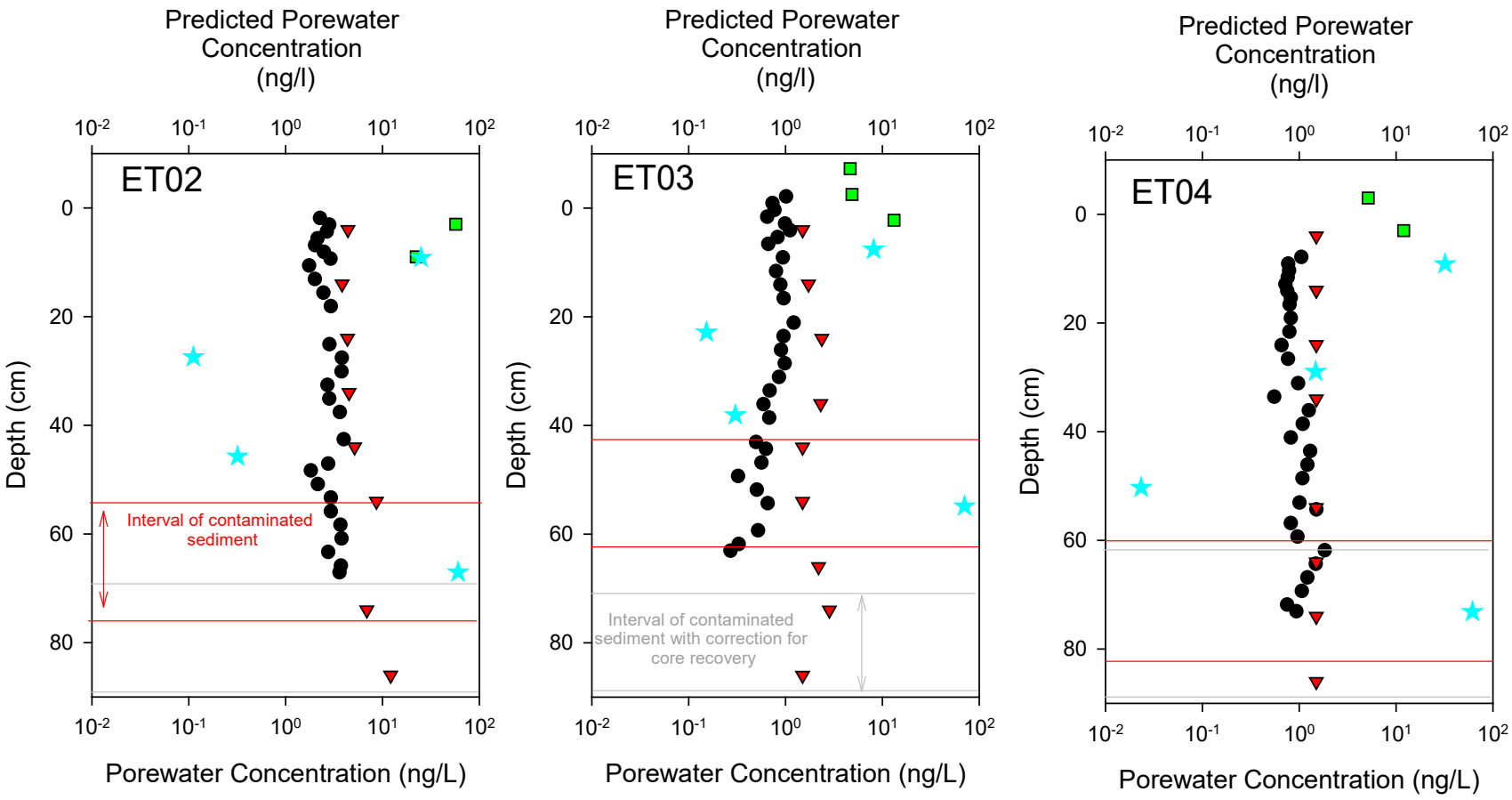


Figure 5.78. Benzo(a)pyrene Porewater Concentration Depth Distribution Across the East Transect

Benzo(a)pyrene porewater concentration depth distribution across the East Transect for sHRPP (black circles), T-Bar (red triangles), PE (green squares), and predicted porewater concentrations based on Koc and measured PAH and organic carbon concentration sediment concentration (blue stars). Red lines denote the core interval identified as including sediment below the cap. Grey lines denote the potential maximum depth interval identified as including sediment below the cap based on core recovery.

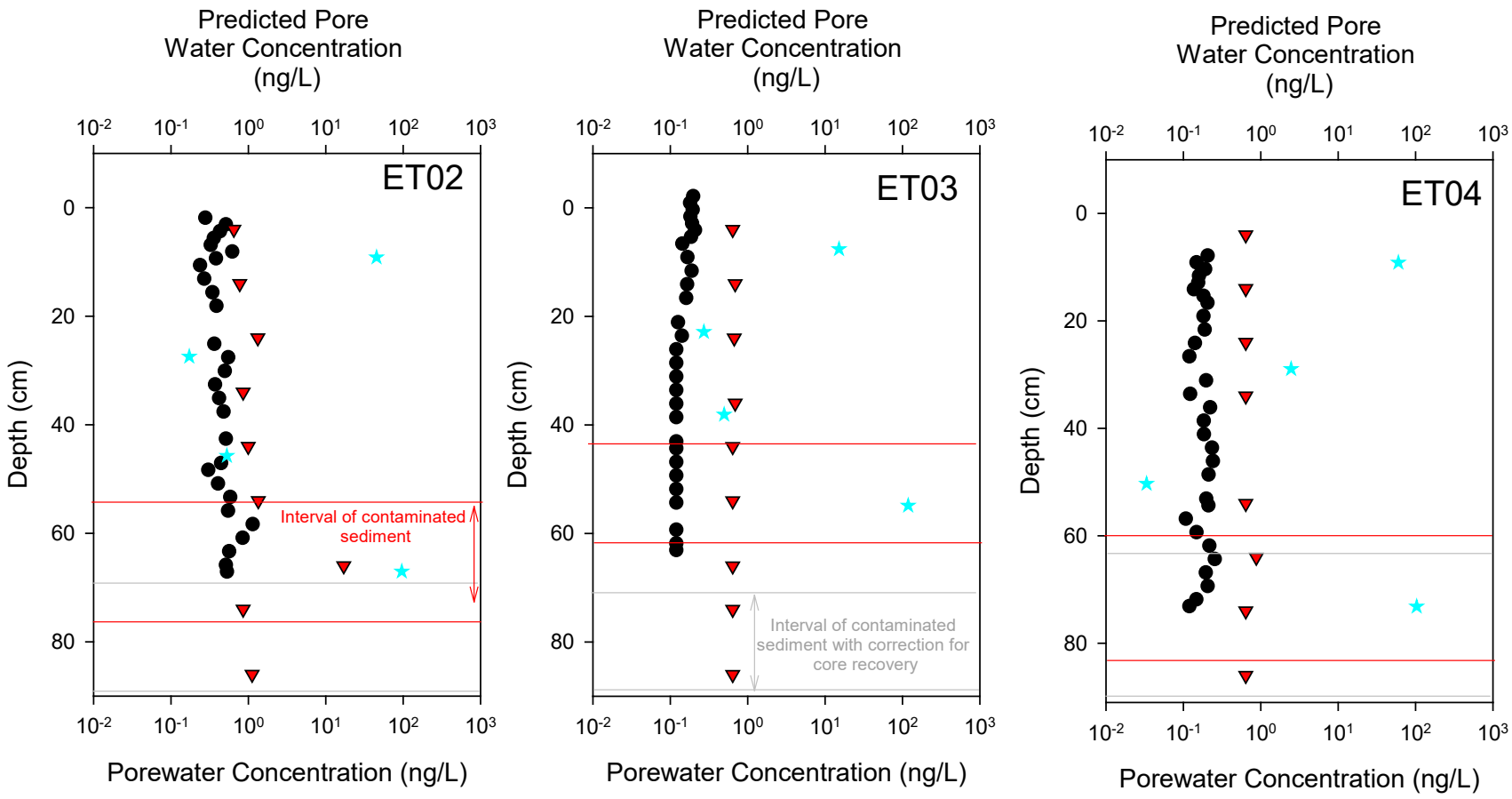


Figure 5.79. Benzo(ghi)perylene + Indenpyrene Porewater Concentration Depth Distribution Across the East Transect

Benzo(ghi)perylene + Indenpyrene porewater concentration depth distribution across the East Transect for sHRPP (black circles), T-Bar (red triangles), PE (green squares), and predicted porewater concentrations based on Koc and measured PAH and organic carbon concentration sediment concentration (blue stars). Red lines denote the core interval identified as including sediment below the cap. Grey lines denote the potential maximum depth interval identified as including sediment below the cap based on core recovery.

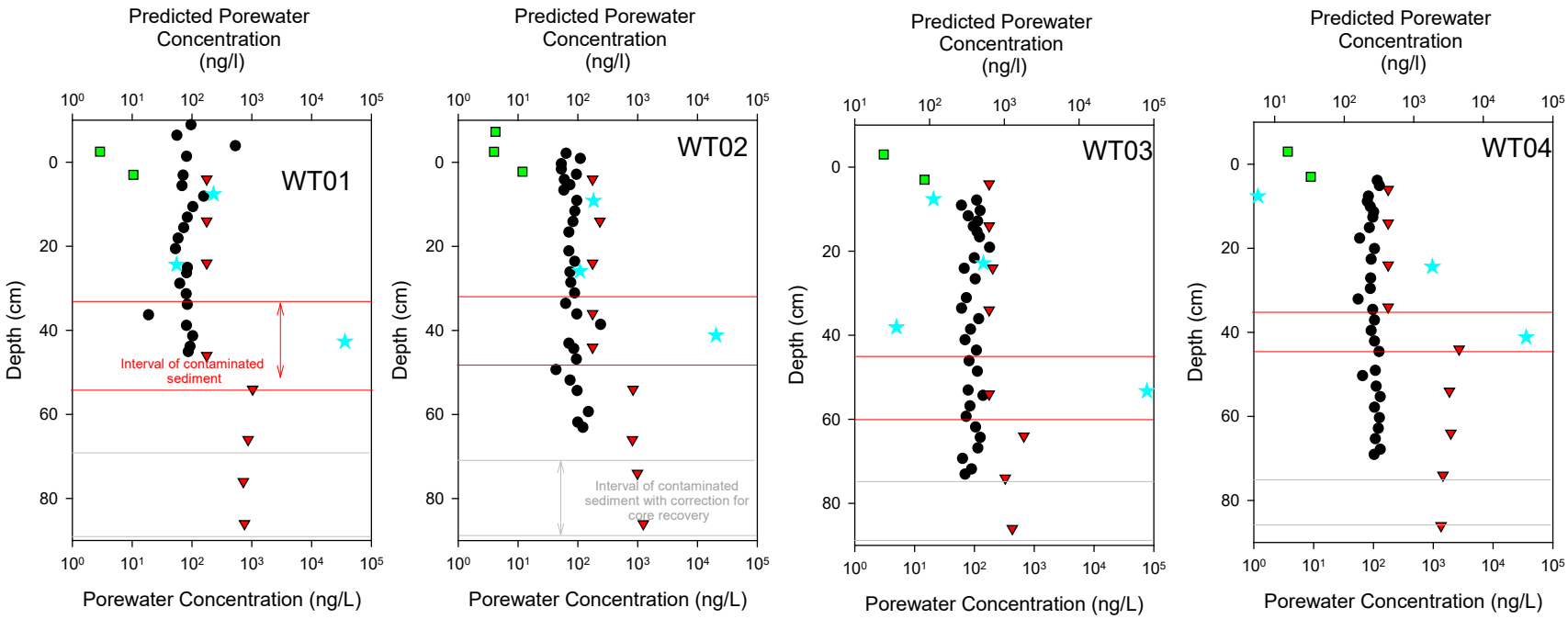


Figure 5.80. Fluorene Porewater Concentration Depth Distribution Across the West Transect

Fluorene porewater concentration depth distribution across the West Transect for sHRPP (black circles), T-Bar (red triangles), PE (green squares), and predicted porewater concentrations based on Koc and measured PAH and organic carbon concentration sediment concentration (blue stars). Red lines denote the core interval identified as including sediment below the cap. Grey lines denote the potential maximum depth interval identified as including sediment below the cap based on core recovery.

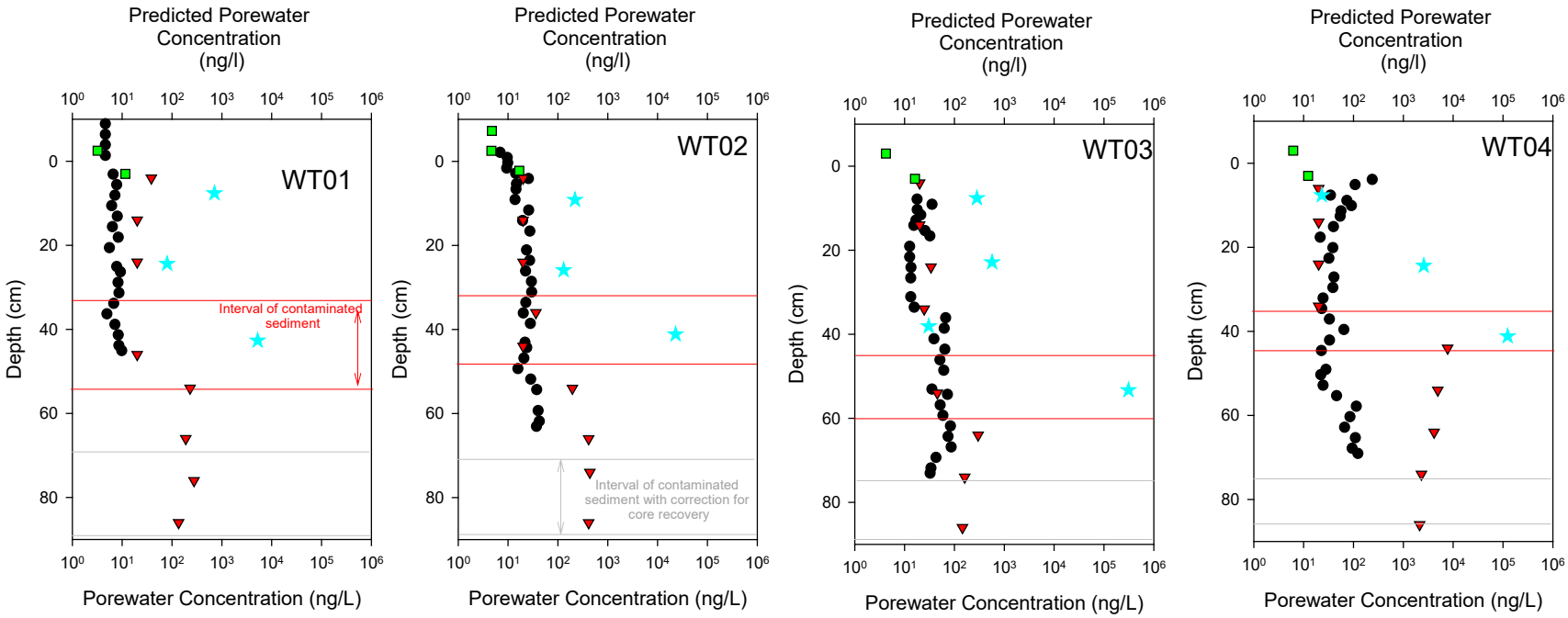


Figure 5.81. Phenanthrene Porewater Concentration Depth Distribution Across the West Transect

Phenanthrene porewater concentration depth distribution across the West Transect for sHRPP (black circles), T-Bar (red triangles), PE (green squares), and predicted porewater concentrations based on Koc and measured PAH and organic carbon concentration sediment concentration (blue stars). Red lines denote the core interval identified as including sediment below the cap. Grey lines denote the potential maximum depth interval identified as including sediment below the cap based on core recovery.

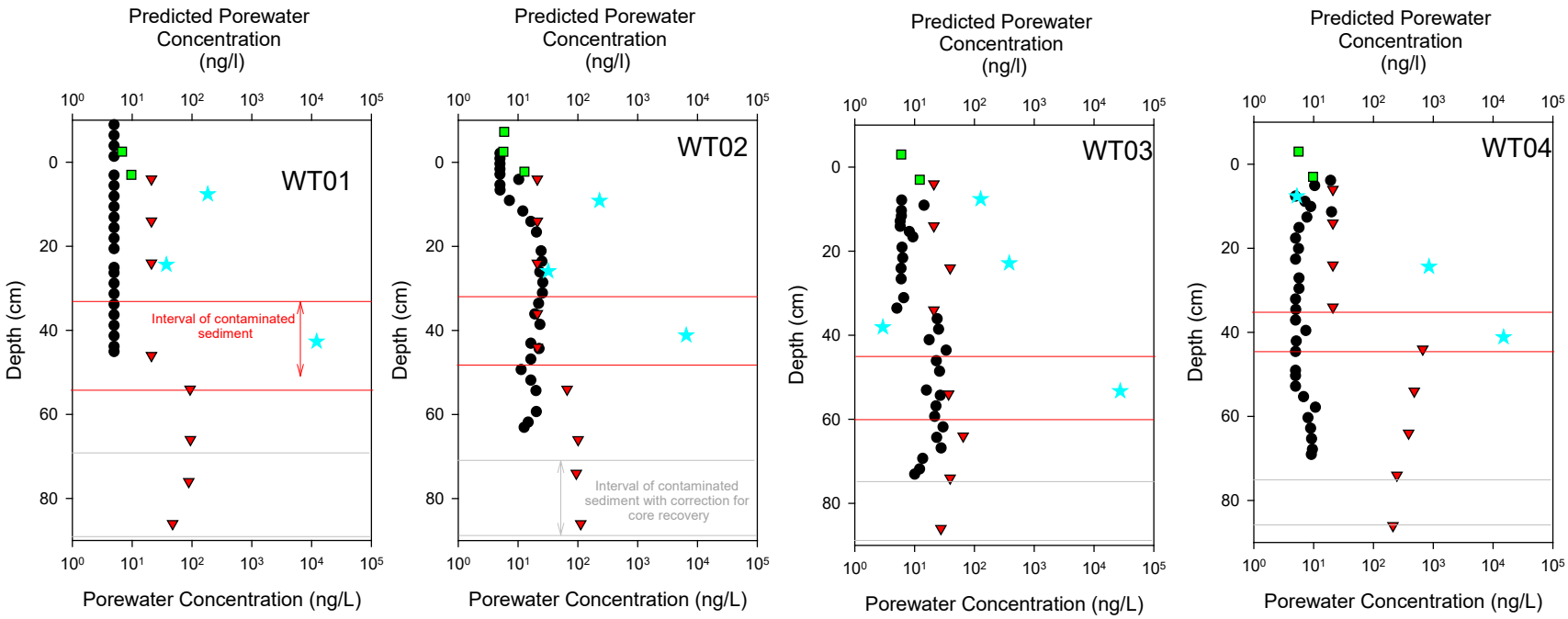


Figure 5.82. Anthracene Porewater Concentration Depth Distribution Across the West Transect

Anthracene porewater concentration depth distribution across the West Transect for sHRPP (black circles), T-Bar (red triangles), PE (green squares), and predicted porewater concentrations based on Koc and measured PAH and organic carbon concentration sediment concentration (blue stars). Red lines denote the core interval identified as including sediment below the cap. Grey lines denote the potential maximum depth interval identified as including sediment below the cap based on core recovery.

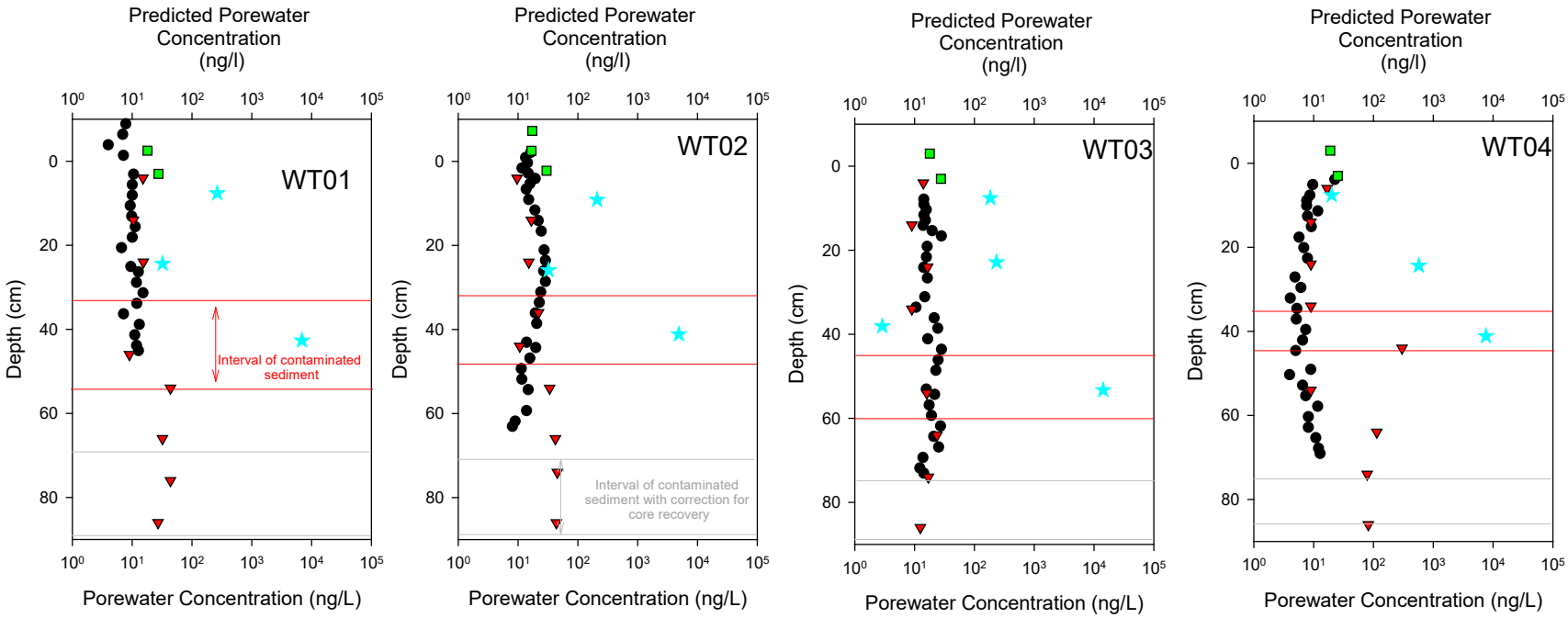


Figure 5.83. Fluoranthracene Porewater Concentration Depth Distribution Across the West Transect

Fluoranthracene porewater concentration depth distribution across the West Transect for sHRPP (black circles), T-Bar (red triangles), PE (green squares), and predicted porewater concentrations based on Koc and measured PAH and organic carbon concentration sediment concentration (blue stars). Red lines denote the core interval identified as including sediment below the cap. Grey lines denote the potential maximum depth interval identified as including sediment below the cap based on core recovery.

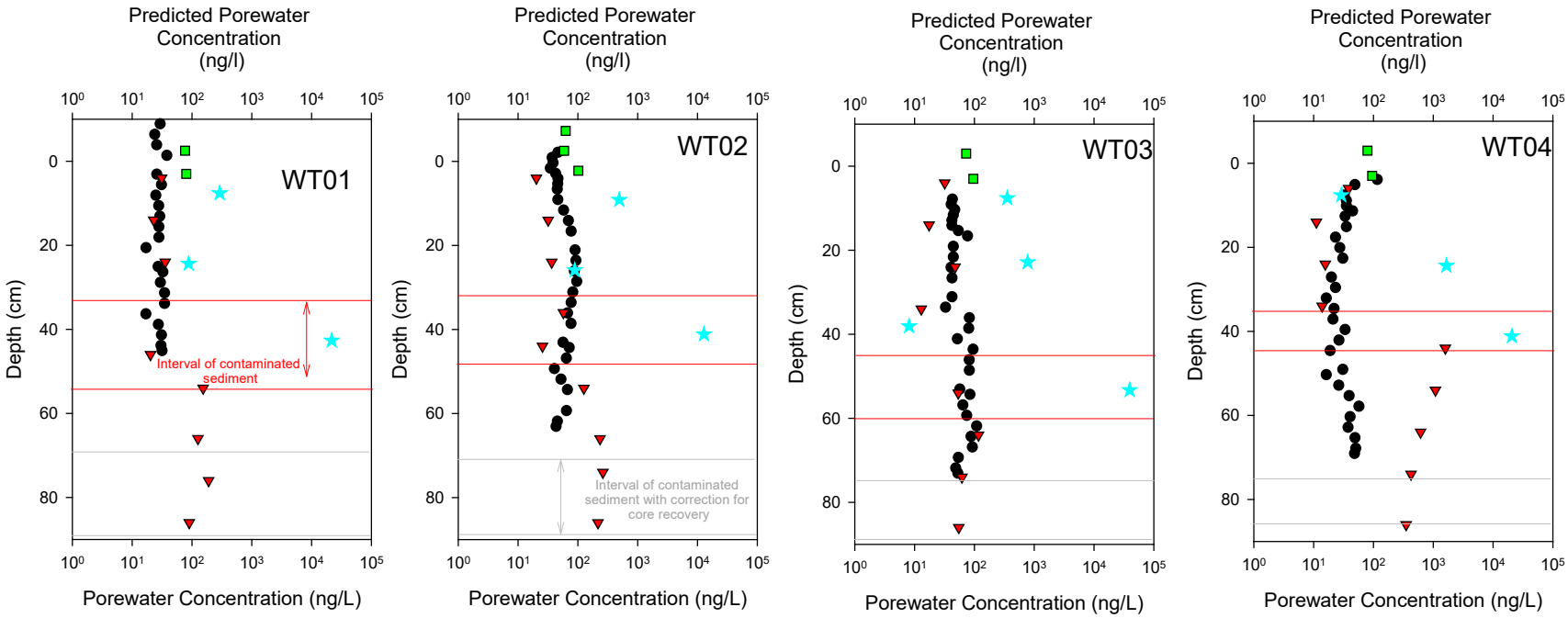


Figure 5.84. Pyrene porewater Concentration Depth Distribution Across the West Transect

Pyrene porewater concentration depth distribution across the West Transect for sHRPP (black circles), T-Bar (red triangles), PE (green squares), and predicted porewater concentrations based on Koc and measured PAH and organic carbon concentration sediment concentration (blue stars). Red lines denote the core interval identified as including sediment below the cap. Grey lines denote the potential maximum depth interval identified as including sediment below the cap based on core recovery.

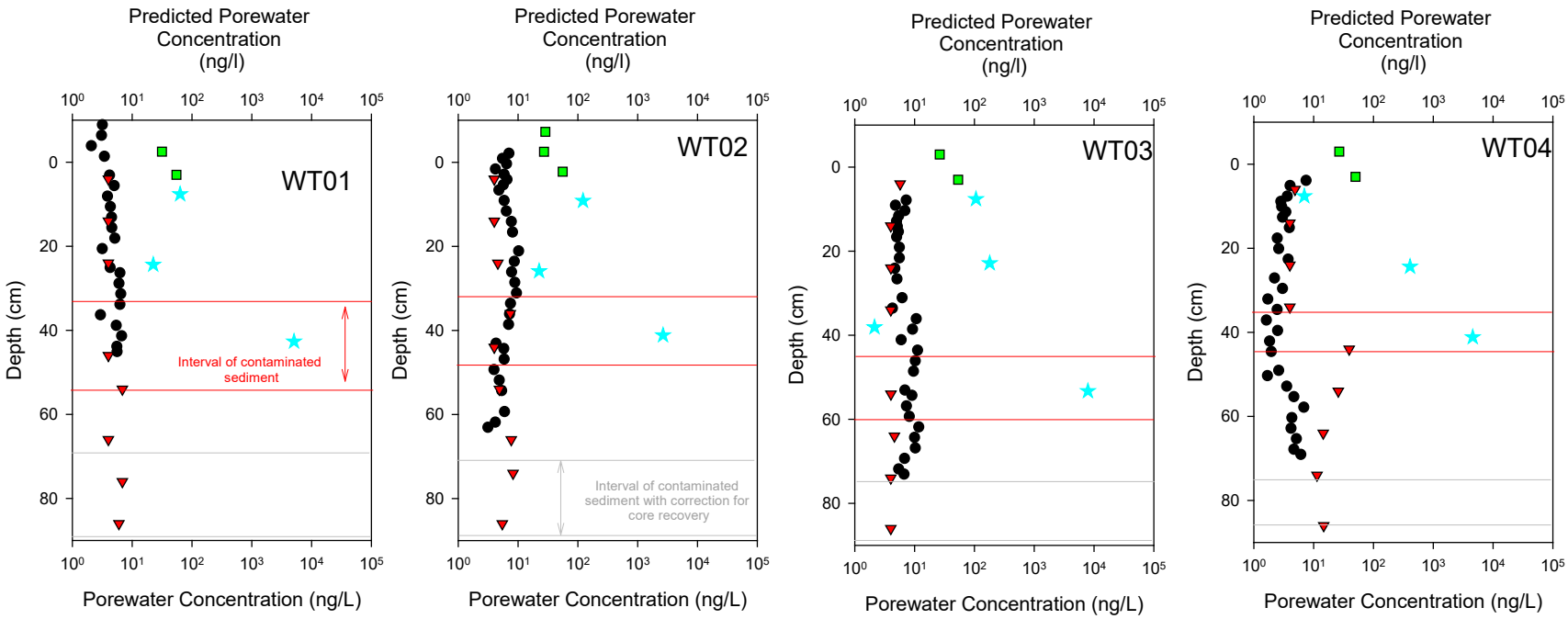


Figure 5.85. Chrysene Porewater Concentration Depth Distribution Across the West Transect

Chrysene porewater concentration depth distribution across the West Transect for sHRPP (black circles), T-Bar (red triangles), PE (green squares), and predicted porewater concentrations based on Koc and measured PAH and organic carbon concentration sediment concentration (blue stars). Red lines denote the core interval identified as including sediment below the cap. Grey lines denote the potential maximum depth interval identified as including sediment below the cap based on core recovery.

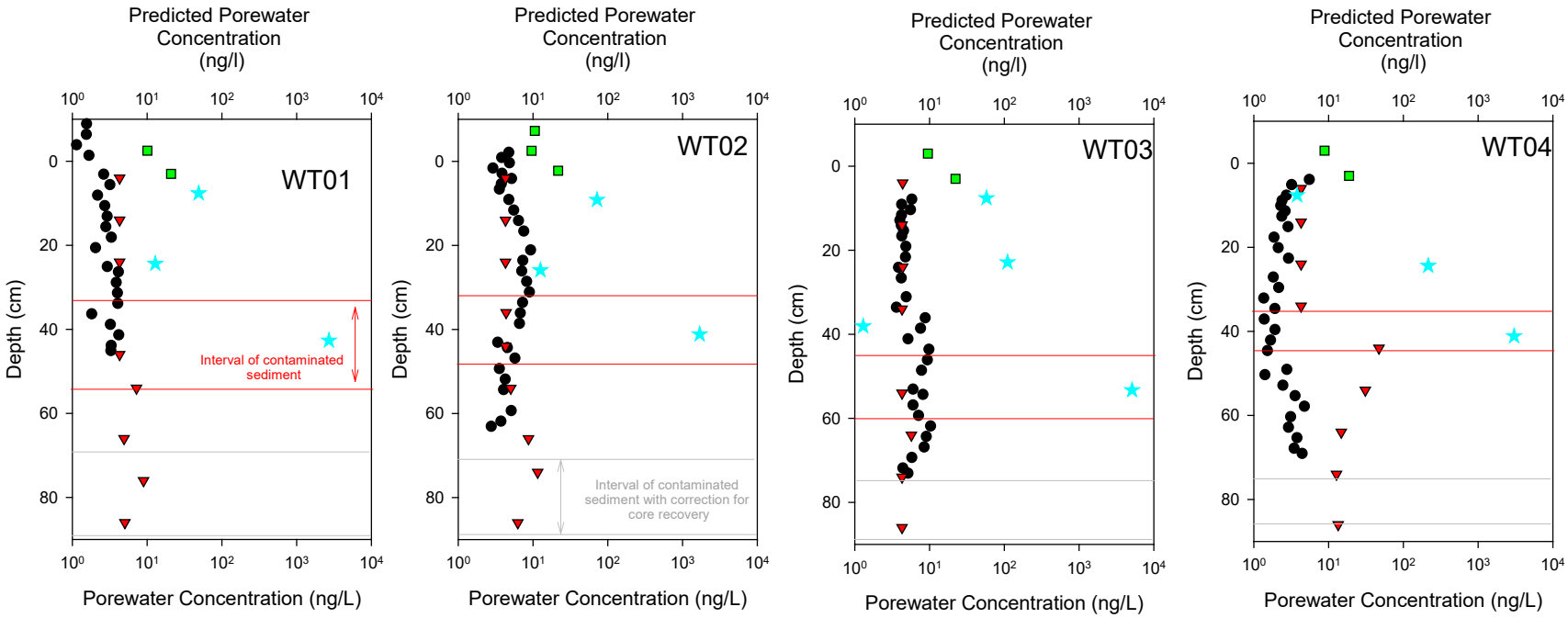


Figure 5.86. Benzo(a)anthracene Porewater Concentration Depth Distribution Across the West Transect

Benzo(a)anthracene porewater concentration depth distribution across the West Transect for sHRPP (black circles), T-Bar (red triangles), PE (green squares), and predicted porewater concentrations based on Koc and measured PAH and organic carbon concentration sediment concentration (blue stars). Red lines denote the core interval identified as including sediment below the cap. Grey lines denote the potential maximum depth interval identified as including sediment below the cap based on core recovery.

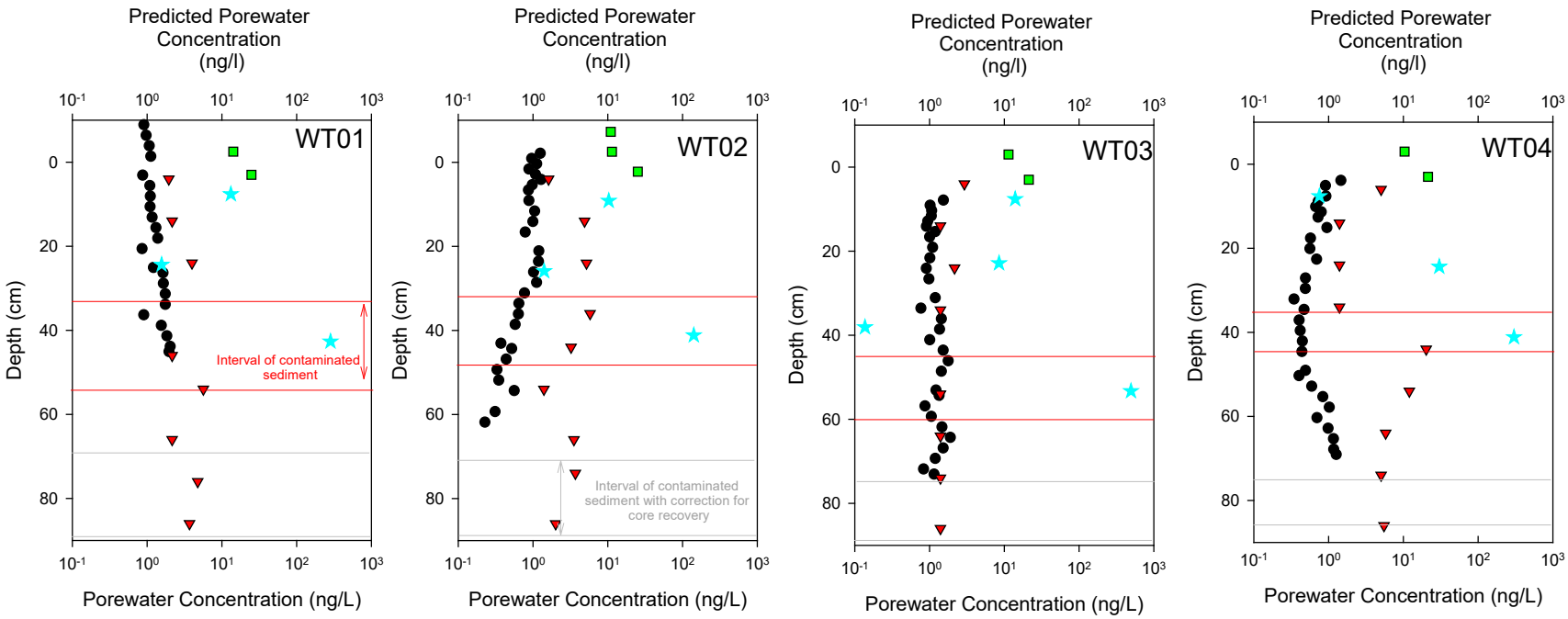


Figure 5.87. Benzo(b)fluoranthene Porewater Concentration Depth Distribution Across the West Transect

Benzo(b)fluoranthene porewater concentration depth distribution across the West Transect for sHRPP (black circles), T-Bar (red triangles), PE (green squares), and predicted porewater concentrations based on Koc and measured PAH and organic carbon concentration sediment concentration (blue stars). Red lines denote the core interval identified as including sediment below the cap. Grey lines denote the potential maximum depth interval identified as including sediment below the cap based on core recovery.

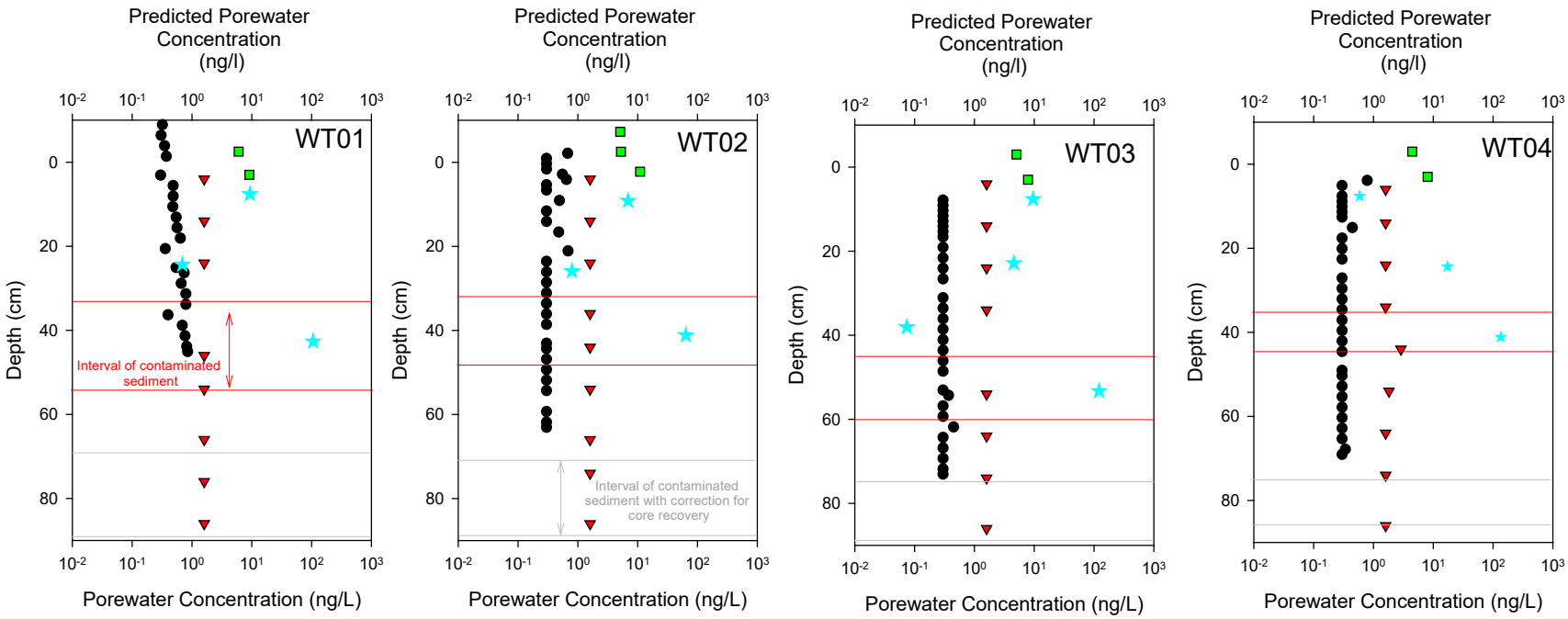


Figure 5.88. Benzo(k)fluoranthene Porewater Concentration Depth Distribution Across the West Transect

Benzo(k)fluoranthene porewater concentration depth distribution across the West Transect for sHRPP (black circles), T-Bar (red triangles), PE (green squares), and predicted porewater concentrations based on Koc and measured PAH and organic carbon concentration sediment concentration (blue stars). Red lines denote the core interval identified as including sediment below the cap. Grey lines denote the potential maximum depth interval identified as including sediment below the cap based on core recovery.

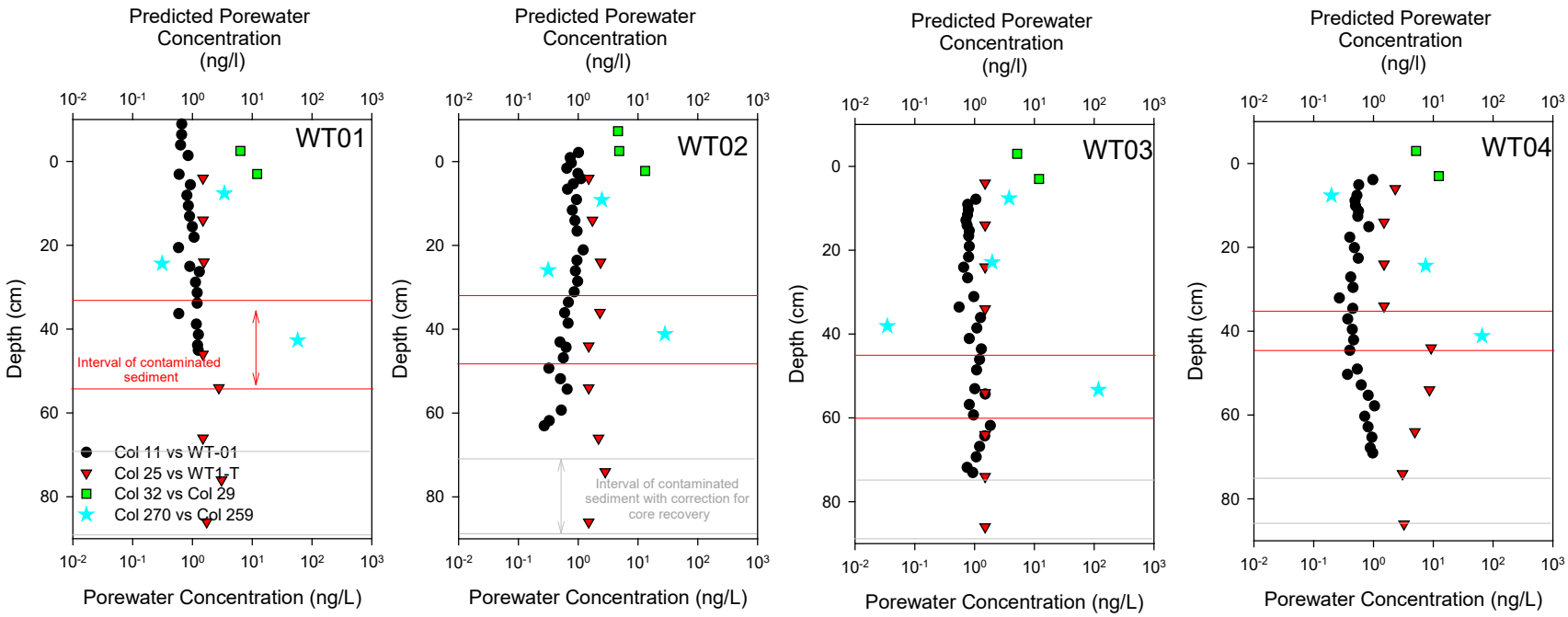


Figure 5.89. Benzo(a)pyrene Porewater Concentration Depth Distribution Across the West Transect

Benzo(a)pyrene porewater concentration depth distribution across the West Transect for sHRPP (black circles), T-Bar (red triangles), PE (green squares), and predicted porewater concentrations based on Koc and measured PAH and organic carbon concentration sediment concentration (blue stars). Red lines denote the core interval identified as including sediment below the cap. Grey lines denote the potential maximum depth interval identified as including sediment below the cap based on core recovery.

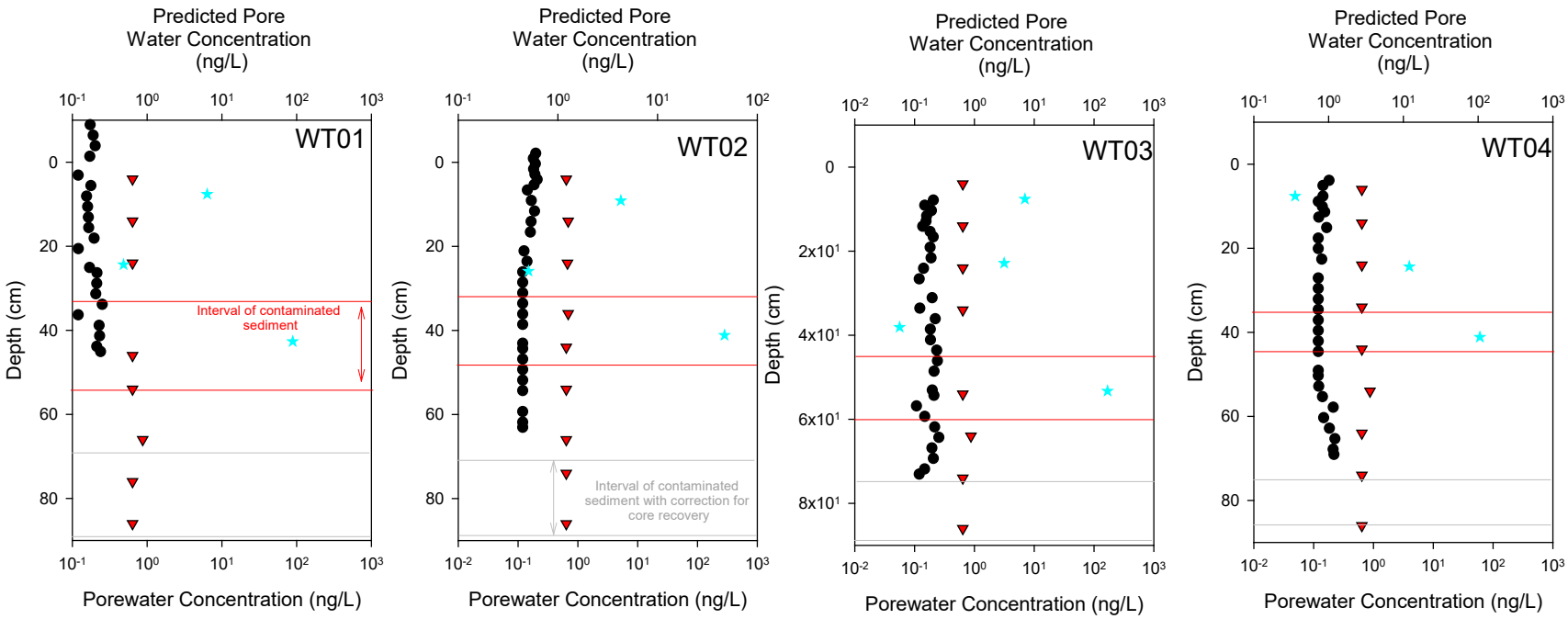


Figure 5.90. Benzo(ghi)perylene + Indenpyrene Porewater Concentration Depth Distribution Across the West Transect

Benzo(ghi)perylene + Indenpyrene porewater concentration depth distribution across the West Transect for sHRPP (black circles), T-Bar (red triangles), PE (green squares), and predicted porewater concentrations based on Koc and measured PAH and organic carbon concentration sediment concentration (blue stars). Red lines denote the core interval identified as including sediment below the cap. Grey lines denote the potential maximum depth interval identified as including sediment below the cap based on core recovery.

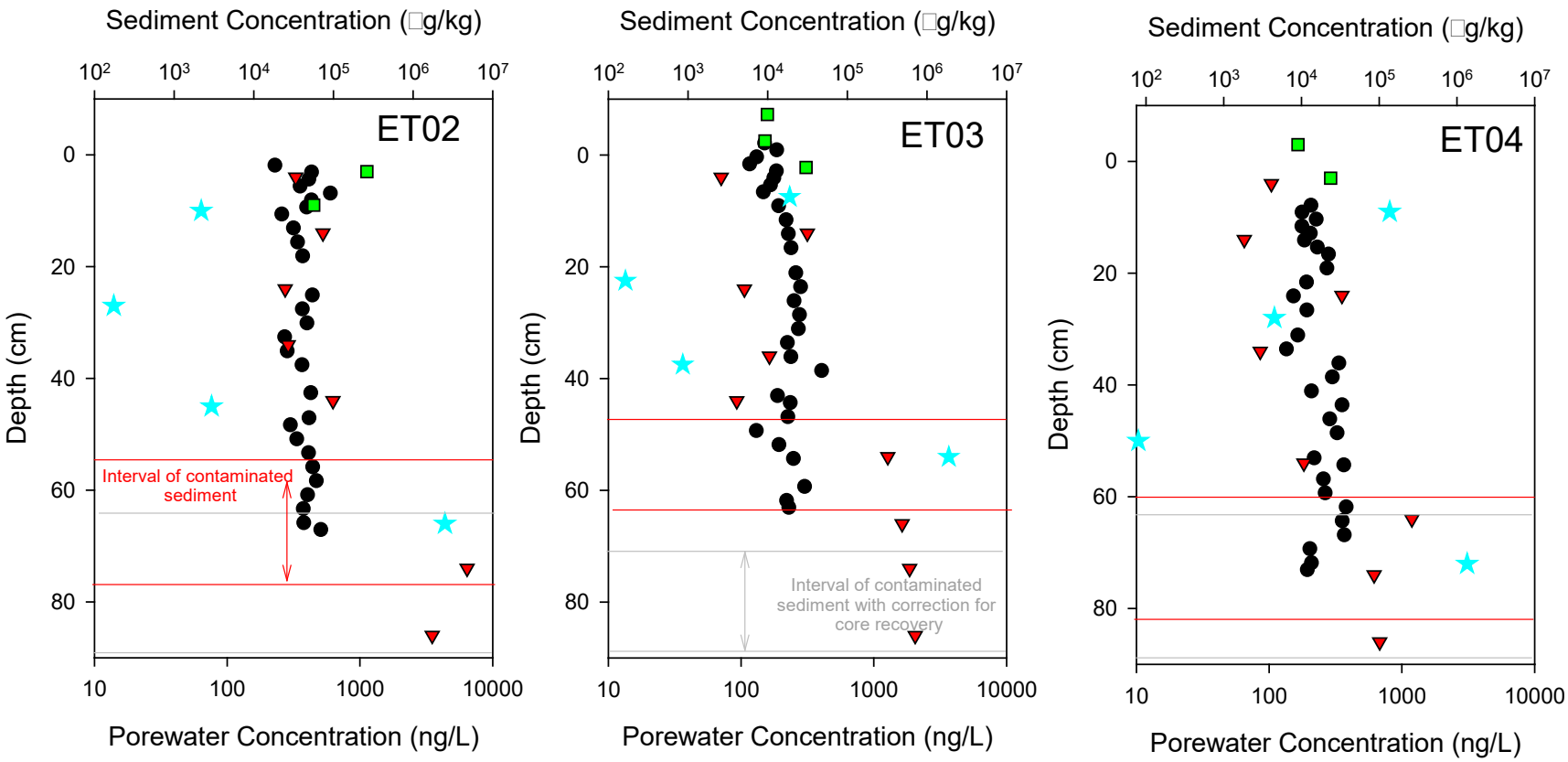


Figure 5.91. Sum of all Measured PAH Porewater Concentrations Depth Distribution Across the East Transect

Sum of all measured PAH porewater concentrations depth distribution across the East Transect for sHRPP (black circles), T-Bar (red triangles), PE (green squares), and sediment concentration (blue stars). Red lines denote the core interval identified as including sediment below the cap. Grey lines denote the potential maximum depth interval identified as including sediment below the cap based on core recovery.

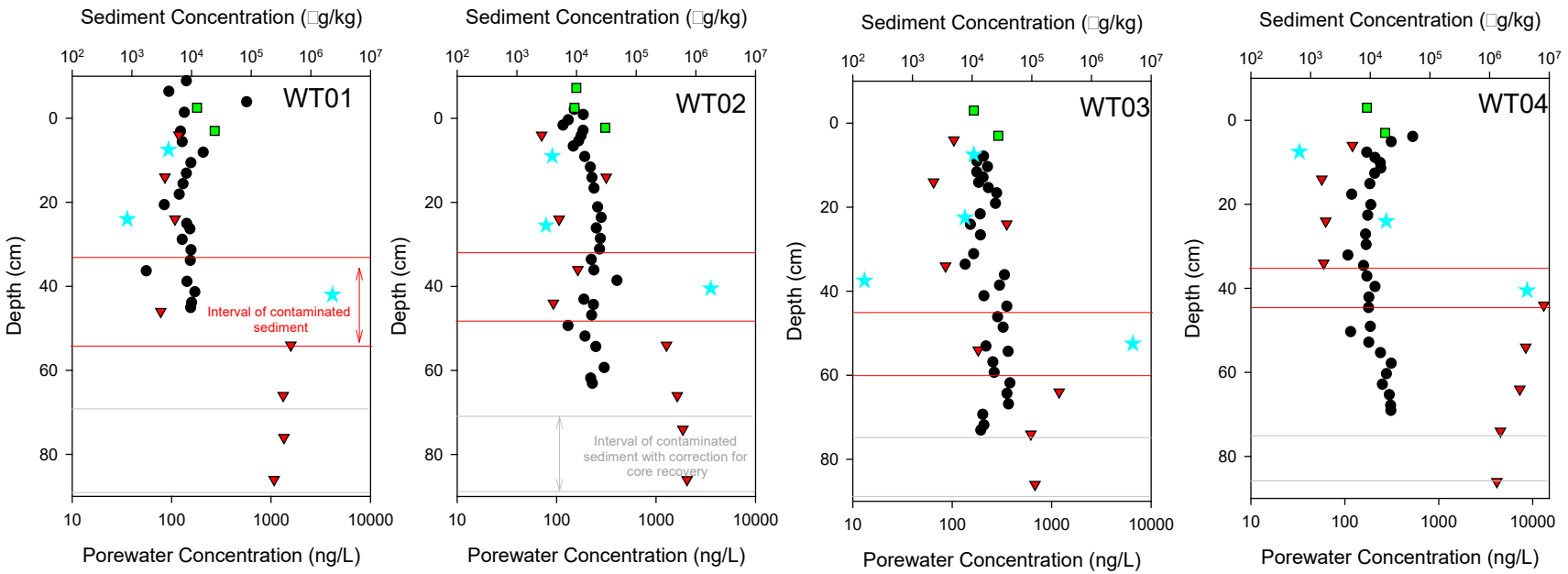


Figure 5.92. Sum of all Measured PAH Porewater Concentrations Depth Distribution Across the West Transect

Sum of all measured PAH porewater concentrations depth distribution across the West Transect for sHRPP (black circles), T-Bar (red triangles), PE (green squares), and sediment concentration (blue stars). Red lines denote the core interval identified as including sediment below the cap. Grey lines denote the potential maximum depth interval identified as including sediment below the cap based on core recovery.

The detection limit and fss varied for each passive sampling method. For the sHRPP and T-Bar, the same four PRCs were used which bracketed a range of log K_{ow} from 5.3 to 7.4, which covered the complete range of PAH evaluated. For the sHRPP the average fss of all depths below the sediment water interface for each location was used to predict porewater concentrations using interpolated fss values based on measured PRC and model results. For SPME located above the sediment interface, fss were calculated separately, and were greater than 0.9. In general, for sHRPP, fss values were similar between sites (Figure 5.93) and there was no systematic difference between upper and lower sediment depths for any location. The variation in PRC fss values for both transects for all depths is displayed in Figure 5.93. For the T-Bar samplers, all depths at all locations were averaged. Values are similar to fss values for co-deployed sHRPP with somewhat lower (10-20%) values for compounds with higher K_{ow} values. Variation of fss values for T-Bar samplers was greater than for sHRPP (Figure 5.94). For PE samplers, only three PRCs were used, and all had $K_{ow} < 5.2$. For compounds with $K_{ow} > 5.2$ fss were estimated based on modeling and extrapolation. Due to this for PAH with log $K_{ow} \geq 6$, the predicted fss values were very low, with those with log $K_{ow} \geq 6.5$ having fss values ~0.1, and for those with log $K_{ow} \geq 7$ having fss values < 0.05 (Table 5.11). These low fss values are likely in error based on a comparison between samplers (as discussed below) in which for all compounds with log $K_{ow} < 6$, porewater concentrations are very similar between sHRPP, T-Bar, and PE but with increasing log K_{ow}, the porewater concentrations predicted by PE samplers greatly increases with respect to both sHRPP and T-Bar. While it's possible that the PE sampler predicted porewater concentrations are correct and sHRPP and T-Bar are underpredicting porewater concentrations, two factors diminish this possibility. First, both the sHRPP and T-Bar utilized PRCs that spanned the whole range of PAH log K_{ow} values allowing interpellation of model results and verification, while for PE samplers fss for PAH with higher log K_{ow} values were modeled and extrapolated. Secondly, using the core data provided by EPA, we calculated the K_{oc} values based on each passive samplers predicted porewater concentration and the measured organic carbon content and sediment PAH concentration and compared this "calculated K_{oc} value, ($K_{oc}C$)" to the theoretical K_{oc} ($K_{oc}T$) value based on Baker (1977). Theoretically, it would be expected that as the carbon quality or attributes are constant, the ratio of $K_{oc}C/K_{oc}T$ would be roughly a constant. For T-Bar and sHRPP samplers this was the actual result with $K_{oc}C/K_{oc}T \sim 10$ across the range of log K_{ow} PAH values (Figure 5.95). A ratio greater than 1 is expected based on previous work (Accardi-Dey and Gschwend, 2002). However, for PE samplers, while the $K_{oc}C/K_{oc}T$ values are also ~ 10 for compounds with log K_{ow} values near those of used PRCs (< 5.3), the $K_{oc}C/K_{oc}T$ ratios rapidly decline with increasing PAH log K_{ow} in some cases to as low as 0.1. This strongly suggests a systematic impact such as underpredicting the fss value. It should be noted that this is not an inherent issue with PE samplers but simply reflects that only PRCs with relatively low K_{ow} were used for PE samplers for this event, which required large extrapolations.

Porewater detection limits are based on a combination of mass of polymer material extracted and final volume of the extracted solvent (Table 5.11). sHRPP detection limits were lower than T-Bar due to longer extracted fiber lengths but also to increased concentration of solvent extracts. PE samplers had much lower detection limits mainly due to the greater mass of polymer available for extraction.

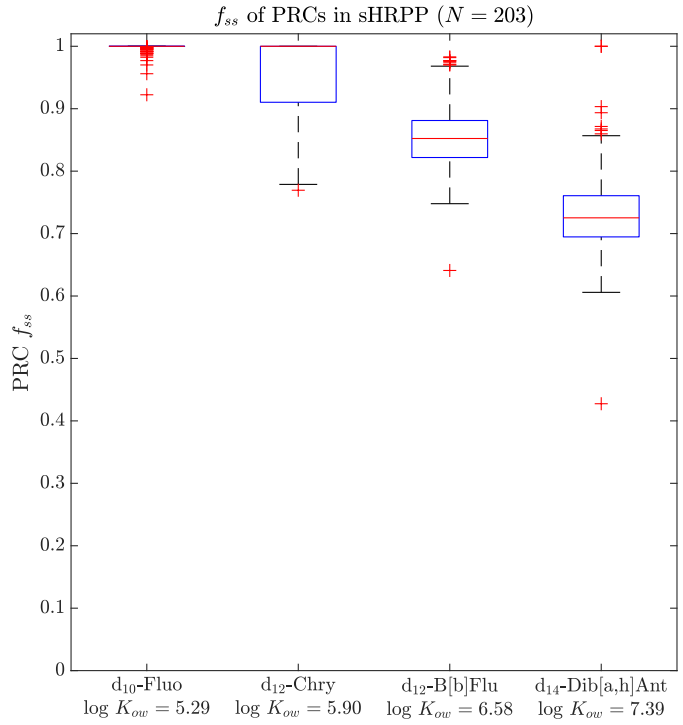


Figure 5.93. Variation in fss Values for all sHRPP Locations and Depths for PRCs

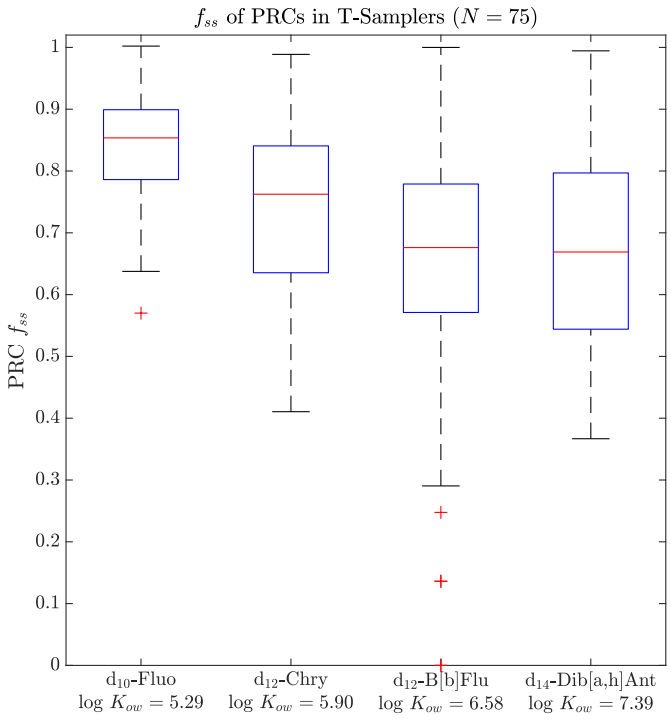


Figure 5.94. Variation in fss Values for all T-Bar Locations and Depths for PRCs.

Table 5.11. PAH Compounds Evaluated and their Associated Porewater Detection Limits and fss Achieved

Compound	sHRPP		T-Bar		PE	
	Detection Limit (ng/l)	Average fss	Detection Limit (ng/l)	Average fss	Detection Limit (ng/l)	Average fss
Fluorene	53	0.98	177	1		1.0
Phenanthrene	4.6	0.97	20	1		1.0
d10-Anthracene	Not used	Not used	Not used	Not used		0.92
Anthracene	5.0	0.97	21	0.96		1.0
d10-Fluoranthrene	53	1.0	21	0.85		0.85
Fluoranthene	2.0	0.95	9	0.97		0.80
d10-Pyrene	Not used	Not used	Not used	Not used		0.81
Pyrene	2.0	0.95	10	0.83		0.9
d12-Chrysene	1.0	0.95	4.0	0.74		Not Used
Chrysene	1.0	0.91	4.0	0.84		0.28
Benzo(a)anthracene	0.8	0.92	4.3	0.69		0.31
d12-Benzo(b)fluoranthene	0.2	0.85	1.4	0.64		Not Used
Benzo(b)fluoranthene	0.2	0.85	1.4	0.64		0.08
Benzo(k)fluoranthene	0.3	0.86	1.6	0.69		0.08
Benzo(a)pyrene	0.3	0.86	1.5	0.64		0.12
d14-Dibenzo(a,h)anthracene	0.1	0.72	0.3	0.67		Not Used
Benzo[a,h], anthracene	0.1	0.72	0.3			0.03
Benzo(ghi)perylene+ indenpyrene	0.1	0.78	0.6	0.64		0.04

The sum of all PAH porewater concentrations measured by each passive sampler is plotted in Figures 5.91 and 5.92 for the ET and WT, respectively. In addition, the sum of the sediment PAH concentrations based on core data is also displayed. It should be noted that the scale of the sediment concentrations (top x axis) is different than the pore water (bottom X axis). A number of general observations can be made. All three samplers have similar concentrations at each depth where they were deployed. PE samplers were only deployed near the interface. sHRPP and T-Bar porewater are similar to depths down to 40 cm BSI. Below these depths, concentrations based on T-Bar samplers rapidly rise by 1 order of magnitude, while concentrations based on sHRPP remain generally unchanged.

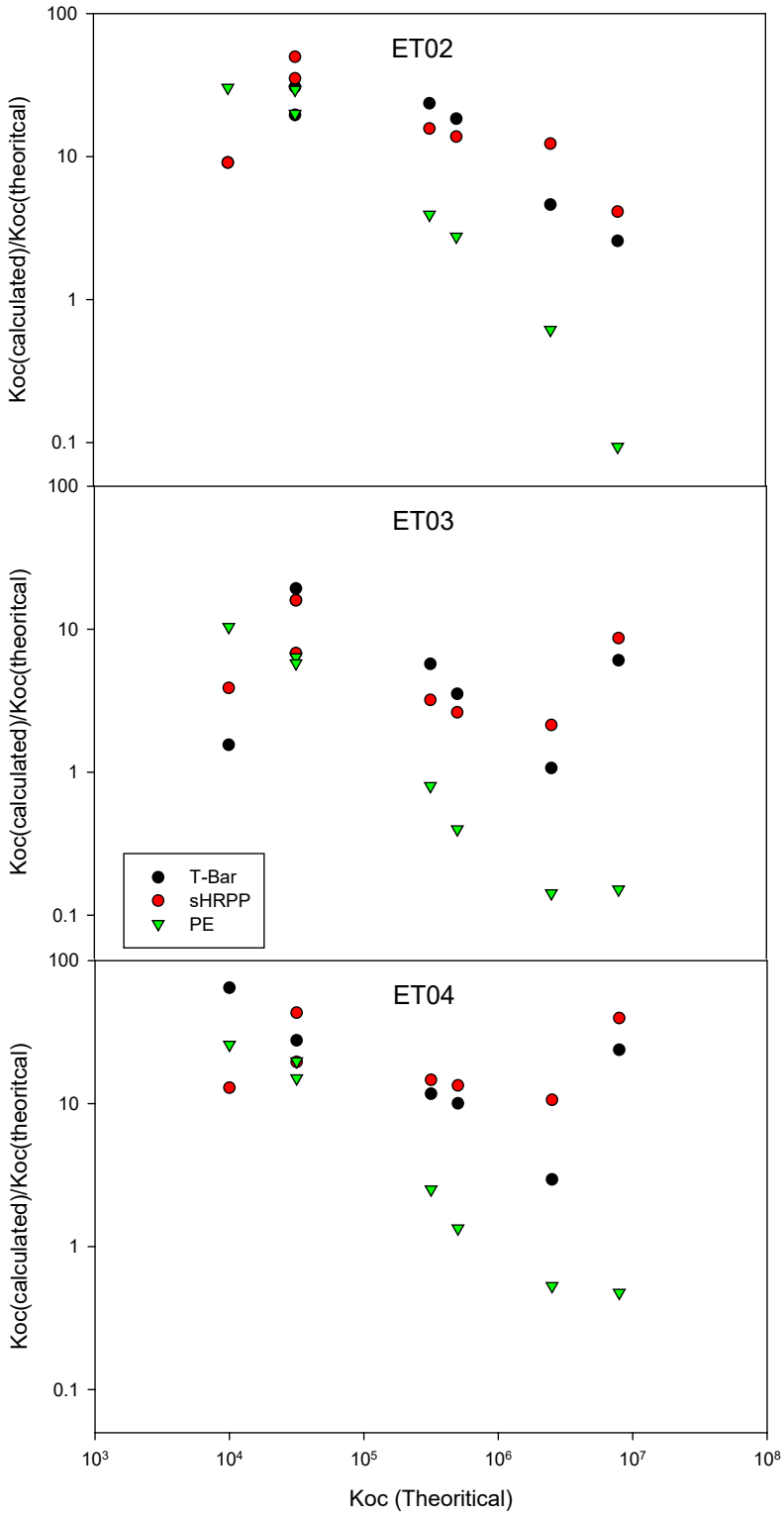


Figure 5.95. Comparison of the Calculated Koc for each Passive Sampler Type to the Theoretical Koc

(Theoretical Koc based on Baker 1977)

Two possibilities occur to explain the lack of increase in sHRPPs porewater concentrations below the cap. One, the sHRPP did not penetrate through the cap; or two, cleaner sediment from the upper layers was packed into the indentions of the sHRPP blocking the fibers from contact with the contaminated sediment (as previously discussed). To evaluate the first possibility, we evaluated the contaminated sediment depth based on core data for which the zone of contamination is > 30 cm BSI. This is generally less deep than that indicated by the T-Bar samplers, for which the porewater concentrations increase at depths ~ 10cm deeper. Due to the incomplete core recovery and potential error in T-Bar placement, this is not unexpected; but it is unlikely that the assigned depths or more than 10 or 15 cm in error. At WT-01 the sHRPP did not penetrate below 50 cm and at this site it probably did not penetrate into the contaminated sediment. At sites WT-02 and WT-03 the sHRPP should have penetrated the contaminated sediment by 7-9 cm based on T-Bar data and by 12-15cm based on core data; and so, it is possible that differences in estimated depths account for the lack of increase in porewater concentrations from the sHRPP at depths that should have apparently been in the contaminated sediment. However, at WT-04, the sHRPP penetrated the contaminated sediment by ~ 25cm based on either T-Bar or core data and so it seems unlikely that the sHRPP was not in contact with contaminated sediment at lower depths. In the ET, similar observations can be made. Porewater concentrations are similar at depths above contaminated zone regardless of sampler type. At locations ET-02 and ET-03 it is possible that the sHRPP did not penetrate the contaminated sediment, assuming a potential error of < 10 cm in deployment depth of the T-Bar and core. However, at ET-04 core recovery was near 100% and T-bar porewater concentrations coincide with core data in terms of the depth at which the contaminated sediment occurs. As the sHRPP, apparently penetrated ~12 cm into the sediment, it seems that an additional issue prevented the sHRPP from responding to the contaminated sediment. As suggested above, this is most likely due to clean sediment becoming packed in the indentation above the SPME fiber as it is driven in, blocking the fiber from contact with the contaminated sediment. As such we recommend that the sHRPP be reconfigured to eliminate the indention and thus ensure the fiber is always in contact with the sediment at the deployed depth.

Fluorene concentrations produced by sHRPP and T-Bar samplers were similar at depths above the contaminated sediment but could only be compared for a few locations and depths as most T-Bar porewater concentrations were below the detection limit. Fluorene concentrations predicted by PE samples were much lower (~ 1 order of magnitude). Predicted porewater concentrations based on core sediment concentrations and estimated K_{oc} values were variable. At some locations and depths predicted porewater concentrations based on cores matched the sHRPP and T-bar (e.g., WT-01,02), while at others (WT-03,04) they were more similar to PE samplers. In the ET, similar observations could be made. Pore water concentrations predicted by PE were lower than T-Bar and sHRPP which were very similar for depths above the contaminated sediment. However, in the ET, predicted core porewater concentrations were more similar to T-Bar and sHRPP. Below the cap in the contaminated sediment, T-Bar porewater concentrations were up to 10 times higher in concentration than sHRPP measured porewater concentrations. Porewater predicted from core data was 1 to 2 orders of magnitude greater than those measured by T-Bar samplers.

Phenanthrene, anthracene, fluoranthene, and pyrene concentrations produced by sHRPP and T-Bar samplers were similar at depths above the contaminated sediment for both transects (ET and WT). In cases where the results were not similar it was generally due to the higher detection limits for T-Bar samplers. Concentrations predicted by PE samplers were generally very similar to both T-Bar and sHRPP porewater concentrations at similar depths.

Predicted porewater concentrations based on core sediment concentrations and estimated K_{oc} values were generally greater than those measured by passive samplers. Similar results were observed for the ET. At depths below the cap in the contaminated sediment, sHRPP porewater concentrations were lower than T-Bar porewater concentrations which were much lower than predicted porewater concentrations based on core data, similar to results for fluorene.

Chrysene, benzo(a)anthracene, and benzo(b)fluoranthene concentrations produced by sHRPP and T-Bar samplers were similar at depths above the contaminated sediment for both the ET and WT (Figures 5.74 through 5.76 and Figures 5.85 through 5.87, respectively). Concentrations predicted by PE samplers were higher (~ 1 order of magnitude). As previously discussed, chrysene is the first PAH with a K_{ow} outside the range of the PRC utilized in the PE samplers. The much higher porewater concentrations are probably due to under-predicted fss values due to extrapolation. Predicted porewater concentrations based on core sediment concentrations and estimated K_{oc} values were generally greater than those based on passive samplers. Below the cap, porewater concentrations were similar between T-Bar and sHRPP for all profiles except WT-04. The similarities in concentrations compared to previously discussed PAHs appear to mainly be due to the lack of increase in T-Bar porewater concentrations below the cap rather than a from a change in behavior of the sHRPP porewater concentration distribution with depth, which remained unchanged with depth similar to other discussed PAHs. Porewater concentrations predicted from core data were highest below the cap and similar to profiles in shape and magnitude to pyrene and fluoranthene so the lack of response by passive samplers is unclear.

Benzo(k)fluoranthene concentrations were generally less than the detection limit at al depths. In the WT transect almost no concentrations were greater than the DL for the T-bar samplers, while for the sHRPP, concentrations were generally measurable for WT-01 and in the upper depths of WT-02 but not generally detectable in WT-03 or -04. This is in spite of the fact that predicted porewater concentrations based on cores were similar between all profiles. As before, PE porewater concentrations were higher (> 1 order of magnitude) than sHRPP or T-Bar but were also higher than predicted porewater concentrations at similar depths. Similar observations were made for the ET, where with one exception all T-Bar concentrations were less than the detection limit and sHRPP were only greater than the detection limit for ET-02. PE concentrations were higher than sHRPP and T-Bar but less than predicted values based on core data.

Benzo(a)pyrene porewater concentrations were above the detection limit for sHRPP samplers and generally greater for T-Bar except profiles ET-04 and WT-03. T-Bar and sHRPP concentrations were similar at depths above the contaminated sediment. In some profiles, concentrations cannot be compared as the sHRPP measured concentrations were lower than the T-Bar detection limit. PE porewater concentrations were generally equal to or greater than predicted porewater concentrations based on cores and much greater (> 1 order of magnitude) than sHRPP or T-Bar. At depths below the cap, T-Bar porewater concentrations were generally similar to those in the cap except for profile WT-04. This is despite the fact that predicted porewater concentrations based on cores were all similar.

Porewater concentrations of Benzo(ghi)perylene+Indenpyrene were almost all below the detection limit for the T-Bar samplers and often below for the sHRPP on both transects. As such the concentrations cannot be compared. No values were available for the PE samplers.

5.5.6.4 Summary of Site Assessment Based on Each Sampling Method

sHRPP samplers appear to provide comparable PAH porewater data to other passive sampling methods at depths less than 30 cm BSI. At lower depths it seems probable that the samplers are not responding to porewater due to a design issue that lets sediment fill in small indentions above the fibers producing a barrier to equilibration. This design flaw is easily fixable, and we propose a solution in the recommendations section. At shallow depths, the sampler produced very high resolution profiles and comparable or lower detection limits to T-Bar samplers but higher than PE. Like most SPME based passive samplers, PRC were closer to equilibrium than PE samplers which equilibrate more slowly but produce lower detection limits. Compared to predicted porewater concentrations based on core data, passive samplers generally measured much lower concentrations with the exception for PAHs with log K_{ow} > 5.5 measured by PE samplers. As previously mentioned, this is not an issue of the samplers but was due only to the PRCs utilized which covered a narrow range of K_{ow} values and forced extrapolation to predict fss values for PAH with higher K_{ow}. The much higher porewater concentrations based on cores is likely due to the nature of the contaminated organic matter. PAHs with higher log K_{ow}, may not be available for equilibration even though they are solvent extractable, producing large errors when using K_{oc} values that assume all PAHs are equally available.

Unlike other passive samplers, the sHRPP also provide data on transport and geochemistry, allowing additional insights into PAH fate as well as better constraints on modeling efforts (See Section 5.5.7). While only sulfate was measured for this deployment due to resource restrictions, it is clear that the sediments have consumed all sulfate within a few cm of the surface and are presumably highly anaerobic, reducing the possibility of biodegradation except in the near surface. Velocity measurements suggest pore velocities of 2-10 cm/d across both transects and chloride profiles support upwelling of groundwater. In the top 15cm much higher velocities are observed, indicating bioturbation impacts. The ability of the sHRPP to aid in modeling efforts is expanded on in Section 5.5.7.

5.5.7 Modeling Sediment Processes using High-Resolution Data

The spatial distribution of species in sediment pore water is determined by transport and transformation processes. The characterization of transport mechanisms (e.g. velocity, dispersion, diffusion) can be obtained from combining direct porewater velocity measurements with spatial profiles of non-reactive species such as Cl^-, which can be considered a natural tracer (de Aragão Nogare, 2020; Houzé et al., 2022). The first step to model the sediment mechanisms consists in developing a conceptual model of the site based on observations. Then, the conceptualization is translated into a mathematical form by using mass balances. The parameters for the different mechanisms in the model are constrained from literature values and direct observations. In this regard, the high-resolution profiles of Cl^- become useful to characterize processes occurring over small lengths (e.g., benthic mixing) and to reduce the uncertainty in the parameters of the models. The following cases demonstrate the use of pore water velocity estimates and Cl^- data to constraint transport processes in two of the demonstration sites. The sHRPP observations are presented followed by a conceptual model of the site. Then, the model is translated to a mathematical form for the estimation of parameters. Finally, we show the implications of the transport model on the contaminants at each site.

5.5.7.1 West Transect of Grand Calumet River

There were 12 sHRPP estimates of pore water velocity in the sediments of the west transect (WT) of the Grand Calumet River with a geometric mean of 5.4 cm/d (95% C.I.: 3.9 and 7.7 cm/d) (Figure 5.96) shows observations and fitted log-normal distribution validating the use of geometric mean). Using the porosity in the cores of 0.45, the average interstitial velocity corresponds to a Darcy's flux of 2.45 cm/d, which is similar to previous estimates in the same area, between 0.5 and 2.0 cm/d (Mills, Crone, Fetters, & Williams, 2015).

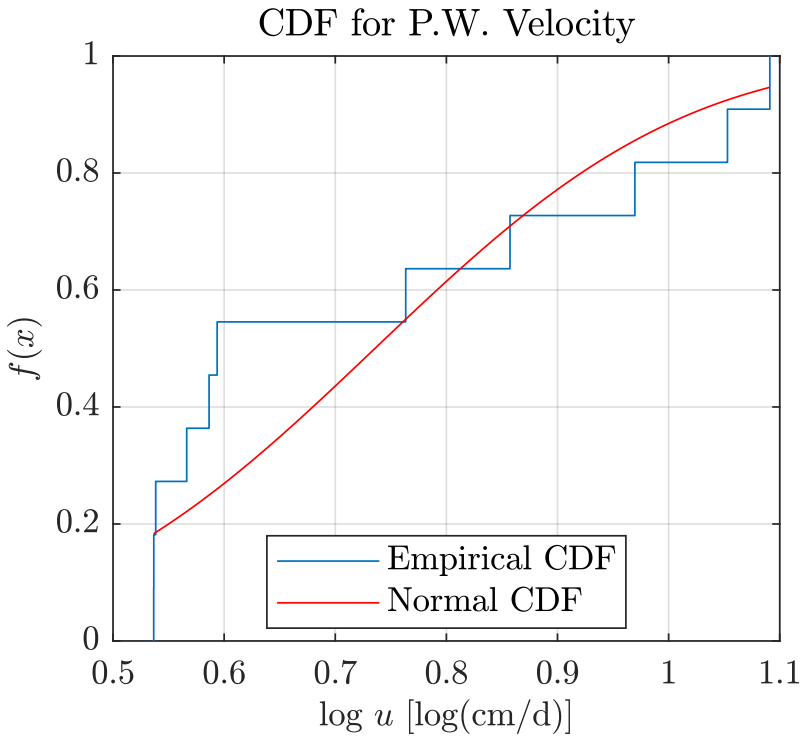


Figure 5.96. Empirical and Normally Fitted Cumulative Distribution Function (CDF) of Estimated Pore Water Velocity (Interstitial Velocity) from the Loss of Tracer in the WT.

The profiles of Cl^- measured through sHRPP in the WT of the river are presented in Figure 5.97. Top cells of samplers WT-01 and WT-02 captured surface water conditions, which are characterized by constant values above 0 cm. The four profiles show a change in pore water from surface water concentration (77.7 ± 0.7 mg/L) to groundwater levels (between 90 and 120 mg/L). The transition occurs in the top ~20 cm, and the shape is characteristic of a steady-state flux composed of advection and diffusion-dispersion. The advection is validated through the estimates of pore water velocity and the dispersion is inherent to flow in porous media (Danny D. Reible, 1998). In addition, some of the profiles show surface water concentrations in the top ~5 cm of the sediments. This observation suggests intrusion of surface water likely due to benthic mixing such as bioturbation and hyporheic exchange (Cardenas, 2009; Chandler, Guymer, Pearson, & Van Egmond, 2016; Thibodeaux & Bierman, 2003).

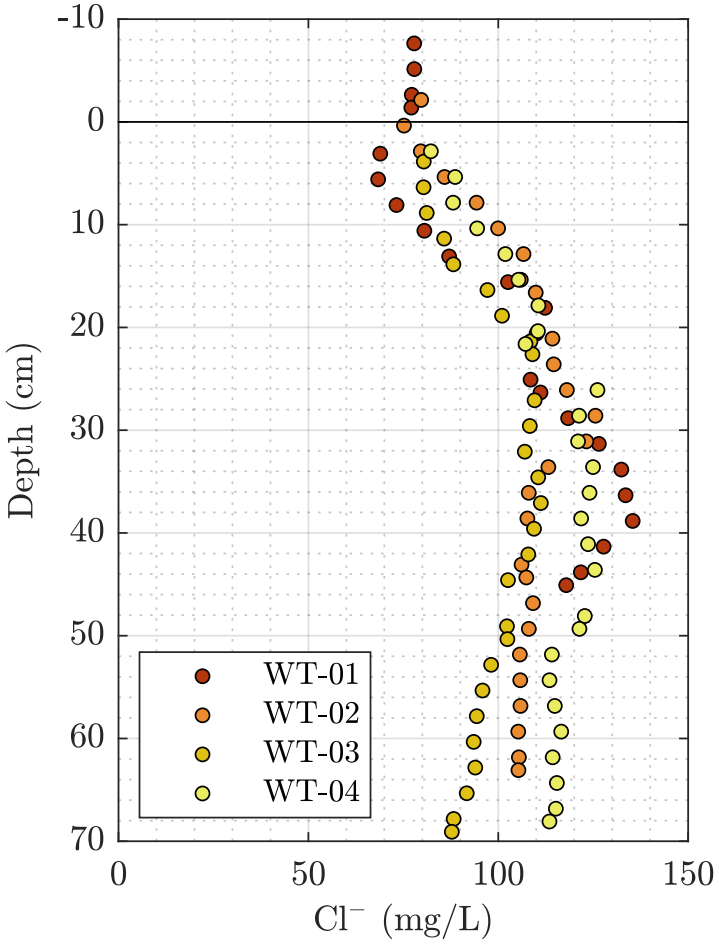


Figure 5.97. Pore water concentration of Cl- in the WT measured through sHRPP.

5.5.7.1.1 Conceptual Site Model

Based on the observations, a conceptual model for the transport mechanisms in the sediments and the cap was developed (see Figure). In this conceptualization, there is groundwater upwelling and diffusion/dispersion of dissolved species. In addition, a rapid mixing between pore water and surface water occurs in the near surface (benthic zone) because of hyporheic exchange and bioturbation.

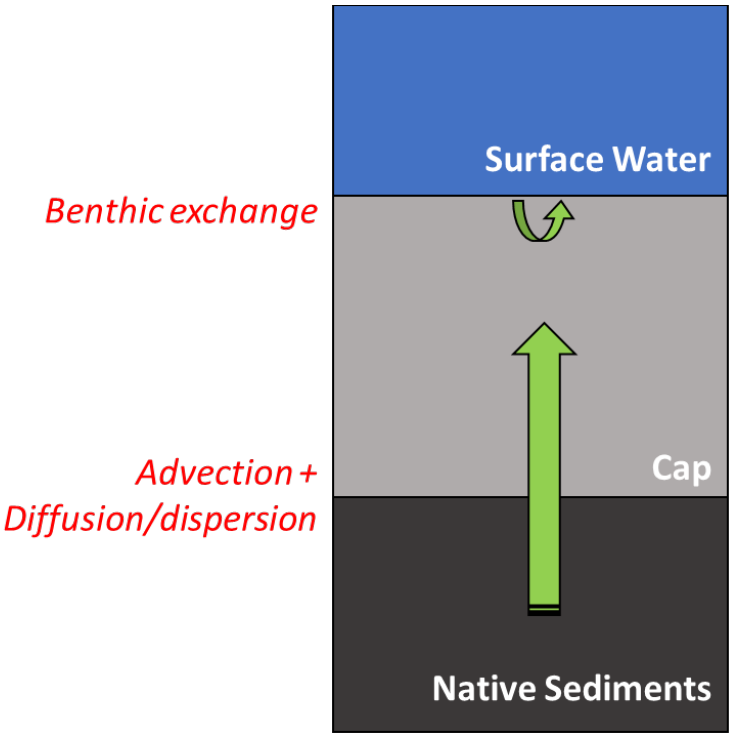


Figure 5.98. Conceptual Model of the WT Sediments.

5.5.7.1.2 Mathematical model and parameter estimation

The profiles of non-reactive Cl^- and the measured upwelling velocity were used to validate the conceptual model and to estimate the intensity of the exchange in the benthic zone. For this purpose, the flux of Cl^- in this model, J_{Cl}, is given by

$$J_{Cl} = q_z C_{Cl} - \left(\alpha_z |q_z| + \frac{D_w \phi}{\tau} + D_{ben}(z)\right)\frac{\partial C_{Cl}}{\partial z} \tag{1.1}$$

where q_z is the Darcy's flux, α_z is the longitudinal dispersivity (3.5 cm, which was assumed to be 5% of total simulated length (Danny D. Reible, 1998)), D_w is the diffusion coefficient in water (1.7 cm^2/d (Vitagliano & Lyons, 1956)), ϕ is the porosity (0.45), τ is the tortuosity of the media ($\tau = \phi^{-1/3}$ (Millington & Quirk, 1961)), and z is the direction of transport (vertical). The benthic processes corresponding to bioturbation of pore water and hyporheic exchange were assumed to fall off with a Gaussian intensity with depth (Shen, Lampert, Ogle, & Reible, 2018),

$$D_{ben}(z) = D_{ben,0} \exp\left\{-\frac{z^2}{2\sigma^2}\right\}, \tag{1.2}$$

where $D_{ben,0}$ is the maximum intensity of benthic exchange and σ is the characteristic length (depth where $D_{ben}(z)$ drops to ~60% its maximum value), which was assumed to be 5 cm, consistent with (Reible, 2014) and the observed chloride transition.

Using the previous definitions, a mass balance for the Cl^- ion in pore water is

$$\phi \frac{\partial C_{\mathrm{Cl}}}{\partial t} + \frac{\partial J_{\mathrm{Cl}}}{\partial z} = 0 \tag{1.3}$$

which was solved with the boundary conditions corresponding to surface water (C_{sw}) and groundwater (C_{gw}) concentrations. In this case, $D_{\mathrm{ben},0}$ and C_{gw} were estimated to fit to the Cl^- observations. The model results are shown in Figure 5.99, and the numerical values of estimations and the 95% confidence intervals are $D_{\mathrm{ben},0} = 110 \pm 72$ cm^2/d and $C_{\mathrm{gw}} = 112 \pm 3$ mg/L (average percent error between model and observations is 7.4 %). The fitted model for Cl^- shows a good agreement with observations and reproduces the transition in the top ~20 cm. The estimated value of $D_{\mathrm{ben},0}$, which is ~2 orders of magnitude higher than D_w, reflects the strong mass exchange because of the benthic processes (Chandler et al., 2016; Thibodeaux, Valsaraj, & Reible, 2001).

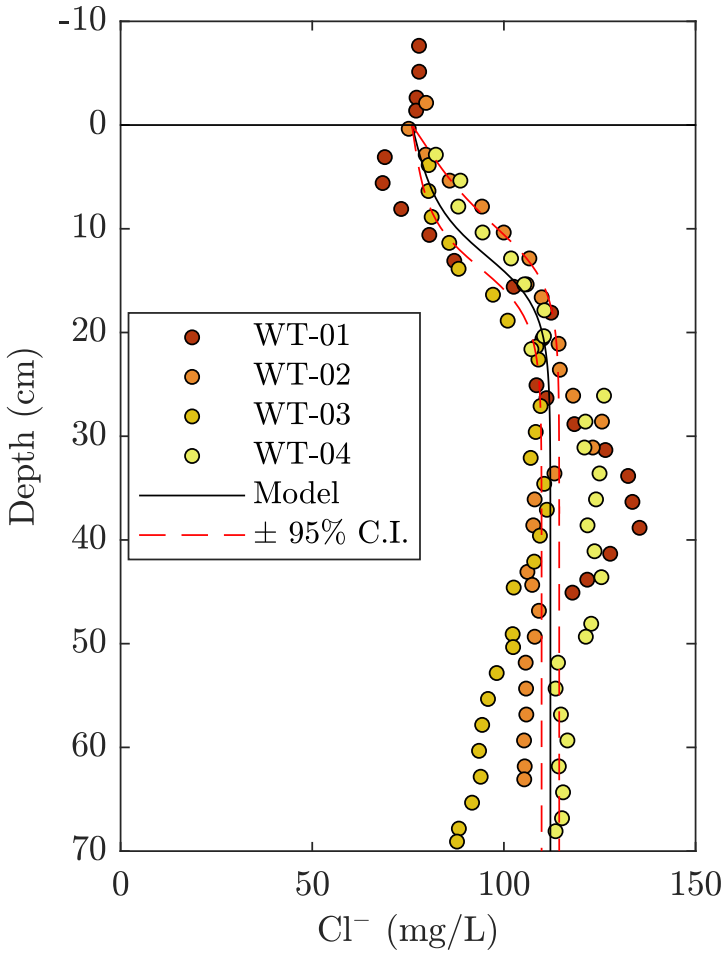


Figure 5.99. Cl^- Observations in the WT and Fitted Transport Model.

5.5.7.1.3 Model implications on the fate and transport of PAHs in the cap

The purpose of the remediation cap in the Grand Calumet River is to create a physical barrier between the contaminated sediments and surface water. In addition, the organophilic constituents of the cap can sorb freely dissolved PAHs and retard the migration in pore water.

The long-term availability and mobility of hydrophobic contaminants in the cap is largely determined by the transport processes. Thus, modeling the transport is fundamental to predict the lifespan of the cap. In this regard, sHRPP data provided valuable information on (1) direction of flow and (2) magnitude of pore water velocity and intensity of benthic exchange.

To illustrate the value of sHRPP data, the system of native sediments and the cap was simulated in CapSim 4.0 to predict the lifespan of the cap. The objective was to model the migration of two representative PAHs, phenanthrene and benzo[a]pyrene (3 and 5 rings respectively), under the assumption that there is no natural attenuation. The parameters used for the simulations are presented in Table 5.12 and Table 5.13, and the simulation results are presented in Figure 5.100.

Table 5.12. Compound Specific Parameters for CapSim Simulation.

Parameter	Phenanthrene	Benzo[a]pyrene
log K_{DOC}	3.81	5.59
log K_d in Cap	2.80	4.01
log K_d in Sediments	5.03	6.46
Initial Concentration in Cap (ng/L)	140	1.05
Initial Concentration in Sediments (ng/L)	1495	3.55

Table 5.13. Cap Specific Parameters for CapSim Simulations.

Parameter	Value
Cap Thickness (cm)	40
Cap Dispersivity (cm)	4
DOC (mg/L)	4.5
Bulk density (kg/L)	1.25

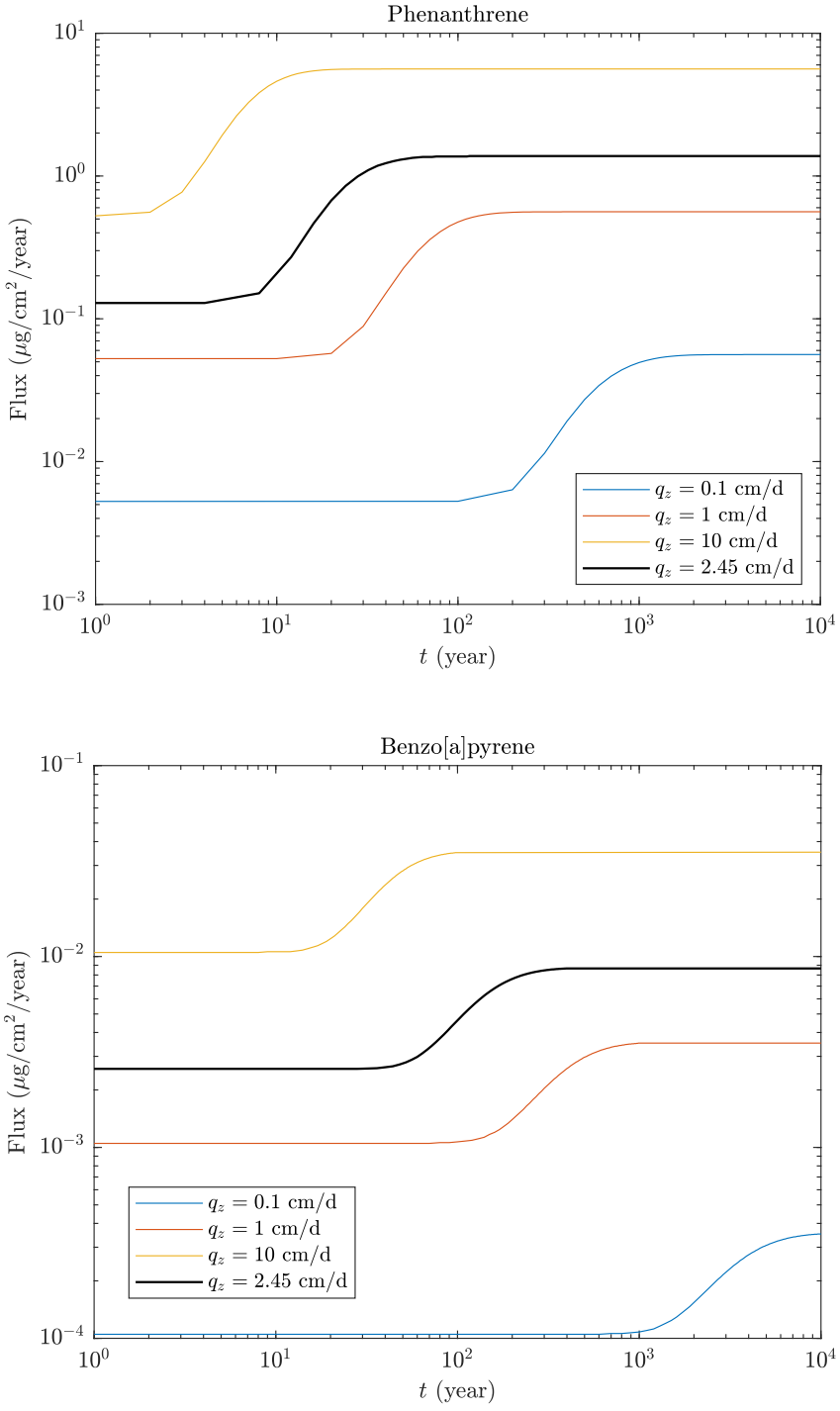


Figure 5.100. Sensitivity Analysis of Darcy's Flux on Predicted Flux of Phenanthrene (Top) and Benzo[a]pyrene (Bottom) from the Cap to Surface Water Immediately After Cap Placement.

Black line ($\boldsymbol{q_z = 2.45\ cm/d}$) indicates estimated flux with transport parameters characterized through sHRPP measurements.

Simulation results presented in Figure 5.99 highlight the effect of Darcy's flux on the magnitude of contaminant leaving the system and the predicted lifespan of the cap. Without the ability to constrain the transport processes, the cap needs to be simulated with typical upwelling flows that can vary by orders of magnitude. By using a Darcy's flux of 10 cm/d, phenanthrene and benzo[a]pyrene break through the cap in approximately 3 and 20 years respectively. However, if Darcy's flux is 0.1 cm/d, breakthrough occurs in approximately 200 and 2000 years respectively. By using the transport processes estimated through sHRPP ($q_z = 2.45$ cm/d), a breakthrough of phenanthrene and benzo[a]pyrene is expected to occur in approximately 10 and 50 years respectively.

A final remark is that this prediction does not account for natural attenuation, which can play a significant role in the availability of contaminants. If there are measurements of contaminants in the cap at different times, the changes could be used to estimate attenuation rates. This would work since observed changes in the cap not derived from the transport processes (already characterized through sHRPP) would be used to characterize attenuation.

5.5.7.2 Canal Creek

At Canal Creek, the estimated pore water velocities provide an indication of groundwater upwelling and tidal exchange in the near surface environment. Net groundwater upwelling is relatively low with a Darcy's flux below the surficial sediments of between 0.06 and 0.08 cm/d according to previous measurements (Majcher, Phelan, Lorah, & McGinty, 2007). The analysis of near surface and bank groundwater movement was focused on the transect where the four locations lie in the same plane (locations "T" in Figure 5.101). The estimates of pore water velocity through sHRPPs are based on calculated mass transfer coefficients for the loss of Br^- and cannot differentiate direction of flow. Therefore, estimations presented in Figure 5.102 are the result of all transport processes occurring in the bank.

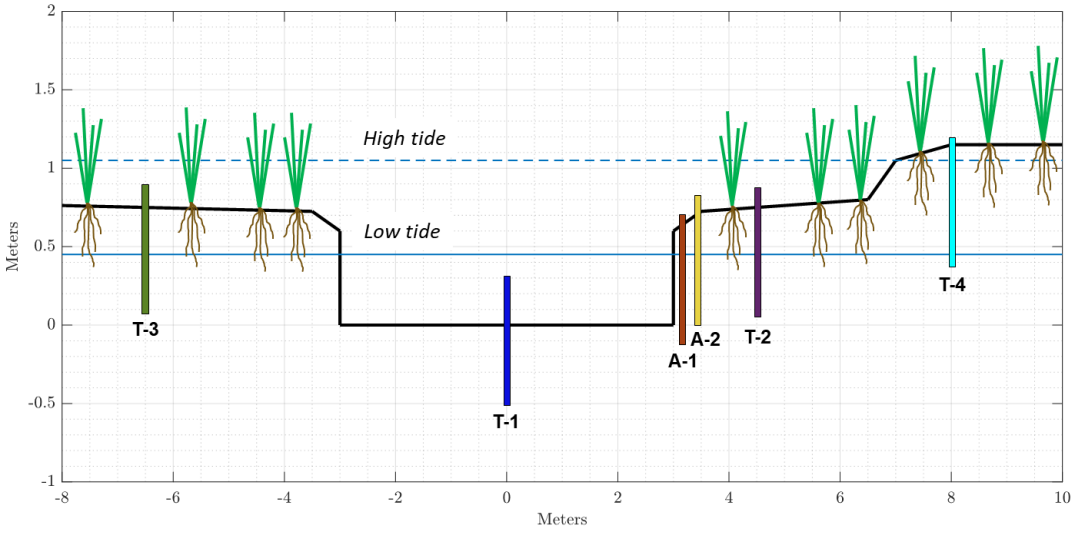


Figure 5.101. Cross-sectional View of Deployed Samplers.

Vertical rectangles represent the sHRPPs at the respective depths and distances from the center and bottom of the canal. Samplers A-1 and A-2 are not in the same transect as the rest of the sHRPPs.

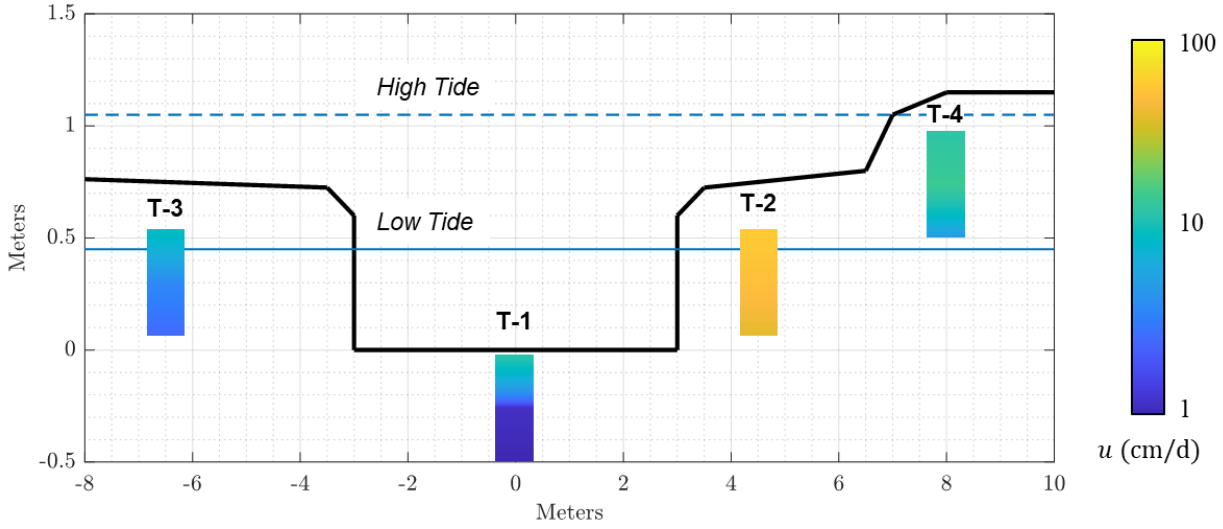


Figure 5.102. Estimates of Pore Water Velocity as a Function of Depth at Locations in the Canal Creek Transect.

For the location T-1, estimates of velocity showed a higher rate of exchange in the top ~10 cm of the sediments, which is consistent with mixing in the benthic zone by bioturbation and hyporheic exchange. For the remaining locations in the bank, estimates were higher near the surface of the sediments and overall velocities decreased with distance from the canal. Estimated velocities in the sediments within the tidal range of the adjacent creek were 10-100 times larger than the prevailing groundwater upwelling. This is consistent with tidal exchange being the primary mechanism for flow in the upper layers of the sediment.

The Cl^- concentrations as a function of depth are displayed in Figure . The profiles reflect groundwater-surface water exchange with surface water Cl^- concentrations near the top and groundwater concentrations of Cl^- at depth. In addition, observations indicate that locations close to the canal had a deeper intrusion of surface water, which is expected due to bank drainage in tidal zones (Musial, Sawyer, Barnes, Bray, & Knights, 2016; Røy, Lee, Jansen, & de Beer, 2008; Alicia M. Wilson & Morris, 2012; Xin, Yuan, Li, & Barry, 2011). In addition, the profiles of Cl^- reached a maximum at or below the level of mean low tide and approached surface water and ground water concentrations at the surface and at depth, respectively. The maximum concentrations were 300-800 mg/L Cl^- despite considerably lower surface water (~45 mg/L) and groundwater concentrations (<200 mg/L). For locations T-3 and T-4 furthest from the creek, concentrations still do not reflect groundwater concentrations even at the deepest depth.

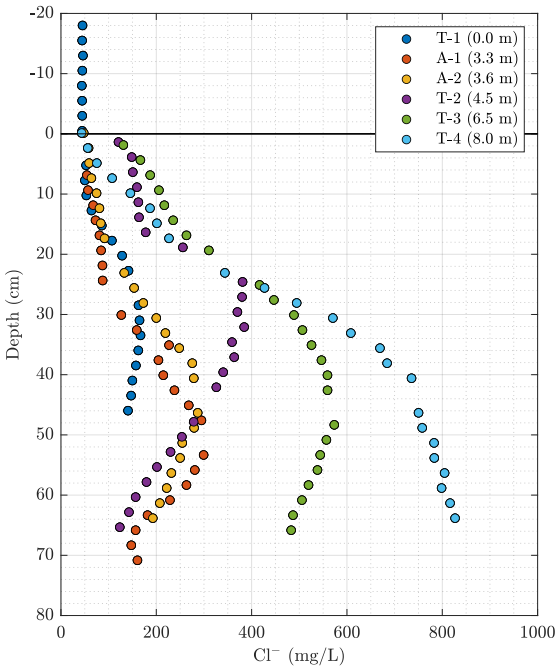


Figure 5.103. Cl^- Profiles as a Function of Depth.

Groundwater concentrations of Cl^- were <200 mg/L and surface water concentrations were ~45 mg/L.

At location T-1 within the channel and always saturated, the surface water concentration was maintained in the first ~10 cm suggesting a rapid exchange between pore and surface water, which is expected from bioturbation and hyporheic exchange in the near surface sediments (Cheng, Song, Wang, & Zhang, 2019; Thibodeaux & Bierman, 2003; Volkenborn, Polerecky, Hedtkamp, van Beusekom, & De Beer, 2007). At location T-4, which did not extend as far down as mean low tide, much higher concentrations of Cl^- were noted with no apparent peak.

The Cl^- profiles indicate a band of high concentration at intermediate depths in the profile, which increased and broadened with distance from the canal. The likely explanation for this behavior is evapotranspiration which removed water from the subsurface and increased the concentration in the root zone relative to the near surface (controlled by surface water exchange) and at depth (controlled by groundwater concentration) (Mguidiche et al., 2015; Saysel & Barlas, 2001; Xin et al., 2017). The dominant plant in this system is Phragmites, which is characterized by deep root structures extending into and below the saturated sediments. Since the intensity of tidal exchange decreases with distance from the canal, the relative effects of evapotranspiration will increase relative to the dilution associated with tidal exchange away from the stream.

5.5.7.2.1 Conceptual Site Model

From the observations and characteristics of the site, the conceptual model of the site includes groundwater upwelling, diffusion and dispersion, evapotranspiration, and a rapid exchange between pore water and surface water near the surface. Figure 5.104 shows the conceptual model of the site, where inundated sediments at the bottom of the canal have no evapotranspiration, and sediments in the bank have inundation/drainage instead of benthic exchange.

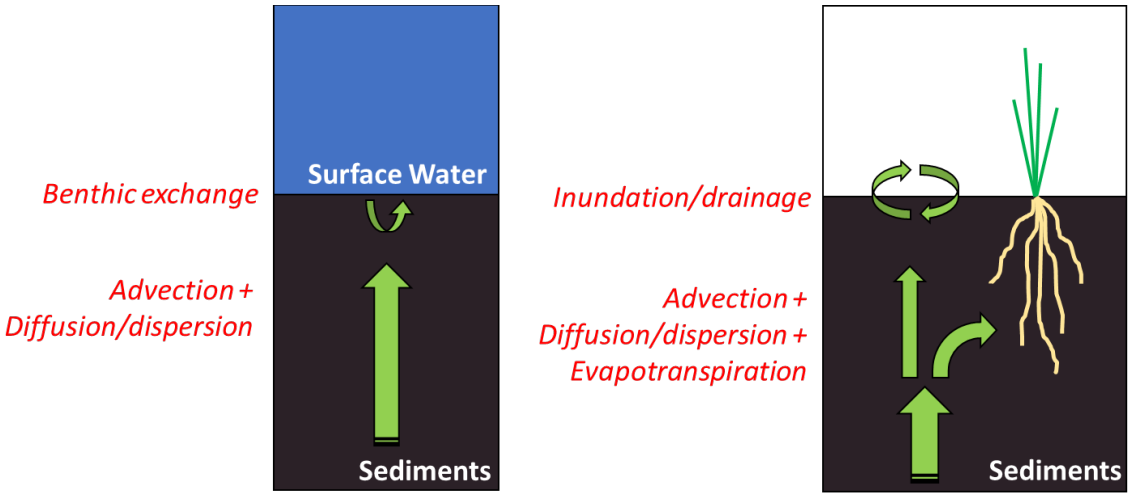


Figure 5.104. Conceptual Model of the Sediments at the Bottom of the Canal (Left) and in the Bank (Right).

5.5.7.2.2 Mathematical Model and Parameter Estimation

The vertical flux (z-direction) for Cl^- is given by

$$J_z = q_z C - \left(\alpha_z |q_z| + \frac{D_w \phi}{\tau} + D_{\text{ben}}\right)\frac{\partial C}{\partial z} \tag{2.1}$$

where C is the concentration in pore water, ϕ is the porosity of the medium, q_z is the Darcy's flux ($q_z = \phi u$), α_z is the dispersivity (which was assumed to be one tenth the simulated length (Danny D. Reible, 1998)). D_w is the diffusion coefficient of Cl^- in water (1.7 cm^2/d (Vitagliano & Lyons, 1956)), $\tau = \phi^{-1/3}$ is the tortuosity in the porous space (Millington & Quirk, 1961), and D_{ben} describes the depth-dependent mixing in the benthic zone by hyporheic and bioturbation processes (Shen et al., 2018), i.e.,

$$D_{\text{ben}}(z) = D_{\text{ben},0}\exp\left\{-\frac{z^2}{2\sigma^2}\right\} \tag{2.2}$$

where $D_{\text{ben},0}$ is the maximum intensity and σ is the characteristic length for the benthic exchange. Since there is water uptake by evapotranspiration, a volumetric water balance in the pore space is given by

$$\frac{\partial q_z}{\partial z} = -\eta(t)\epsilon(z) \tag{2.3}$$

where $\eta(t)$ is a factor to account for the intensity of evapotranspiration through the year ($\eta \in [0,1]$), which is a function of the weather and vegetation type, and $\epsilon(z)$ is the rate of water uptake per volume of sediments per time (Li, 2001; Raats, 1974; J. Vrugt, van Wijk, Hopmans, & Šimunek, 2001; J. A. Vrugt, Hopmans, & Šimunek, 2001), that assumes a normally distributed root activity with depth

$$\epsilon(z) = \epsilon_m \exp\left\{-\frac{(z-\delta_\epsilon)^2}{2\sigma_\epsilon^2}\right\} \tag{2.4}$$

where ϵ_m is the maximum rate, δ_ϵ the depth where the maximum occurs, and σ_ϵ is the characteristic width of the function (distance from δ_ϵ where ϵ drops to ~60% of its maximum value). Therefore, from Equations 3.5 and 3.6, the Darcy's flux is spatially and temporally variable, i.e.,

$$q_z(z,t) = q_{gw} - \eta(t)\int_\infty^z \epsilon(\zeta)d\zeta \tag{2.5}$$

where q_{gw} is the flux of groundwater before root water uptake. Note that quantity $\int_0^\infty \epsilon(z)\,dz$ indicates the rate of volume of water removed by evapotranspiration per area of soil surface.

Given the previous definitions, a mass balance for Cl^- in the sediments is given by

$$\phi\frac{\partial C}{\partial t} + \frac{\partial J_z}{\partial z} = \xi(C_{sw} - C) \tag{2.6}$$

where ξ is a depth-dependent irrigation term (Boudreau, 1997) (volume of water mixed per volume of sediments per time) to account for the exchange between pore and surface water due to inundation and drainage of the bank as a function of the distance from the canal:

$$\xi(z) = \frac{1}{2}\xi_m \operatorname{erfc}\left(\frac{z-\delta_\xi}{\sqrt{2}\sigma_\xi}\right) \tag{2.7}$$

where ξ_m is the maximum exchange rate (volume of pore water per time per volume of sediment), δ_ξ is the characteristic depth (inflection point) where the exchange drops to zero, and σ_ξ is the characteristic length for the drop to occur. Based on this model, the quantity $\int_0^\infty \xi(z)\,dz$ indicates the rate of water volume exchange per area of bank surface. Note that in this approach, $D_{\text{ben}} = 0$ for sediments in the bank, and $[\epsilon, \xi] = [0,0]$ for sediments in the canal.

The solution of Equation 2.6 requires the definition of boundary conditions, that in this case are the surface and ground water concentrations of Cl^- (C_{sw}, C_{gw}) and model parameters.

Collected data in this study only captures a picture of averaged pore water conditions during December of 2018. However, some reasonable assumptions were used to reproduce observations. The assumed Darcy's flux at the bottom of the formation was between 0.06 and 0.08 cm/d according to previous measurements (Majcher et al., 2007). For evapotranspiration, it was assumed that vegetation at this location was represented by Phragmites, which are active in the second and third quarters of the year (see Figure 5.105), exhibit most of the root activity in the top 60 cm, and cause evapotranspiration rates between 0.2 and 0.4 cm/day (Borin, Milani, Salvato, & Toscano, 2011; Moore, Burdick, Peter, & Keirstead, 2012; Zhou, Zhou, Liu, & Sui, 2010). The maximum evapotranspiration rate (ϵ_m) and the depth where it occurs (δ_ϵ) were fitted to reproduce observations (see Figure and Table).

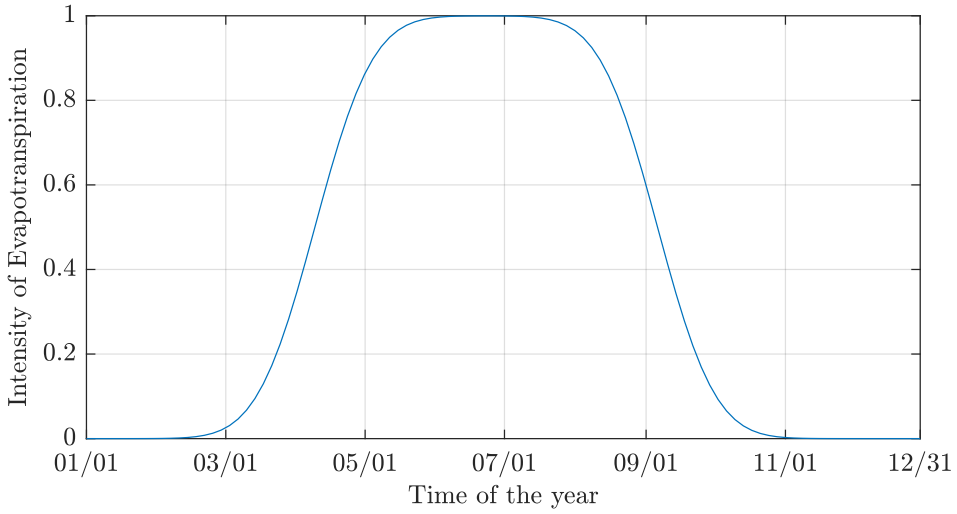


Figure 5.105. Assumed Intensity of Evapotranspiration Rate Throughout the Year.

(Term $\boldsymbol{\eta(t)}$ in Equation 2.3)

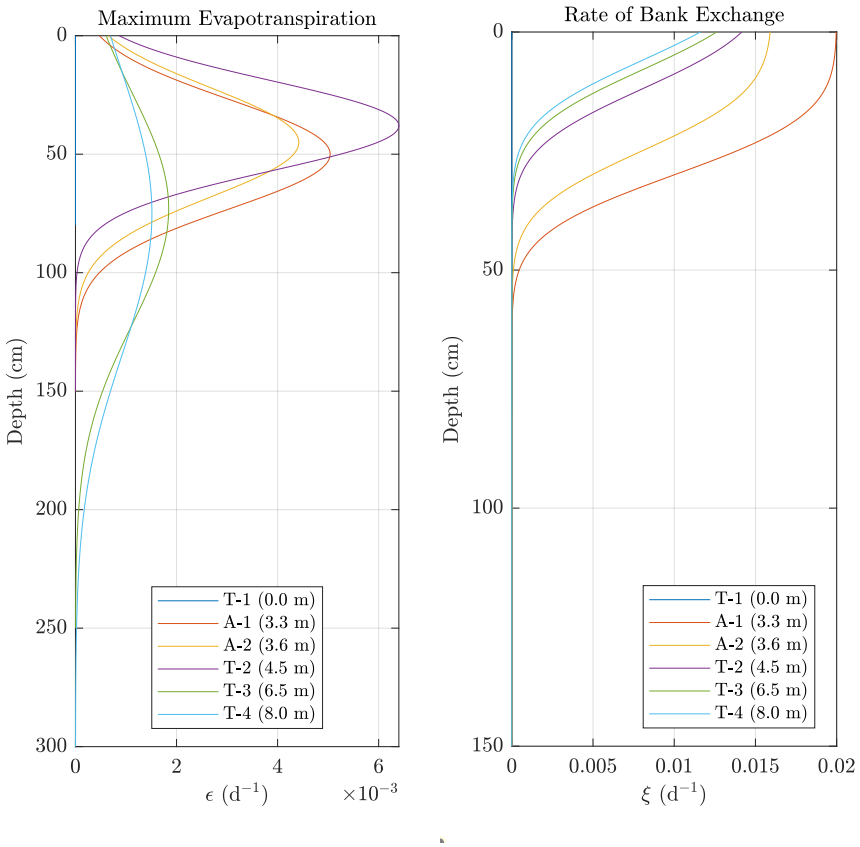


Figure 5.106. Fitted Rates of Evapotranspiration (Left) and Surface Exchange (Right) to Reproduce Cl^- Observations.

Table 5.14. Fitted Parameters to Reproduce Cl^- Observations.

Location	Distance from the center of the canal (m)	Maximum benthic zone mixing, $D_{\text{ben},0}$ (cm^2/d)	Average evapotranspiration rate, $\int_0^\infty \epsilon(z)\,dz$ (cm/d)	Rate of water exchange per area of sediment surface, $\int_0^\infty \xi(z)\,dz$ (cm/d)	Average percent error between model and observations (%)
T-1	0	10	0	0	4.7
A-1	3.3	0	0.29	0.60	13.9
A-2	3.6	0	0.25	0.40	10.0
T-2	4.5	0	0.30	0.20	12.9
T-3	6.5	0	0.21	0.15	15.7
T-4	8.0	0	0.20	0.12	6.6

For the benthic exchange at T-1, an intensity of $D_{\text{ben},0} = 10$ cm^2/d was assumed and a characteristic length of 5 cm was used in line with observations at other fresh water systems (Danny D Reible, 2014). For the surface water-pore water exchange in the bank, values of ξ_m and δ_ξ were fitted to reproduce observations. ξ_m was of the order of 10^{-2} d^{-1} and dropped with distance with the canal, which means a full replacement of the pore volume in less than 100 days, consistent with (Alicia Marie Wilson & Gardner, 2006). For δ_ξ, fitted values dropped also with distance and were between 5 and 30 cm, which meant an intrusion of surface water at smaller depths than tidal fluctuations during the sampling period.

Using the previous assumptions and fitted values, Figure shows that the model reproduced the observed behavior of Cl^- in pore water (average percent errors were between 5 and 16%), which suggests that the model captured the main transport mechanisms. Note that the model implies that during the sampling period (winter), there was no root uptake of pore water and the Cl^- peaks were vanishing due to inundation-drainage of the bank and the groundwater upwelling. In this regard, Figure shows the predicted Cl^- concentration in pore water as a function of the time of the year at the location closest to the canal (A-1) and the location farther from it (T-4). The model assumes that the tides are consistent from day to day and that seasonal processes, such as precipitation, do not strongly affect the measured profiles.

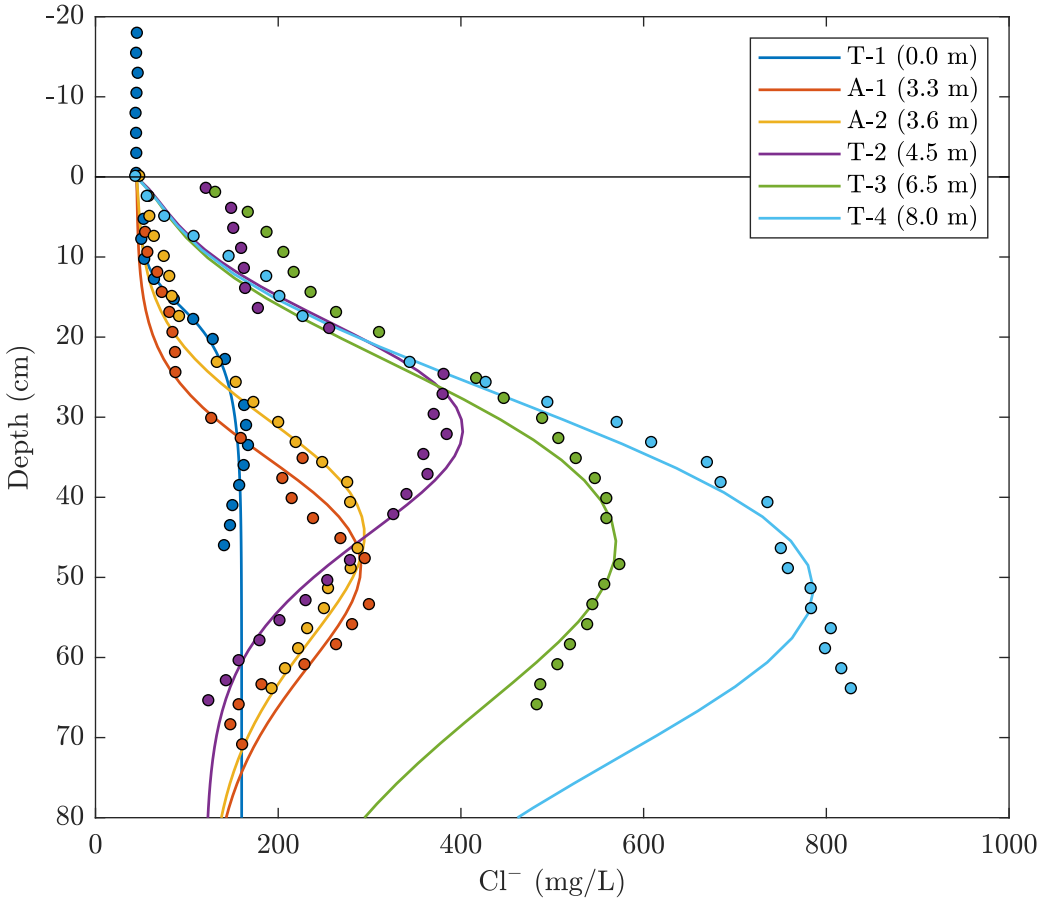


Figure 5.107. Observed Concentrations of Cl^- in Pore Water and Qualitative Reproduction Based on the Proposed Model.

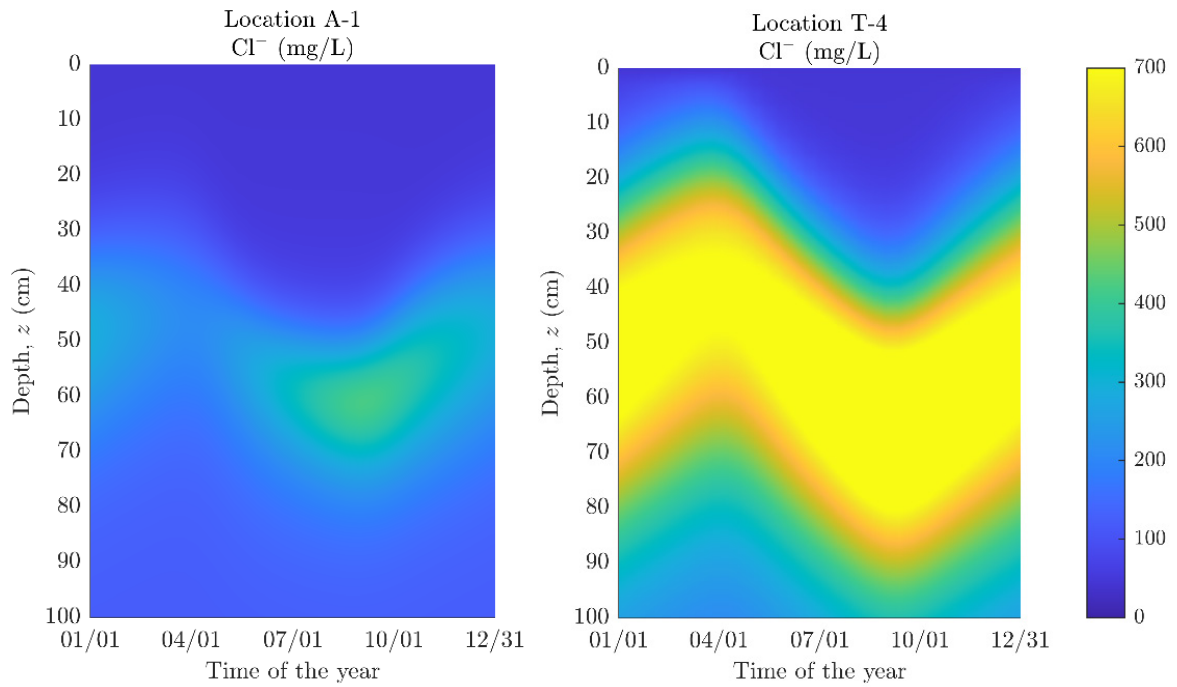


Figure 5.108. Predicted Pore Water Concentration of Cl^- as a Function of Depth and Time of the Year at Locations A-1 (Closest to the Canal) and T-4 (Farther from the Canal).

5.5.7.2.3 Model Implications on the Fate and Transport of Heavy Metals in the Bank

The observations and the model of the site indicate that in near surface sediments, groundwater upwelling is a slow process to renew pore water compared to tidal inundation-drainage and evapotranspiration. This implies a periodic intrusion of oxic water and subsequent depletion of favorable electron acceptors by biogeochemical processes. Consequently, there is a cyclic variation of chemical conditions resulting from the tidal inundation and drainage that can affect the availability of redox sensitive species.

Figure shows the profiles of two sensitive species, SO_4^{2-} and Zn. In the case of SO_4^{2-}, pore water concentrations peaked at certain locations with no correlation to evapotranspiration peaks in Cl^- profiles. Therefore, SO_4^{2-} profiles are likely the result of S^{2-} oxidation by intrusion of oxic water. This implies that redox sensitive molecules, such as Zn compounds, can change speciation because of the mixing of surface and pore water in the near surface. In oxic conditions, Zn oxidizes to Zn^{2+}, which is soluble while in reduced environments it is expected to be present mostly as insoluble zinc sulfide ($ZnS_{(s)}$). The transition from one phase to another is reversible, therefore sequestration and release of Zn could occur in sediments exposed to cyclic redox conditions (Kumar, Chaurand, Rose, Diels, & Bastiaens, 2015; Liber et al., 1996). Observations in total dissolved Zn show that most of the pore water values were below the surface water concentration, except at three locations (A-1, A-2, and T-4), where Zn concentrations peaked at depths where SO_4^{2-} did.

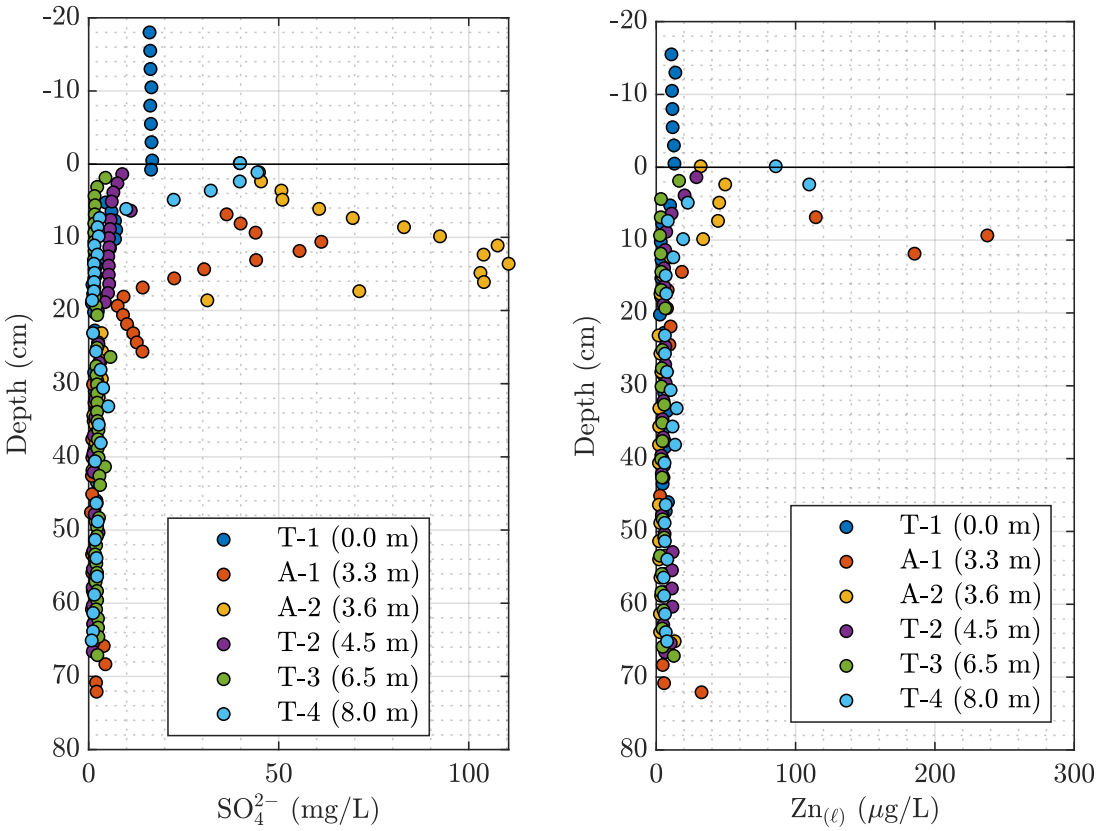


Figure 5.109. Measured Pore Water Concentration of SO_4^{2-} and Dissolved Zn.

Based on the previous discussion, the tidal inundation of the bank has the potential to cause two opposite effects on Zn: release from $ZnS_{(s)}$ by the introduction of dissolved O_2 that oxidizes S^{2-} to SO_4^{2-}, and sequestration of dissolved Zn^{2+} by S^{2-} from the reduction of SO_4^{2-}. Based on the site model, the effects should be evident in the near surface sediments. To evaluate this, bulk measurements of Zn were split into top and bottom groups, where the separating depth was 25 cm (based on an average depth for inundation and drainage obtained from observations and the modeling efforts). The groups were analyzed for normality of data and the means were compared (Figure 5.110). Results showed that sediments in the near surface group had 45% more Zn than in the bottom ($p < 0.001$ for values of 4606 ± 308 mg/kg and 3182 ± 208 mg/kg respectively). Therefore, it was evident that sequestration of Zn from surface water was the dominant process, which is in line with studies showing that precipitation kinetics of Zn^{2+} and S^{2-} are much faster than oxidation of $ZnS_{(s)}$ (Bowles et al., 2002; Hong, Kinney, & Reible, 2011; Sukola, Wang, & Tessier, 2005).

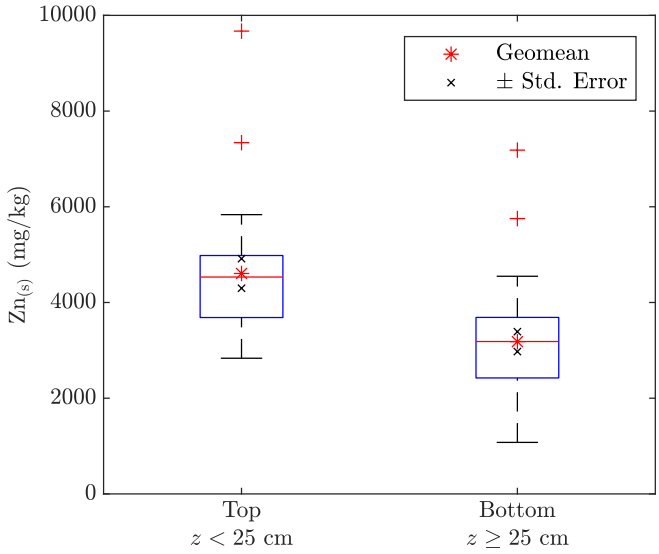


Figure 5.110. Distribution of Bulk Concentrations of Zn in Top and Bottom of Sampled Sediments.

As a conclusion, characterized transport processes in the bank help develop a conceptual model of the site in which variable redox conditions can affect the sequestration and release of redox sensitive contaminants.

5.6 QUALITY ASSURANCE FOR PORE WATER SAMPLING AND ANALYSIS

5.6.1 Calibration Procedures and Frequency

Calibration refers to the checking of physical measurements of both field and laboratory instruments against accepted standards. It also refers to determining the response function for an analytical instrument, which is the measured net signal as a function of the given analyte concentration. These determinations have a significant impact on data quality and are performed regularly. In addition, preventative maintenance is important to the efficient collection of data. For preventative maintenance purposes, critical spare parts were obtained from the instrument manufacturer.

All field and laboratory instruments were calibrated according to manufacturers' specifications. All laboratory instruments were calibrated in accordance with established SOPs (see Appendix C). Certified standards were used for all calibrations and calibration check measurements. A calibration logbook was maintained by laboratory quality assurance (QA) personnel. Calibration of field instruments (Hach methods) followed all manufacturer guidelines.

5.6.2 Quality Control Samples

Internal quality control (QC) data provides information for identifying and defining qualitative and quantitative limitations associated with measurement data. Analysis of sHRPP preparation water, distilled water spiked with NaBr (100 mg/l-Br), provided the primary basis for quantitative evaluation of field data quality. These field blank samples are used to evaluate the presence of contamination from handling errors or cross-contamination during sHRPP preparation prior to deployment.

Trip blanks can also be used to assess handling errors and cross-contamination but are often not necessary when the contaminants of concern are non-volatile or have low volatility (e.g., PCBs, DDX, PAHs, anions, etc.). Trip blanks were not analyzed during this demonstration.

5.6.3 Sample Documentation

Project staff coordinated shipment and receipt of sample bottles, coolers, ice, and custody seals. An important consideration for the collection of environmental data is the ability to demonstrate that the analytical samples have been obtained from predetermined locations and that they have reached the laboratory without alteration. Evidence of collection, shipment, laboratory receipt, and laboratory custody until disposal must be documented to accomplish this. Upon completion of sampling, typically a chain of custody form is filled out and returned with the samples to the laboratory. However, due to the sheer volume of samples collected during this demonstration, chain of custody forms were not utilized; instead using the field logbook as evidence of sample collection, custody seals as evidence that the samples were not tampered with between collection and analysis, and commercial carrier shipment documentation (waybill) as evidence of shipping. Samples were packaged appropriately to prevent breakage or leakage during transport and shipped to the laboratory via commercial carrier.

Upon receipt of the samples by the Texas Tech laboratory, the laboratory QC Coordinator, or designated representative, opened the shipping container(s) and compared the contents with records contained in the field book. Any discrepancies would have been noted in the project file (none were noted during this demonstration).

5.6.4 Sample Identification

A discrete sHRPP cell number or sample location identification number, in the case of T Bar and sediment core samples, was assigned to each sample. This discrete identifier was placed on each bottle and was recorded, along with other pertinent data in a field notebook dedicated to the project. The sample identification number designated the sample location (e.g., "sHRPP-4-1" for this specific sampler cell). The bottle label also contained the site name, the sampling date and time, any preservatives added to the bottle, and the initials of the sampler.

5.6.5 Laboratory Sample Receipt

Following sample receipt, the Laboratory Manager or qualified personnel:

- Examined all samples and determined if proper temperature has been maintained during transport. If samples had been damaged during transport, the remaining samples were carefully examined to determine whether they were affected. Though no samples were damaged during the demonstration, if any samples had been considered damaged, those samples would have been removed from the sampling program.
- Compared samples received against those listed in the field book.
- Verified that sample holding times were not exceeded.
- Recorded samples in the laboratory sample log-in book containing, at a minimum, the following information:

- Project identification number
- Sample numbers
- Type of samples
- Date and time received.

The field book was placed in the project file.

5.6.6 Other Documentation

Following sample receipt at the laboratory, the Laboratory Manager or sample custodian clearly documented the processing steps applied to the sample. The analytical data from laboratory QC samples were identified with each batch of related samples. The laboratory logbook includes the time, date, and name of the person who logged each sample into the laboratory system. This documentation is thorough enough to allow tracking of the sample analytical history without aid from the analyst. At a minimum, laboratory documentation procedures provide the following:

- Recording in a clear, comprehensive manner using indelible ink.
- Corrections to data and logbooks made by drawing a single line through the error and initialing and dating the correction.
- Consistency before release of analytical results by assembling and cross-checking the information on the sample tags, custody records, bench sheets, personal and instrument logs, and other relevant data to verify that data pertaining to each sample are consistent throughout the record.
- Observations and results identified with the project number, date, and analyst and reviewer signatures on each line, page, or book as appropriate.
- Data recorded in bound books or sheaf of numbered pages, instrument tracings or hard copy, or computer hard copy.
- Data tracking through document consolidation and project inventory of accountable documents: sample logbook, analysis data book, daily journal, instrument logbook, narrative and numerical final reports, etc.

6.0 PERFORMANCE ASSESSMENT

The extent to which each performance objective presented in Section 3.0 was met is discussed in detail below and summarized in Table 6.1.

6.1 MEASURE CONCENTRATIONS OF KEY CONTAMINANTS AT EQUAL SENSITIVITY AND WITH LOWER ERROR ESTIMATES WITH DEPTH

One of the primary objectives of this demonstration was to demonstrate that the sHRPP can measure concentrations of key contaminants [PCBs, DDX, PAHs, metals] with depth in sediments with the same or better levels of detection and with greater confidence than traditional methods (either *in- situ* passive sampling or core processing).

6.1.1 Data Requirements

This performance objective was evaluated through the 4-wk deployment of multiple sHRPPs at the field sites. Following retrieval, the sHRPP SPME PDMS fibers were analyzed for dissolved HOCs (PCBs, PAHs or DDX) according to EPA 8270 (PAHs), EPA 8081A (DDX), and EPA 1668c (PCBs). Remaining concentrations of PRCs were analyzed in the SPME fibers by the appropriate methods above, depending on which analyte was of interest. For sites with PCBs, DDX, or PAHs we also measured concentrations in pore water using traditional vertical *in-situ* SPME sampling and/or ex-situ SPME sampling and at Grand Cal we also compared to PE sheet samplers at shallow depths. At sites where heavy metals are present, a portion of the equilibrated pore water in the sHRPP cells was analyzed for heavy metals (Hg, , Pb, As, Zn).

6.1.2 Success Criteria

This objective was considered to be met if the concentrations of organic hydrophobic contaminants (PAHs, PCBs, DDX), measured in pore water:

1) were acquired by the sHRPP at the desired resolution (~2 cm) and were detected with comparable or improved sensitivity compared to current industry-standard (e.g., *in-situ* vertical SPME sampling) passive sampling methods.
2) had statistically smaller confidence intervals (smaller uncertainty) than concentrations provided by standard vertical samplers.

For metals, the objective was met if the concentrations in the equilibrated pore water of the sHRPP cells:

1) had the desired resolution (~2 cm) and were detected with comparable or improved sensitivity compared to current industry-standard pore processing methods.
2) had measured and predicted (spatial) concentrations at depths of concern that have statistically smaller confidence intervals (smaller uncertainty) than concentrations provided by core processing.

Table 6.1. Performance Objectives Assessment

Performance Objective	Data Requirements	Success Criteria	Results
Quantitative Performance Objectives			
Measure concentrations of key contaminants [PCBs, PAHs, metals] in sediments using HRPPs that decrease uncertainty in depth dependent measurements of COCs and modeled predicted concentrations at a detection limit and resolution that provides statistically lower error estimates of concentration with depth.	SPME - EPA 1668c (PCBs) (Abraham's Creek) SPME-EPA 8270 (DDX) (Quantico Embayment) Aqueous ICP-MS (metals) (Canal Creek) SPME - EPA 8270 (PAHs) (Grand Calumet)	Quantification of key contaminants with depth with sensitivity (e.g., DL) comparable to traditional methods (in-situ vertical SPME for HOCs and core processing for metals). Quantification of COCs at a resolution that produces statistically lower error estimates with respect to sediment depth.	Partial Success
Measure changes in geochemical conditions and conservative species at a scale equal to the scale in change of depth due to redox changes or conservative transport.	Anions - EPA 300 (all sites) DOC (EPA 5310) (Abraham's Creek and Quantico Embayment)	Quantification of key geochemical parameters with depth at a scale that equals the distance redox changes occur and conservative transport processes occur and with sufficient sensitivity to measure redox transitions and transport processes.	Success
Measure pore water velocity in sediments using HRPPs	Br^- - EPA 300 (all sites)	Quantification of pore velocity with depth	Success
Measure microbial community structure and key degradative organisms/genes	qPCR analysis of Bio-Sep beads in HRPP cells for key organisms/genes (contaminant dependent) (Canal Creek, Abraham's Creek) but each site may evaluate different groups/ capabilities)	Quantification of key organisms/genes with depth at comparable resolution to cores.	Success
Measure quantitative parameters required to evaluate remediated and unremediated sediments.	Quantitative data from above parameters (Abraham's Creek, Quantico Embayment, Grand Calumet)	Demonstrate that measured concentrations (e.g., COCs, bioaugmented bacteria, and presence of lower chlorinated PCB congeners) based on sHRPP data have lower error estimates and lead to higher statistical power (significance) than data produced by standard sampling measurements. (Abrahams Creek and/or Embayment).	Success
Qualitative Performance Objectives			
Quantify differences in site evaluation based on traditional existing data and cores/traditional passive sampling from this study and new high resolution integrated data	Compare attenuation and transport of contaminants at sites for both unaltered and remediated areas where present using existing data and data from sHRPP above (Abraham's Creek, Quantico Embayment, Grand Calumet)	Quantify differences in site interpretation, model predictions, resolution, confidence interval, and cost of data collection	Partial Success
Ease of HRPP deployment and sampling	Feedback from field technician on usability of technology and time required (all sites)	Deployment time is comparable or less than traditional measures (site dependent). Technical skill required to utilize samplers is comparable to that required for traditional methods.	Partial Success

6.1.3 Outcome

For HOCs this objective was considered to be mostly met. Detection limits for HOCs (PCBs, PAHs, DDx) are a function of the length of fiber extracted and final volume of solvent. sHRPP provide greater fiber mass per depth (~5-7 cm every ~2cm) due to horizontal rather than vertical integration and therefor had lower detection limits than traditional vertical SPME sampling (See Figures 5.31-5.33). The sHRPP HOC detection limits were higher than ex-situ SPME (more fiber per mass of soil) and PE sheet samplers. However ex-situ SPME analysis does not represent field conditions (e.g., benthic exchange) and PE samplers have slow equilibration rates and are not able to penetrate to deeper depths or through consolidated sediment. Traditional SPME must average 5-7cm of depth to produce the same detection limit. sHRPP therefore have increased spatial resolution providing ~ 3X the fiber length over any sampled depth compared to vertical SPME. Ex-situ resolution using cores is also lower due to the need for sufficient material (see Figures 5.62-5.64). sHRPP also sample a longer sampling length per sample depth compared to vertical placement providing a more spatially integrated concentration (5-7cm sampled each ~2cm) compared to vertical placement (2cm sampled per 2cm of depth). This reduces error due to spatial variation in sediment and decreases the uncertainty in concentration (See Figures 5.39, 5.40, 5.78-5.92). For instance, in order to sample an equivalent sediment area, ~ 3 vertically deployed SPME samplers would have to be installed and for each horizontal deployment 3 independent measures of HOC concentration are produced by the sHRPP compared to the vertical deployment, assuming equal detection limits. In addition, vertical SPME or PE sheet placement and ex-situ SPME using cores produces more uncertainty in sampled depth, as the only way to determine depth of vertical SPME or PE sheet placement is by measuring the depth of water to the sediment interface. This can be difficult in sediments with deep overlying water (e.g., Grand Cal and Abrahams Creek) and soft bottomed sediment. Incomplete core retrieval and compression also impact ex-situ depth assignment (see figures 5.62-5.64; 5.69-5.92). The sHRPP depth of deployment was verified by evaluating the concentration of conservative species (e.g., Cl^-) with depth which can clearly show the sediment/water interface (See Figures 5.6, 5.2, 5.26, 5.55, 5.66).

For metals this objective was also considered partially met as detection limits were theoretically similar to processing cores based on maximum porewater available from cores sectioned at the same resolution. However, due to issues with oxidation of processed core material (Figure 5.18) no metal analysis was performed on core extracts and so no data is available for comparison. The sHRPP resolution was greater than achieved with cores (Figure 5.17 and 5.18) with less depth error, and changes (compression, porewater extrusion, and oxidation) due to core shipping and processing were avoided. Metal concentrations measured by the sHRPP are a function of the instrument detection limit and any dilution factor required to produce sufficient volume for analysis. The sHRPP provided a total of 10ml of volume every 2cm for metal analysis based on reserving 4ml for analysis of major anions (Cl^-, Br^-, NO_3^-, NO_2^-, SO_4^{-2}), sulfide, and iron concentrations. Metal analysis (ICP) requires ~10ml and Hg_T analysis requires 20mls for maximum sensitivity. In this study we diluted the sample for metal analysis by 2.5X (4ml in 10ml) and for Hg_T 4X (5ml in 20ml). This increased our quantification limit by the same factors. In comparison, traditionally cores would be acquired and sectioned, followed by centrifugation, and filtration in a glove bag to prevent redox changes. In this study we acquired 10cm diameter cores. The amount of porewater produced is a function of the length of core homogenized, porosity and sediment type (silt, clay, plant material). In theory the 2cm core section could provide much more porewater but in practice the volume is only slightly greater or similar (as in this study).

This is due to the loss of material while filling the centrifuge bottles, some material having little free water content (plant roots), and limits on sediment compaction. However, even assuming the cores can provide equivalent or greater water per depth, it is almost impossible to process a core at 2cm intervals without freezing the core. Extensive plant roots and the soft nature of the sediment limit the spatial resolution. Secondly, processing the cores anaerobically to prevent oxidation while homogenizing the sections is also problematic. In this study, although we used a glove bag and continuous nitrogen purge, significant sulfides were oxidized to sulfate (Figure 5.18) potentially releasing metals and altering concentrations of geochemical species. Finally, significant core compaction and incomplete recovery occurs during sampling, this reduces the depth resolution, depth confidence, and can allow porewater to be extruded altering the depth dependence of measured parameters. Finally, it should be noted that unless cores are frozen in the field, the shipping of cores can allow for mixing and will alter the redox conditions of the upper core.

6.2 MEASURE KEY GEOCHEMICAL PARAMETERS

The second primary objective was to effectively measure changes in geochemical parameters [NO_3^-, NO_2^-, Cl^-, Fe^{+2}, SO_4^{2-}, DOC] and conservative species (e.g., Cl^-) at a scale equal to the scale in change of depth due to redox changes or transport of conservative species.

6.2.1 Data Requirements

In addition to the previous objective, this performance objective was evaluated through the same 4-wk deployment of multiple sHRPPs at the field sites. Following retrieval, a portion of the equilibrated pore water in the sHRPP cells was analyzed for concentrations of key geochemical indicators (e.g., NO_3^-, NO_2^-, Cl^-, SO_4^{2-}). Depending on the site, we also analyzed Fe^{+2} and S^{-2} on site and DOC. Diffusion equilibrium sampling is the accepted method for monitoring of geochemical species with depth and so we did not compare concentrations with alternate methods (e.g., core processing), as it is well established that cores cannot produce reliable and spatially relevant distributions of geochemical indicators.

6.2.2 Success Criteria

This objective was considered to be met if the data allowed quantification of key geochemical parameters with depth, at a scale less than the distance redox changes and conservative transport processes occur, and with sufficient sensitivity to measure redox transitions and transport processes. It should be noted that the sHRPP uses the "traditional" passive sampling method for geochemical indicators and comparisons were made on the sensitivity from past applications and to the processes being evaluated. For instance, does the sHRPP produce data that can be used to evaluate SO_4^{2-} reduction with a resolution that is less than the distance over which the reduction occurs? Major processes we evaluated include transport of Cl^-, SO_4^{2-} reduction (measuring both SO_4^{2-} and S^{2-}) and Fe reduction.

6.2.3 Outcome

This objective was met. We measured changes in NO_3^-, SO_4^{2-}, sulfide, and Fe^{+2} with depth at both Canal Creek, Abrahams Creek, and the Embayment (e.g., Figures 5.6, 5.7, 5.9, 5.11, 5.13,5.15, 5.27, 5.68). In many cases redox transitions between major electron acceptors were observed to occur over a scale of centimeters often within a few centimeters of the surface water interface.

These depth profiles can also be complex due to vertical and horizontal flow as well as tidal fluctuations. We also show that Cl^- profiles can be used to establish the sediment interface depth more precisely (all sites) (see Figures 5.6, 5.2, 5.26, 5.55, 5.66), and qualitatively (all sites, see sections 5.5.6.1, 5.4.6.3.1, 5.3.6.1, 5.2.6.3) and quantitively (Canal Creek and Grand Cal) evaluate transport (see Section 5.5.7). This includes in some cases the ability to constrain transport increasing the confidence on HOC transport modeling.

6.3 MEASURE PORE WATER VELOCITY

The third primary objective was to measure pore water velocity in sediments using HRPPs.

6.3.1 Data Requirements

In addition to previous objectives, this performance objective was evaluated through the 3-wk deployment of multiple sHRPPs at the field sites. Following retrieval, the equilibrated pore water from the specialized velocity cells in the sHRPP was analyzed for the remaining concentration of a conservative tracer (Br^-). The depletion of Br^- was used to determine pore water velocity.

6.3.2 Success Criteria

The performance objective was considered to be met if the pore water velocity measured with the sHRPP was at the desired resolution (~0.5 m) and with comparable or improved sensitivity compared to current industry-standard sampling methods. It should be noted that at some sites (e.g., lower Canal Creek) no field deployable alternative devices were available and so, although we measured velocity at all sites, only some sites were able to provide alternative measurement techniques for comparison. This approach represents a significant advance over current technologies.

6.3.3 Outcome

This performance objective was considered to be met. Pore velocity was measured at all sites at a resolution greater than 0.5m (5.6, 5.7, 5.9, 5.11, 5.13, 5.15, 5.27, 5.44, 5.52, 5.55, 5.67). Pore velocity can be measured down to a lower resolution of ~2 cm/d. Estimates of pore velocity by other methods were only available at Grand Cal, where historical estimates based on seepage meters ranged from 1-5 cm/d while estimates based on sHRPP were 2-12 cm/d. It should be noted that while the sHRPP cannot differentiate between horizontal and vertical fluxes, it can capture the magnitude of either. At Canal Creek and the Embayment, it appears that there is a significant horizontal component. We are unaware of any system than can be direct driven into sediments to measure horizontal flow.

6.4 MEASURE MICROBIAL COMMUNITY STRUCTURE AND KEY DEGRADATIVE ORGANISMS/GENES

The fourth primary objective was to measure microbial community structure and key degradative organisms/genes using micro-Bio-Traps.

6.4.1 Data Requirements

In addition to previous objectives, this performance objective was evaluated through the 3-wk deployment of multiple sHRPPs at the field sites. Following retrieval, the Bio-Sep beads were collected from the micro-Bio-Traps and shipped on ice to Microbial Insights (Knoxville, TN) for QuantArray analysis. We also quantified bacteria known to dechlorinate PCBs.

6.4.2 Success Criteria

The performance objective was considered to be met if microbial population densities were acquired at the desired resolution (~2 cm) and were detected above background values. There are currently no corresponding standard methods for comparison, thus this approach represents a significant advance in this area.

6.4.3 Outcome

This performance objective was partially met. We measured concentrations of two species of bacteria capable of PCB reductive dehalogenation (DHC and DECO) throughout the profile (Figure 5.28). Due to budget constraints, we only analyzed selected depths. However, Biosep beads were available in all micro-biotrap cells (resolution ~ 3cm) which could have been analyzed.

6.5 QUANTIFY DIFFERENCES IN SITE EVALUATION (EXISITING DATA VS NEW SHRPP DATA)

The fifth primary objective was to quantify differences in site evaluation based on existing data from traditional sampling methods and new, high-resolution, integrated data from the sHRPPs.

6.5.1 Data Requirements

This performance objective was evaluated using the data obtained for two sites (Grand Cal and Canal Creek). Predicted attenuation and transport of contaminants were compared using data based on 1) existing data and/or data produced from traditional methods (e.g., from soil cores, traditional 1D SPME) or 2) data from the sHRPP. For sites that have both unaltered and remediated areas, we also compared the transport and fate of COC using each data set (e.g., traditional vs sHRPP). Emphasis was on evaluating model resolution and reliability.

6.5.2 Success Criteria

The performance objective was considered to be partially met by both quantitative and qualitative measures. Quantitative measures include demonstrating that modeled concentrations with time and depth have lower error terms using data collected by sHRPP than by traditional methods. Qualitative measures were met if differences in site interpretation and cost of data collection for traditional sampling methods compared to the sHRPP are quantified.

6.5.3 Outcome

This objective was partially met. At Canal Creek, sHRPP comprehensive data (velocity, conservative profiles) produced a transport model that predicted accumulation of dissolved species do to evapotranspiration, bank drainage, and tidal fluctuation (5.5.7.2). This model when qualitatively coupled with geochemistry and metal concentrations suggest metals are concentrated from surface water and sequestered due to reduced conditions. A dynamic zone near the surface exists with dynamic fluctuations in metal concentrations, due to tidal and seasonal changes. We are unaware of any other sampling methods that could produce the required data to perform this evaluation. At Grand Cal, transport of HOCs were modeled using CapSim (5.5.71). The effort combined the velocity estimates, and Cl^- depth profiles to determine the magnitude of benthic exchange and then verified the conservative transport model which was applied to PAHs.

Without the sHRPP data there is no way to constrain the transport parameters and thus predictions of long-term transport have large uncertainties. Treatment efficacy was evaluated at Abraham's Creek (see section 6.7) where we show that sHRPP produced more statistical power for comparing treatments. However, we were not able to compare the cost and effort for each method directly as no other methods exist even in combination to give all of the data produced by the sHRPP at the same resolution.

6.6 MEASURE QUANTITATIVE PARAMETERS REQUIRED TO EVALUATE REMEDIATED AND UNREMEDIATED SEDIMENTS

6.6.1 Data Requirements

Quantitative data from Sections 5.3 taken from remediated and unremediated areas of some demonstration locations were compared based on the technologies deployed at each site (e.g., activated carbon). Multiple sHRPPs were deployed in control and treated areas and we also used traditional evaluation methods as appropriate for the site (e.g., vertical 1D SPME, etc.). Using the data produced by each method we evaluated the efficacy of the treatment. Our intention was to both highlight the ability to evaluate remedial efforts but also to compare the power of each data set. Our main focus was not specifically to determine whether there is or is not a difference based upon the remedial approach (i.e., this was not a remediation technology evaluation) but rather whether the sHRPP can better measure such differences versus traditional sampling. As such, we compared qualitative measures such as resolution (sHRPP vs traditional) and quantitative measures, such as contaminant concentrations confidence intervals. We used appropriate statistical analyses (e.g., ANOVA) as a measure of past treatment effect(s) on measured sediment parameters where appropriate but our focus was on comparing the confidence of any given comparison using data produced by the sHRPP compared to traditional methods.

6.6.2 Success Criteria

Documentation of the increase in the precision of the measurement of concentration with depth for each sampling method.

6.6.3 Outcome

This objective was met. Using a one way ANOVA, the sHRPP data passed the normalcy test and there was a statistical difference between treatments ($p=0.002$). The control treatment was statistically lower in concentration compared to both the sedimite ($p=0.004$) and sedimite+ bioaugmentation ($p=0.011$) treatments but there was no difference between plots with sedimite ($p=0.782$). The T-bar data from the sedimite+ bioaugmentation plot had a much larger range of values. As such, the normalcy test failed. Using a Kruskal-Wallis one-way analysis of variance by ranks, there was no difference in means ($p=0.068$) between treatments. In order to better compare the statistical power of each data set (sHRPP and T-bar), only the control and sedimite treatment were compared using a t-test. Both the sHRPP and T-bar data for those two treatments pass the normalcy test. Using the sHRPP data the concentrations of PCBs in the control plot were higher ($p=0.001$) than in the sedimite plot, while using the T-bar data set there was no statistical difference ($p=0.803$). It should be noted as both T-bar and sHRPP use the same SPME technique.

However, the sHRPP produces more samples per depth and more spatial integration per depth, reducing spatial variation.

6.7 EASE OF SHRPP DEPLOYMENT AND SAMPLING

The final performance objective was to determine the ease of sHRPP deployment and sampling.

6.7.1 Data Requirements

This performance objective is qualitative; therefore, a quantifiable data set was replaced with feedback from the field technician(s) on usability of technology and time required to deploy, retrieve, and sample sHRPPs in the field trials.

6.7.2 Success Criteria

The success criteria are partially qualitative, but the performance objective was considered to be met if time and cost efficiency of the sHRPPs are comparable to or less than industry-standard sampling methods. The improved resolution of sHRPP data relative to traditional sampling methods was considered when evaluating time and cost efficiency.

6.7.3 Outcome

This objective was met. The cost of site evaluation using the sHRPP and traditional methods was compared assuming the same spatial resolution was required (Table 6.2). It should be noted that for all parameters this resolution cannot be achieved by traditional methods and for some parameters traditional sampling is unable to measure the parameters (e.g., unstable constituents such as sulfide or reduced iron). For the analysis, we assumed 12 sample locations and that there would be three field technicians on site for both methods, and that divers would be required to install seepage meters as part of traditional sampling. Finally, assuming that both methods had similar resolution, we did not include the cost of the sample laboratory analysis, as it would be the same for both methods. Also not included in the cost analysis, are the costs of the sHRPP. Including cost in the comparison is difficult, as they can only currently be acquired through Texas Tech University, but the design is publicly available, and any contractor could purchase or manufacture their own leading to a range of equipment costs based on the number of total deployments. For a general comparison, the sHRPP cost ~ $2,500 to manufacture. The samplers can be reused indefinitely, and the current rental cost is ~ $800/sampler. The cost comparison was made solely based on personnel labor time, which is the major cost of site sampling excluding the analytical costs. For this analysis total labor cost for traditional methods is estimated at ~$32,000 and for the sHRPP is estimated at ~$20,400.

Table 6.2. Cost Comparison of Site Evaluation using Traditional Methods vs. sHRPP

Costs are based solely on person time to complete sample collection and processing. Analytical costs are excluded assuming each method would produce similar number of samples. For most constituents' traditional methods are unable to produce the resolution

Required Activities		Sampling Method								Comments
		Traditional						sHRPP		
		Geochem & Metals Cores	Velocity Seepage Meter	HOC SPME or PE	Geochem & Metals Cores	Velocity Seepage Meter	HOC SPME or PE	Geochem, Metals, HOC, & Velocity		Analysis based on 12sample locations, assumes 3 field technicians on site for both methods. Traditional sampling also includes divers to install seepage meters.
		Time Required (person days)			Cost			Time Required (person days)	Cost	
Deployment	Mobilization	3	2	0	$2,400	$2,000	$0	3	$2,400	Time required to get to site Seepage meter assumed to require a diver to install.
	Preparation	0.25	0.5	0.25	$300	$600	$300	1.5	$1,200	Time required to prepare equipment for field activities (e.g. sHRPP assembly, core acquisition/ seepage meters)
	Sample Acquisition	3	0	0	$2,400	$0	$0	0	$0	Core acquisition and preparation for shipping
	Installation/ Removal*	0	4	1.5	$0	$3,800	$1,350	6	$4,800	Install sHRPP or seepage meters *seepage meters
	Demobilization	3	2	0	$2,400	$2,000	$0	3	$2,400	Pack up equipment/ship samples/equipment/waste disposal /travel
Retrieval	Mobilization	0	0	2	$0	$0	$1,800	3	$2,400	Time required to get to the site
	Removal/Sampling	0	0	2	$0	$0	$3,600	6	$4,800	Time to remove sHRPP, prepare samples and measure unstable species (Fe and HS)
	Demobilization	0	0	2	$0	$0	$1,800	3	$2,400	Pack up equipment/ship samples/equipment/waste disposal etc.
Sample Processing prior to Analysis	Section and homogenize cores, centrifuge, filter	9	0	0	$7,200	$0	$0	0	$0	Only required for cores. Assumes 3 hours per core to fully process with 2 people working.
Total Person Time / Sub Total Cost		**18.25**	**8.5**	**7.75**	**$14,700**	**$8,400**	**$8,850**	**25.5**	**$20,400**	
Total Time/Cost per Sampling Method		**34.5**			**$31,950**			**25.5**	**$20,400**	

7.0 COST ASSESSMENT

As discussed in Section 6.7.3 and summarized on Table 6.2, the cost of site evaluation using the sHRPP and traditional methods was compared under the assumption that the same spatial resolution was required. It again should be noted that this resolution cannot be achieved for all parameters by traditional methods and for some parameters (e.g., unstable constituents such as sulfide or reduced iron) traditional sampling is unable to measure the parameters. Therefore, there is no real way to directly compare the sHRPP to traditional methods and achieve the same sample resolution for all parameters. That said, the cost analysis presented in Section 6.7.3 did assume the same resolution and was made solely based on personnel labor time, which is the major cost of site sampling when excluding the analytical costs. As states, the total labor cost for traditional methods is estimated at ~$32,000 and for the sHRPP is estimated at ~$20,400.

8.0 IMPLEMENTATION ISSUES

Currently the sHRPP is not widely available commercially as a turnkey service similar to most passive sampling methods such as SPME, PE or DGT. It is available through Texas Tech University in cooperation with other consultants or a new company called Envirostatus, LLC, which specializes in passive sampling. However, we have developed a SOP and informational voice over power point which is posted on the ESTCP website that covers the use, applications, and detailed instructions on how to prepare, deploy and sample the sHRPP. This presentation includes imbedded videos that demonstrate these activities.

9.0 REFERENCES

Army Defense Environmental Restoration Program (ADERP) 2017. FY2016 Aberdeen Proving Ground Installation Action Plan. https://www.aec.army.mil/application/files/1815/0060/3452/MD-APG.pdf

Battelle and Neptune, 2004. Final Quantico Watershed Study, Post Interim Remedial Action (Post IRA) Study Report. Prepared for the U.S. Navy, Chesapeake Division Naval Facilities Engineering Command, Washington, Washington, D.C.

Battelle, Neptune and Company. 2005. Draft Survey Report Quantico Watershed Study Chopawamsic Creek Investigation (Site 100 Chopawamsic and Abraham's Creek, Site 101 Potomac River, and Site 99 Quantico Embayment). Prepared for the U.S. Navy, NAVFAC Washington, Washington, D.C. September 2005.

Battelle, Otten M, Neptune and Company. 2007. Final Quantico Embayment (Site 99) Southern Wetlands (Site 96), and Potomac River Southern Area 1 Feasibility Study.

Battelle, Otten, Mark, Neptune & Company. 2008. Final Site 100 Chopawamsic Creek (Including Abrahams Creek) Feasibility Study. US Navy NAVFAC-Washington. September 2008.

Battelle. 2009. Draft-Final Remedial Design IR Site 96 Southern Wetlands and IR Site 99 Quantico Embayment Marine Corps Base Quantico, Quantico, Virginia Revision No. 00. Contract N62470-D-08-1006. Prepared for NAVFAC Washington, Washington D.C.

Battelle, Neptune & Company. 2014. Final Site 102 Abrahams Creek Supplemental Remedial Investigation Report. US Navy NAVFAC-Washington. June 2014.

Bedard D.L., H. VanDort, and K.A. Deweerd. 1998. Brominated biphenyls prime extensive microbial reductive dehalogenation of Aroclor 1260 in Housatonic River sediment. Appl. Environ. Microbiol. 64:1786–1795.

Borin, M., Milani, M., Salvato, M., & Toscano, A. 2011. Evaluation of Phragmites australis (Cav.) Trin. evapotranspiration in Northern and Southern Italy. Ecological Engineering, 37(5), 721--728. doi:10.1016/j.ecoleng.2010.05.003

Boudreau, B. P. 1997. Diagenetic models and their implementation (Vol. 505): Springer Berlin.

Bowles, K. C., Bell, R. A., Ernste, M. J., Kramer, J. R., Manolopoulos, H., & Ogden, N. 2002. Synthesis and characterization of metal sulfide clusters for toxicological studies. Environmental Toxicology and Chemistry: An International Journal, 21(4), 693-699. doi:10.1002/etc.5620210402

Busch-Harris, J., Sublette, K., Roberts, K. P., Landrum, C., Peacock, A. D., Davis, G., and Yang, X. (2008). Bio-traps coupled with molecular biological methods and stable isotope probing demonstrate the in situ biodegradation potential of MTBE and TBA in gasoline-contaminated aquifers. Groundwater Monitoring & Remediation, 28(4), 47-62.

Cardenas, M. B. (2009). Stream-aquifer interactions and hyporheic exchange in gaining and losing sinuous streams. Water Resources Research, 45(6). doi:10.1029/2008WR007651

Chandler, I., Guymer, I., Pearson, J., & Van Egmond, R. (2016). Vertical variation of mixing within porous sediment beds below turbulent flows. Water Resources Research, 52(5), 3493-3509. doi:10.1002/2015WR018274

Chapman, P.M., F. Wang, J.D. Germano, and G. Batley. 2002. Pore water testing and analysis: the good, the bad, and the ugly. Mar. Pollut. Bull. 44:359-366.

Cheng, D., Song, J., Wang, W., & Zhang, G. (2019). Influences of riverbed morphology on patterns and magnitudes of hyporheic water exchange within a natural river confluence. Journal of Hydrology, 574, 75-84. doi:10.1016/j.jhydrol.2019.04.025

Cho, Y-M et al. 2009. Field application of activated carbon amendment for in-situ stabilization of polychlorinated biphenyls in marine sediment. Environ. Sci. Technol. 43:3815-3823.

Cohen, D.A., Greeman, T.K., and Buszka, P.M. 2002. Surface-Water and Ground-Water Hydrology and Contaminant Detections in Ground Water for a Natural Resource Damage Assessment of the Indiana Harbor Canal and Nearshore Lake Michigan Watersheds, Northwestern Indiana. U.S. Department of the Interior, U.S. Geological Survey. June 2002.

Davis G et al. 2008. Integrated approach to PCE-impacted site characterization, site management, and enhanced bioremediation. Remediation, Fall, 5-17 (DOI:10.1002/rem.20178).

de Aragão Nogare, M. (2020). Measuring and modeling sediment dispersion in small streams. (Ph.D. Dissertation), University of British Columbia.

EA Engineering, Science, and Technology, Inc. (EA). 2008. Baseline Ecological Risk Assessment for Site EACC1K: Canal Creek Marsh and Landfill. Prepared for U.S. Army Environmental Center, Aberdeen Proving Ground, MD.

Environmental Chemical Corporation (ECC). 2018. Remedial Investigation Report, West Canal Creek Study Area, Aberdeen Proving Ground, Maryland. Draft. May 2018.

Ghosh, U., et al. 2014. Passive sampling methods for contaminated sediments: Practical guidance for selection, calibration, and implementation. Integ. Environ. Assess. Manag. 10(2): 210-223.

Hatzinger, P.B., J.K. Bohlke and N.C. Sturchio. 2013. Application of stable isotope ratio analysis for biodegradation monitoring in groundwater. Cur. Opinion. Biotechnol. 24:542-549.

Hong, Y. S., Kinney, K. A., & Reible, D. D. (2011). Acid volatile sulfides oxidation and metals (Mn, Zn) release upon sediment resuspension: Laboratory experiment and model development. Environmental Toxicology and Chemistry, 30(3), 564-575. doi:10.1002/etc.411.

Houzé, C., Durand, V., Mügler, C., Pessel, M., Monvoisin, G., Courbet, C., & Noûs, C. (2022). Combining experimental and modelling approaches to monitor the transport of an artificial tracer through the hyporheic zone. Hydrological Processes, e14498. doi:10.1002/hyp.14498.

Jackson, W.A., L. Martino, S. Hirsh, J. Wrobel, and J. Pardue. 2005. Application of a dialysis sampler to monitor phytoremediation processes. Environ. Monitor. Assess. 107:155-171.

Kiehl-Simpson, Caryn, John Nolan, W.A. Jackson, and Danny Reible. 2007. Porewater sampling for cap design: An assessment of three methods. 2007 Battelle Conference.

Kumar, N., Chaurand, P., Rose, J., Diels, L., & Bastiaens, L. (2015). Synergistic effects of sulfate reducing bacteria and zero valent iron on zinc removal and stability in aquifer sediment. Chemical Engineering Journal, 260, 83-89. doi:10.1016/j.cej.2014.08.091

Kupryianchyk, D., Rakowska, M. I., Reible, D., Harmsen, J., Cornelissen, G., van Veggel, M., ... & Koelmans, A. A. (2015). Positioning activated carbon amendment technologies in a novel framework for sediment management. Integ. Environ. Assess. Manag 11(2), 221-234.

Lampert, D., C. Thomas, and D. Reible. 2015. Internal and external transport significance for predicting contaminant uptake rates in passive samplers. Chemosphere 119: 910-916.

Li, K. Y. a. (2001). An exponential root-water-uptake model with water stress compensation. Journal of Hydrology, 252(1-4), 189--204. doi:10.1016/S0022-1694(01)00456-5.

Liber, K., Call, D. J., Markee, T. P., Schmude, K. L., Balcer, M. D., Whiteman, F. W., & Ankley, G. T. (1996). Effects of acid-volatile sulfide on zinc bioavailability and toxicity to benthic macroinvertebrates: a spiked-sediment field experiment. Environmental Toxicology and Chemistry: An International Journal, 15(12), 2113-2125. doi:10.1002/etc.5620151207.

Lorah, M.M., Olsen, L.D., Smith, B.L., Johnson, M.A., and Fleck, W.B. 1997. Natural attenuation of chlorinated volatile organic compounds in a freshwater tidal wetland, Aberdeen Proving Ground, Maryland. USGS Water-Resources Investigations Report 97-4171.

Lorah, M.M., and Olsen, L.D. 1999. Degradation of 1,1,2,2-tetrachloroethane in a freshwater tidal wetland: field and laboratory evidence. Environ. Sci. Technol. 33:227–234.

Lu, X., Skwarski, A., Drake, B., and Reible, D. (2011) Predicting bioavailability of PAHs and PCBs with porewater concentrations measured by solid-phase microextraction fibers. Environmental Toxicology and Chemistry, (30)5, 1109-1116.

Lydy, M. J., Landrum, P. F., Oen, A. M., Allinson, M., Smedes, F., Harwood, A. D., & Liu, J. (2014). Passive sampling methods for contaminated sediments: State of the science for organic contaminants. Integ. Environ. Assess. Manag, 10(2), 167-178.

Majcher, E. H., Phelan, D. J., Lorah, M. M., & McGinty, A. L. (2007). Characterization of Preferential Ground-Water Seepage From a Chlorinated Hydrocarbon-Contaminated Aquifer to West Branch Canal Creek, Aberdeen Proving Ground, Maryland, 2002-04 (Scientific Investigations Report 2006-5233). Retrieved from Reston, VA.

Majcher, E.H., Lorah, M.M., Phelan, D.J., and McGinty, A.L., 2009, Design and performance of an enhanced bioremediation pilot test in a tidal wetland seep, West Branch Canal Creek,

Aberdeen Proving Ground, Maryland: U.S. Geological Survey Scientific Investigations Report 2009–5112, 70 p. plus appendices.

Menzie, C., Amos, B., Driscoll, S., Ghosh, U., and Gilmour, C. (2016) Evaluating the Efficacy of a low Impact Delivery System for In Situ Treatment of Sediments Contaminated with Methylmercury and other Hydrophobic Chemicals. Final Report ESTCP Project ER-200835.

Mguidiche, A., Provenzano, G., Douh, B., Khila, S., Rallo, G., & Boujelben, A. (2015). Assessing Hydrus-2D to Simulate Soil Water Content (SWC) and Salt Accumulation Under an SDI System: Application to a Potato Crop in a Semi-Arid Area of Central Tunisia. Irrigation and Drainage, 64(2), 263-274. doi:10.1002/ird.1884.

Millington, R., & Quirk, J. (1961). Permeability of porous solids. Transactions of the Faraday Society, 57, 1200-1207. doi:10.1039/TF9615701200.

Mills, M., Crone, B., Fetters, K., & Williams, H. (2015, January 12-15, 2015). Cap Performance Monitoring Using Forensic Chemistry Methods. Paper presented at the Eighth International Conference on Remediation and Management of Contaminated Sediments, New Orleans, Louisiana.

Moore, G. E., Burdick, D. M., Peter, C. R., & Keirstead, D. R. (2012). Belowground Biomass of Phragmites australis in Coastal Marshes. Northeastern Naturalist, 19(4), 611--626. doi:10.1656/045.019.0406.

Musial, C. T., Sawyer, A. H., Barnes, R. T., Bray, S., & Knights, D. (2016). Surface water–groundwater exchange dynamics in a tidal freshwater zone. Hydrological Processes, 30(5), 739-750. doi:10.1002/hyp.10623.

NAVFAC. 2013. Third Five-Year Review Report for Marine Corps Base Quantico Virginia. Naval Facilities Engineering Command Washington. September 2013.

NRC; National Research Council. 2007. Sediment Dredging at Superfund Megasites: Assessing the Effectiveness. The National Academies Press, Washington DC.

Payne, R.B., C. Chun, H.D. May, and K.R. Sowers. 2011. Enhanced reductive dechlorination of polychlorinated biphenyl impacted sediment by bioaugmentation with a dehalorespiring bacterium. Environ. Sci. Technol. 45:8772–8779.

Raats, P. (1974). Steady flows of water and salt in uniform soil profiles with plant roots. Soil Science Society of America Journal, 38(5), 717-722. doi:10.2136/sssaj1974.03615995003800050012x.

Reible, D. D. (1998). Fundamentals of Environmental Engineering: CRC Press.

Reible, D. D. (2014). Processes, assessment and remediation of contaminated sediments: Springer.

Røy, H., Lee, J. S., Jansen, S., & de Beer, D. (2008). Tide-driven deep pore-water flow in intertidal sand flats. Limnology and Oceanography, 53(4), 1521-1530. doi:10.4319/lo.2008.53.4.1521.

Ruiz, N.E., J. Bleiler, and K. Gardner. June 2016. Final Report – In Situ Wetland Restoration Demonstration, ESTCP Project Number ER-200825, June 2016.

Saysel, A. K., & Barlas, Y. (2001). A dynamic model of salinization on irrigated lands. Ecological Modelling, 139(2-3), 177--199. doi:10.1016/S0304-3800(01)00242-3.

SERDP/ESTCP. 2012. Workshop Report: SERDP and ESTCP Workshop on Research and Development Needs for Long Term Management of Contaminated Sediments. Available online [www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Sediments].

Shen, X., Lampert, D., Ogle, S., & Reible, D. (2018). A software tool for simulating contaminant transport and remedial effectiveness in sediment environments. Environmental Modelling and Software, 109(January), 104--113. doi:10.1016/j.envsoft.2018.08.014

Sowers, K.R., and H.D. May. 2013. In situ treatment of PCBs by anaerobic microbial dechlorination in aquatic sediment: Are we there yet? Curr. Opin. Biotechnol. 24:482-488.

Sowers, K.R., B. Kjellerupp, and U. Ghosh. 2015. Organic biofilm substrata as a microbial inoculum delivery vehicle for bioaugmentation of persistent organic pollutants in contaminated sediments and soils. US Patent US20150158064 A1. Available online [http://www.google.com/patents/US20150158064].

Sowers, K.R., U. Ghosh, and H.D. May. 2017. Final Technical Report, Evaluating the Efficacy of Bioaugmentation for In-situ Treatment of PCB Impacted Sediment at Abraham's Creek, Quantico, Virginia, ESTCP Project Number ER-201215, Version 2, June 29, 2017.

SPAWAR Pacific. 2017. Technical Report 3052, Demonstration and Commercialization of the Sediment Ecosystem Assessment Protocol, ESTCP Project ER-201130. January 2017.

Sukola, K., Wang, F., & Tessier, A. (2005). Metal-sulfide species in oxic waters. Analytica Chimica Acta, 528(2), 183-195. doi:10.1016/j.aca.2004.10.009.

Tan, K., Todd A. Anderson, and W. Andrew Jackson. 2005. Temporal and spatial variation of perchlorate in streambed sediments: Results from in-situ dialysis samplers. Environ. Pollut. 136(2):283-291.

Tcaciuc, A. P., Borrelli, R., Zaninetta, L. M., & Gschwend, P. M. (2018). Passive sampling of DDT, DDE and DDD in sediments: accounting for degradation processes with reaction–diffusion modeling. *Environmental Science: Processes & Impacts, 20*(1), 220-231. doi:10.1039/C7EM00501F

Tetra Tech NUS. 2007. Final Remedial Investigation Report for Site 100 – Chopawamsic Creek. Marine Corps Base (MCB) Quantico, Virginia. Prepared for NAVFAC-Washington. February 2007.

Tetra Tech NUS. 2010. Final Proposed Remedial Action Plan (PRAP) for Site 100. Marine Corps Base (MCB) Quantico, Virginia. Prepared for Naval Facilities Engineering Command Washington. October 2010.

Texas Technical University (Texas Tech) and APTIM. 2018. Site Selection Memorandum, High Resolution Passive Profiling to Monitor Contaminated Sediments in Support of Remediation Evaluation and Risk Characterization. ESTCP Project ER-201734, April 2018.

Thibodeaux, L. J., & Bierman, V. J. (2003). Peer reviewed: the bioturbation-driven chemical release process. Environmental science & technology, 37(13), 252A-258A. doi:10.1021/es032518j.

Thibodeaux, L. J., Valsaraj, K. T., & Reible, D. D. (2001). Bioturbation-driven transport of hydrophobic organic contaminants from bed sediment. Environmental engineering science, 18(4), 215-223. doi:10.1089/109287501753113124.

Thomas, C., D.J. Lampert, and D. Reible. 2014. Remedy Performance Monitoring at Contaminated Sediment Sites Using Profiling Solid Phase Microextraction (SPME) Polydimethylsiloxane (PDMS) Fibers. Environmental Science: Processes & Impacts 16:445-452.

U.S. Army. 2008. Canal Creek Study Area Record of Decision – Remedial Action at 10 Soil Sites in the Canal Creek Study Area (Sites EACC1F-A, EACC1F-B, EACC1G-A,EACC1H-D, EACC1I-B, EACC3E, EACC3F, EACC3I, EACC3O, EACC3P). Environmental Conservation and Restoration Division, US Army Garrison Aberdeen Proving Ground. September 2008.

USEPA. 2015. Cap Performance Monitoring using Forensic Chemistry Methods, slides presented by Marc A. Mills (USEPA Office of Research and Development), Brian Crone (Student Contractor to USEPA ORD), Kyle Fetters (University of Michigan intern to USEPA ORD), and Heather Williams (USEPA Great Lakes National Program Office). January 6, 2015.

Vitagliano, V., & Lyons, P. A. (1956). Diffusion coefficients for aqueous solutions of sodium chloride and barium chloride. Journal of the American Chemical Society, 78(8), 1549-1552. doi:10.1021/ja01589a011.

Volkenborn, N., Polerecky, L., Hedtkamp, S., van Beusekom, J. E., & De Beer, D. (2007). Bioturbation and bioirrigation extend the open exchange regions in permeable sediments. Limnology and Oceanography, 52(5), 1898-1909. doi:10.4319/lo.2007.52.5.1898.

Vroblesky, D.A., Lorah, M.M., and Trimble, S. 1991. Mapping Zones of Contaminated Ground-Water Discharge Using Creek-Bottom-Sediment Vapor Samplers, Aberdeen Proving Ground, Maryland. Ground Water. 29(1):7-12.

Vroblesky, D.A., Rhodes, L.C., Robertson, J.F., and Harrigan, J.A. 1996. Locating VOC contamination in a fractured rock aquifer at the ground water/surface water interface using passive vapor collectors. Ground Water. 34:223–230.

Vroblesky, D.A. and Hyde, W.T. 1997. Diffusion samplers as an inexpensive approach to monitoring VOCs in ground water. Ground Water Monitor and Remed. 17(3):177–184.

Vrugt, J., van Wijk, M. T., Hopmans, J., & Šimunek, J. (2001). One-, two-, and three-dimensional root water uptake functions for transient modeling. Water Resources Research, 37(10), 2457-2470. doi:10.1029/2000WR000027.

Vrugt, J. A., Hopmans, J. W., & Šimunek, J. (2001). Calibration of a two-dimensional root water uptake model. Soil Science Society of America Journal, 65(4), 1027-1037. doi:10.2136/sssaj2001.6541027x.

Wilson, A. M., & Gardner, L. R. (2006). Tidally driven groundwater flow and solute exchange in a marsh: Numerical simulations. Water Resources Research, 42(1). doi:10.1029/2005WR004302

Wilson, A. M., & Morris, J. T. (2012). The influence of tidal forcing on groundwater flow and nutrient exchange in a salt marsh-dominated estuary. Biogeochemistry, 108(1-3), 27-38. doi:10.1007/s10533-010-9570-y.

Xin, P., Yuan, L. R., Li, L., & Barry, D. A. (2011). Tidally driven multiscale pore water flow in a creek-marsh system. Water Resources Research, 47(7). doi:10.1029/2010WR010110.

Xin, P., Zhou, T., Lu, C., Shen, C., Zhang, C., D'Alpaos, A., & Li, L. (2017). Combined effects of tides, evaporation and rainfall on the soil conditions in an intertidal creek-marsh system. Advances in Water Resources, 103, 1--15. doi:10.1016/j.advwatres.2017.02.014.

Zhou, L., Zhou, G., Liu, S., & Sui, X. (2010). Seasonal contribution and interannual variation of evapotranspiration over a reed marsh (Phragmites australis) in Northeast China from 3-year eddy covariance data. Hydrological Processes: An International Journal, 24(8), 1039-1047. doi:10.1002/hyp.7545.

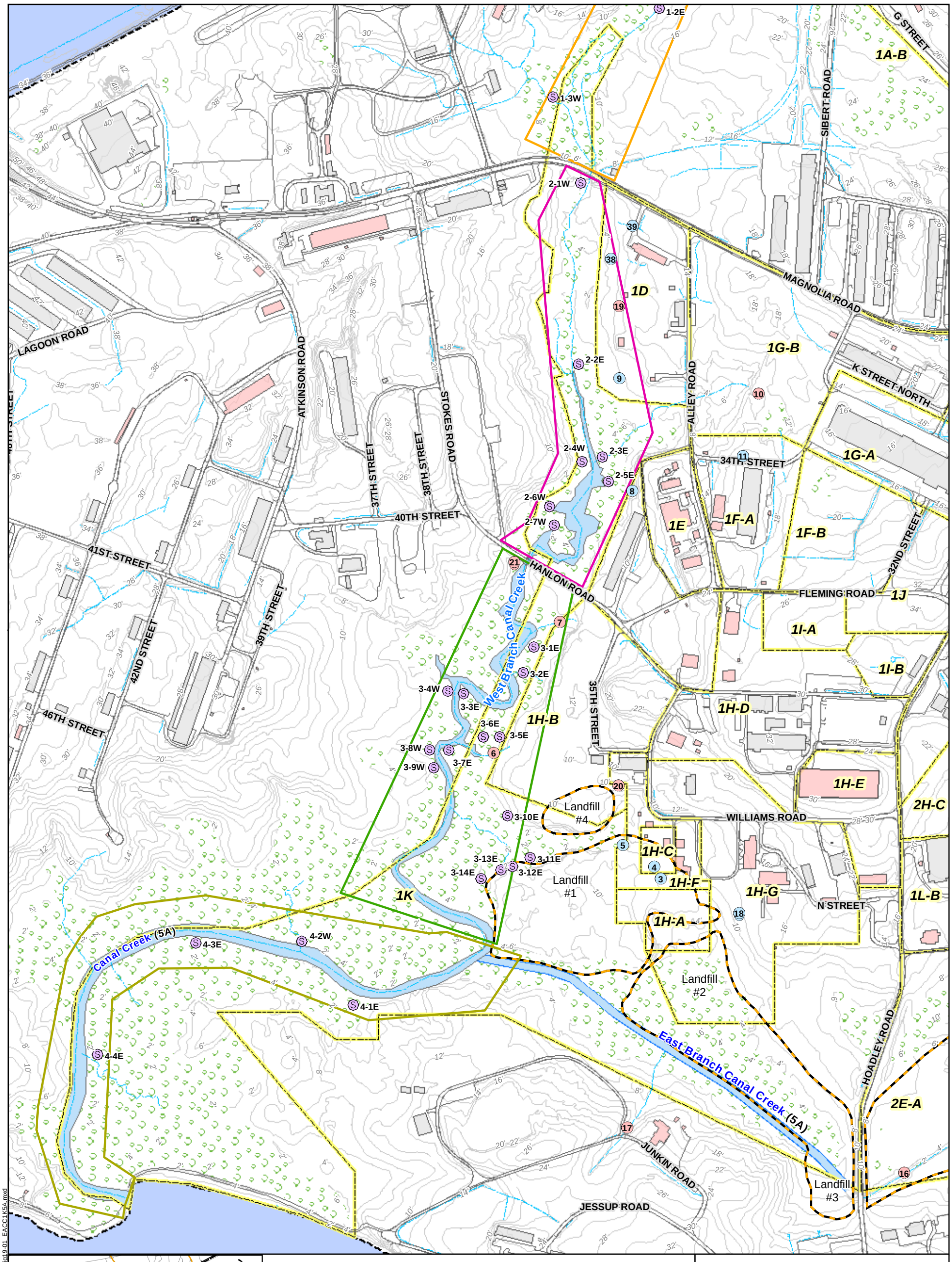
Zimmerman, J.R., D. Werner, U. Ghosh, R.N. Millward, T.S. Bridges, and R.G. Luthy. 2005. Effects of dose and particle size on activated carbon treatment to sequester polychlorinated biphenyls and polycyclic aromatic hydrocarbons in marine sediments. Environ. Toxicol. Chem. 24:1594-1601.

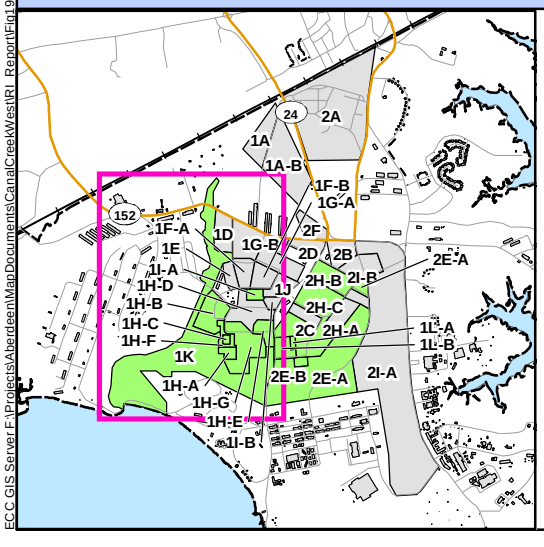
Zoumis, T., A. Schmidt, L. Grigorova, and W. Calman0. 2001. Contaminants in sediments: remobilization and demobilization. Sci. Tot. Environ. 266:195-202.

APPENDIX A POINTS OF CONTACT

POINT OF CONTACT Name	ORGANIZATION Name Address	CONTACT INFORMATION Phone E-mail	ROLE IN PROJECT
Andrew Jackson, PhD, PE, BCEE	Texas Tech University 911 Boston Box 41023 Lubbock, TX 79409-1023	806-834-6575 direct 806-438-9580 cell andrew.jackson@ttu.edu	Principal Investigator
Danny Reible, PhD, PE, BCEE, NAE	Texas Tech University 911 Boston Box 41023 Lubbock, TX 79409-1023	806-834-8050 direct 512-992-3634 cell danny.reible@ttu.edu	Co-Principal Investigator
Paul B. Hatzinger, PhD	APTIM Federal Services 17 Princess Road Lawrenceville, NJ 08648	609-895-5356 direct 267-337-4003 cell paul.hatzinger@aptim.com	Co-Principal Investigator
Graig Lavorgna	APTIM Federal Services 17 Princess Road Lawrenceville, NJ 08648	609-895-5343 direct 908-309-7651 cell graig.lavorgna@aptim.com	Project Engineer Field Task Manager
Uriel Garza-Rubalcava	Texas Tech University 911 Boston, Box 41023 Lubbock, TX 79409-1023	u.garza-rubalcava@ttu.edu	Research Assistant
Andrea Leeson, PhD	SERDP/ESTCP 4800 Mark Center Drive Suite 17D03 Alexandria, VA 22350-3605	703-696-2118 direct 703-696-2114 fax andrea.leeson@gmail.com	ESTCP Environmental Restoration Program Manager
Allison O'Brien	US Army - Aberdeen Proving Ground Installation Restoration Program	410-436-3767 direct allison.c.obrien.civ@mail.mil	Canal Creek Study Area Restoration Program Manager
Lyndsay Kelsey	Naval Facilities Engineering Command (NAVFAC) Washington DC	(202) 685-3266 direct lyndsay.kelsey@navy.mil	MCB Quantico Remedial Project Manager
Marc Mills	EPA Office of Research and Development	mills.marc@epa.gov	Lead Engineer - Grand Calumet River AOC

APPENDIX B CANAL CREEK MARSH/SEDIMENT METALS CONCENTRATIONS MAPS AND CONTAMINANT CONCENTRATIONS - NOVEMBER 2017 (ECC, 2018)





Legend

- Storm Sewer Line Outfall
- Former Chemical Sewer Line Outfall
- Groundwater Seep
- Landfill Area
- Existing Building
- Former Building
- Site Boundary
- Drainage Ditch
- Topographic Contour (2 ft interval)

WBCC Reaches

- Reach A
- Reach B
- Reach C
- Reach D
- Wetland

N

0 240 480 Feet

1 inch = 480 feet

NOTES & SOURCES

Map Coordinates: NAD 83, State Plane, Maryland in US Feet
Map Size: 11"x17" (B-size)

Figure 19-1

Sites EACC1K/EACC5A Canal Creek Marsh and Landfill West and Canal Creek Sediments Site and Features

Aberdeen Proving Ground
Maryland

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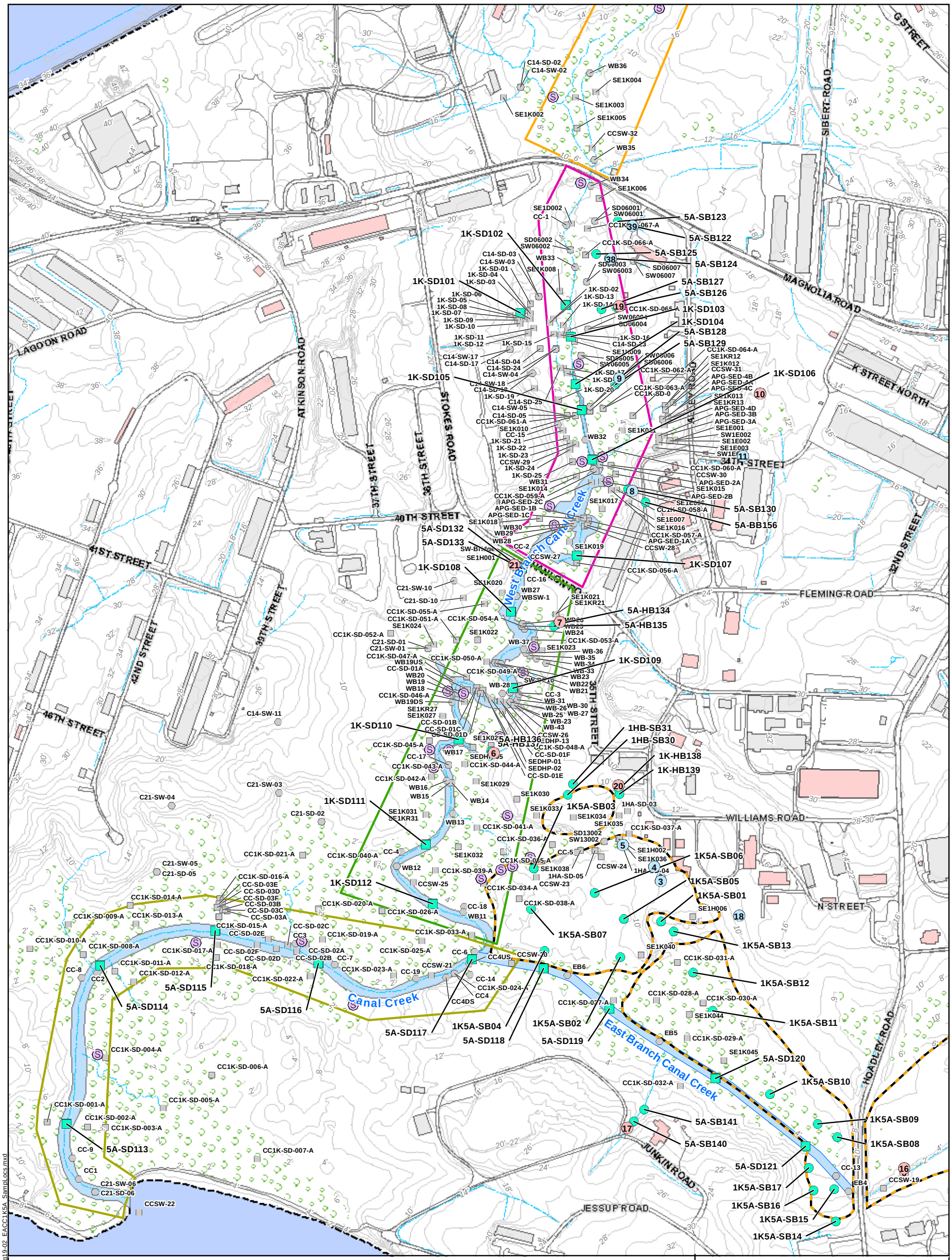

Legend

- 2016/2017 Surface and Subsurface Soil Sample
- 2016/2017 Sediment Sample
- Historical Sediment Sample
- Historical Surface Water Sample
- Storm Sewer Line Outfall
- Former Chemical Sewer Line Outfall
- Groundwater Seep
- Landfill Area
- Existing Building
- Former Building

WBCC Reaches

- Reach A
- Reach B
- Reach C
- Reach D
- Drainage Ditch
- Wetland
- Topographic Contour (2 ft interval)

N

0 240 480 Feet

1 inch = 480 feet

NOTES & SOURCES

Map Coordinates: NAD 83, State Plane, Maryland in US Feet
Map Size: 11"x17" (B-size)

Figure 19-2

Sites EACC1K/EACC5A Canal Creek Marsh and Landfill West and Canal Creek Sediments Sample Locations

Aberdeen Proving Ground
Maryland

ECC GIS Server:F:\Projects\Aberdeen\MapDocuments\CanalCreekWest\RI Report\Fig19-02 EACC1K5A SampLocs.mxd

CCSA Identified COC Risk Drivers

COC	Surface and Subsurface Soil			Hydric Soil and Sediment		
	Industrial Soil RSL	Eco-SSL	95% UPL	Industrial SED RSL	Eco FW SED	95% UPL
Arsenic (mg/kg)	3	18	7.6	30	9.8	14.6

Subsurface soil samples from depths greater than 2 ft. bgs compared only to Industrial Soil RSLs and 95% UPL

COC	chemical of concern
95% UPL	95% Reference Background Upper Prediction Limit
RSL	regional screening level
SSL	soil screening level

Data Qualifiers
B - Analyte found at a level greater than the MDL but less than the Contract Required Quantitation Limit (CRQL).
J - Detected but below the Reporting Limit/Limit of Quantitation; therefore, result is an estimated concentration.
K - Analyte present. Reported value may be biased high.
L - Analyte present. Reported value may be biased low.
N - The MS/MSD criteria and/or precision are outside criteria. The predigested spike recovery is not within control limits for the associated parameter.
Dup - Reported value is from duplicate sample.
ND - Not Detected
NS - Not Sampled
Red Bold - Above Industrial Soil RSL/Industrial SED RSL
Blue Bold - Above Eco-SSL/Eco FW SED
Yellow Highlight - Above both RSL and Eco-SSL/Eco FW SED
Italic Bold - Above Reference Background Value (95% upper prediction limit)
(0.XX) = concentration and [X'] = depth
All analytical results in mg/kg

5A-SB123 13.2 D [0.5'] 15.9 D Dup [2']
5A-SB124 2.61 [0.5'] 3.57 JD [2']
5A-SB125 2.2 JD [0.5'] 3.26 JD [2']
5A-SB127 2.5 J [0.5'] 5.8 Dup [2']
5A-SB122 7.17 D [0.5'] 16.3 D [2']
1K-SD102 3.05 [0.5'] 6.43 [2']
1K-SD101 1.28 J Dup [0.5'] ND [2']
1K-SD104 33.5 Dup [0.5'] 2.97 [2']
1K-SD105 8.37 [0.5'] 4.34 J [2']
5A-SB126 4.4 [0.5'] 3.8 [2']
1K-SD103 2.66 J [0.5'] 4.76 J [2']
5A-SB128 5.01 [0.5'] 2.67 [2']
5A-SB129 3.3 J [0.5'] 4.6 [2']
1K-SD106 9.69 [0.5'] 6.09 J [2']
5A-SB130 1.73 J [0.5'] 2.15 J [2']
5A-BB156 2.82 [0.5']
1K-SD107 12.5 [0.5'] 4.76 J [2']
5A-HB134 4.59 [0.5'] 3.15 J [2']
5A-HB135 2.97 J [0.5'] 27.6 [2']
1K-SD109 36.4 [0.5'] 4.82 [2']
5A-HB136 5.72 [0.5'] 4.44 [2']
5A-HB137 9.29 [0.5'] 4.93 [2']
1HB-SB31 3.09 N [2']
1HB-SB30 13.1 [0.5']
1K-HB138 2.55 [0.5'] 6.25 [2']
1K-HB139 2.01 J [0.5'] 2.6 [2']
1K5A-SB06 3.98 [0.5'] 2.97 [2']
1K5A-SB05 7.63 [0.5'] 3.95 [2']
1K5A-SB01 20.3 [0.5'] 3.52 [2'] 4.85 [5']
1K5A-SB13 4.81 [0.5'] 3.92 [2'] 5.61 [5']
1K5A-SB12 2.4 J [0.5'] 4.43 [2']
1K5A-SB11 6.62 Dup [0.5'] 2.49 [2']
5A-SD120 4.79 J [0.5'] 3.68 [2']
1K5A-SB10 2.72 J [0.5'] 5.39 [2']
1K5A-SB09 4.38 [0.5'] ND [2']
1K5A-SB08 5.74 [0.5'] 5.14 [2']
1K5A-SB14 2.81 [0.5'] 2.57 [2']
1K5A-SB15 3.51 [0.5'] 12.7 [2']
1K5A-SB16 3.56 [0.5'] 4.23 [2']
1K5A-SB17 2.61 [0.5'] 1.64 J [2']
5A-SD121 3.12 [0.5'] 4.82 [2']
5A-SB141 4 [0.5'] 5.4 [2']
5A-SB140 3.4 [0.5'] 3.9 [2']
1K5A-SB04 3.73 [0.5'] 3.65 [2']
1K5A-SB02 3.87 [0.5'] 3.66 [2'] 3.09 [5']
1K5A-SB03 4.11 [0.5'] 2.02 J [2']
1K5A-SB07 5.23 [0.5'] 3.55 [2']
5A-SD132 (10.7 [0.5'] 3 [2']
5A-SD133 24.1 J [0.5'] 23.5 [2']
1K-SD108 66.8 [0.5'] 8.95 [2']
1K-SD110 57.8 [0.5'] 8.49 [2']
1K-SD111 25.4 Dup [0.5'] 40.2 [2']
1K-SD112 78.2 [0.5'] 125 [2']
5A-SD114 19 [0.5'] 20.8 [2']
5A-SD115 20.3 [0.5'] 31.4 [2']
5A-SD116 129 [0.5'] 9.49 [2']
5A-SD117 4.51 [0.5'] 2.65 [2']
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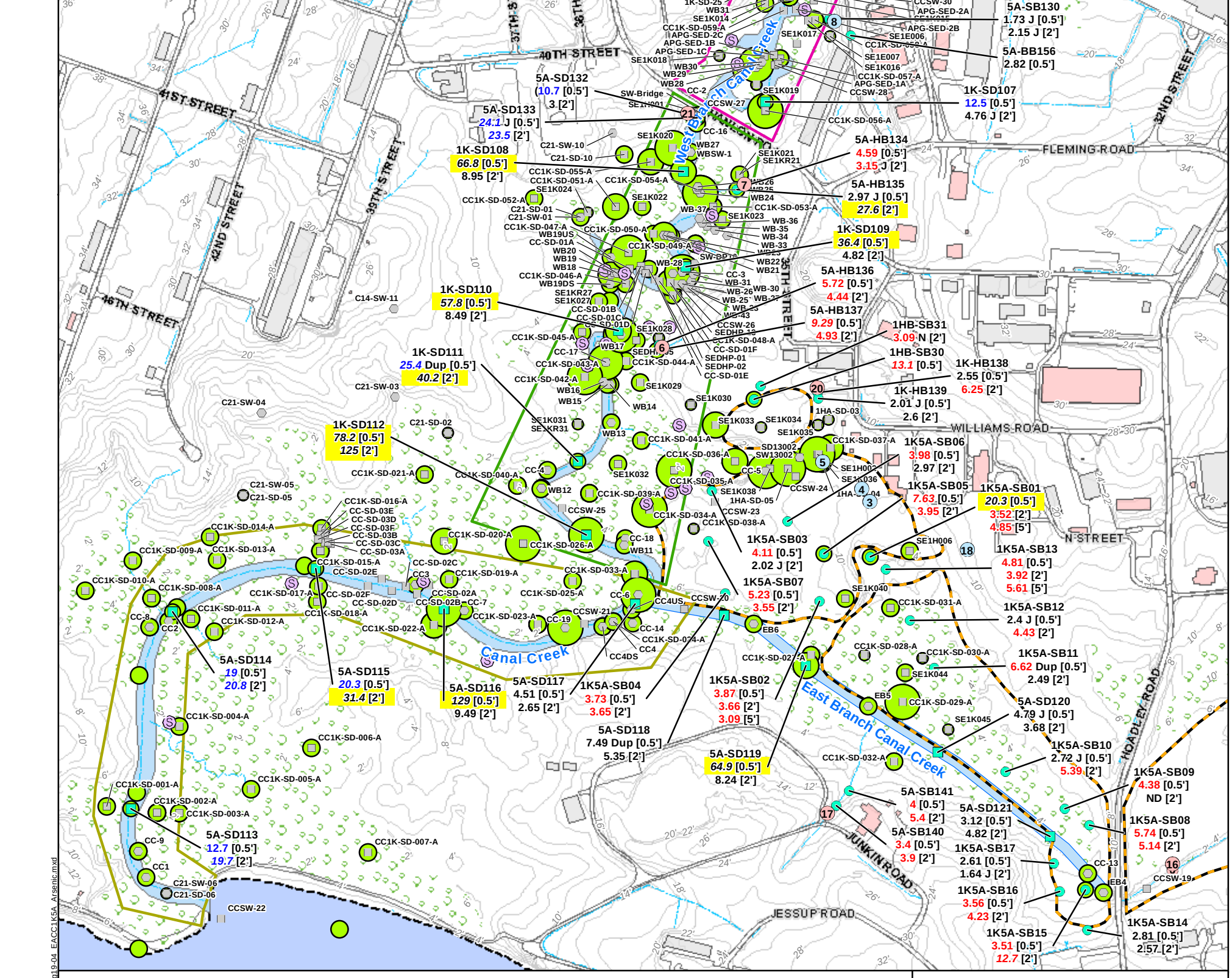
5A-SD113 12.7 [0.5'] 19.7 [2']



Legend

- 2016/2017 Surface and Subsurface Soil Sample
- 2016/2017 Sediment Sample
- Historical Sediment Sample
- Historical Surface Water Sample
- Storm Sewer Line Outfall
- Former Chemical Sewer Line Outfall
- Groundwater Seep

Arsenic in Soil and Sediment (mg/kg)

- Non-detect
- 0 - 7.6
- 7.6 - 50
- 50 - 100
- 100 - 539

WBCC Reaches

- Reach A
- Reach B
- Reach C
- Reach D
- Drainage Ditch
- Wetland
- Topographic Contour (2 ft interval)
- Existing Building
- Former Building
- Landfill Area

N

0 240 480 Feet

1 inch = 480 feet

NOTES & SOURCES

Map Coordinates: NAD 83, State Plane, Maryland in US Feet
Map Size: 11"x17" (B-size)

Figure 19-4

Sites EACC1K/EACC5A Canal Creek Marsh and Landfill West and Canal Creek Sediments Arsenic Sampling Results

Aberdeen Proving Ground
Maryland

ECC GIS Server:F:\Projects\Aberdeen\MapDocuments\CanalCreekWestIRI Report\Fin19-04 EACC1K5A Arsenic.mxd

CCSA Identified COC Risk Drivers

COC	Surface Soil			Hydric Soil and Sediment		
	Industrial Soil RSL	Eco-SSL	95% UPL	Industrial SED RSL	Eco FW SED	95% UPL
Chromium (mg/kg)	6.3	26	33.5	63	43.4	117

Subsurface soil samples from depths greater than 2 ft. bgs compared only to Industrial Soil RSLs and 95% UPL

COC	chemical of concern
95% UPL	95% Reference Background Upper Prediction Limit
RSL	regional screening level
SSL	soil screening level

Data Qualifiers
B - Analyte found at a level greater than the MDL but less than the Contract Required Quantitation Limit (CRQL).
J - Detected but below the Reporting Limit/Limit of Quantitation; therefore, result is an estimated concentration.
N - The MS/MSD criteria and/or precision are outside criteria. The predigested spike recovery is not within control limits for the associated parameter.
Dup - Reported value is from duplicate sample.
ND - Not Detected
NS - Not Sampled
Red Bold - Above Industrial Soil RSL
Blue Bold - Above Ecological SSL
Yellow Highlight - Above both RSL and Eco-SSL
Italic Bold - Above Reference Background Value (95% upper prediction limit)
(0.XX) = concentration and [X'] = depth
All analytical results in mg/kg

5A-SB124 13.2 [0.5'] 18.1 B [2']
5A-SB122 22 B [0.5'] 29.4 B [2']
5A-SB123 25.1 B [0.5'] 28.4 B Dup [2']
5A-SB125 10.8 B [0.5'] 14.6 B [2']
1K-SD102 10.7 N [0.5'] 20.2 [2']
1K-SD101 36.8 [0.5'] 11.1 [2']
5A-SB126 12.2 [0.5'] 12.8 [2']
5A-SB127 19.2 [0.5'] 22.7 [2']
1K-SD103 10.6 [0.5'] 19 [2']
5A-SB128 20.7 [0.5'] 9.92 [2']
1K-SD104 43.9 Dup [0.5'] 6.5 [2']
5A-SB129 12 [0.5'] 19.8 [2']
1K-SD105 48.3 [0.5'] 94.1 [2']
1K-SD106 62.9 [0.5'] 38.9 [2']
5A-SB130 20 [0.5'] 22.8 [2']
5A-BB156 17.9 [0.5']
5A-SD132 13.4 J [0.5'] 12.8 J [2']
5A-SD133 63.5 J [0.5'] 69.7 J [2']
1K-SD107 43.4 [0.5'] 30.1 [2']
1K-SD108 54.8 [0.5'] 37.8 [2']
5A-HB134 22.7 [0.5'] 23.2 [2']
5A-HB135 14.5 [0.5'] *151* [2']
1K-SD109 69.1 [0.5'] 25 [2']
1K-SD110 47.9 [0.5'] 44.1 [2']
5A-HB136 15.7 [0.5'] 18.7 [2']
5A-HB137 20.7 [0.5'] 19.5 [2']
1HB-SB31 16.1 N [2']
1HB-SB30 14.1 [0.5']
1K-HB138 *55.7 J [0.5']* *51.5* [2']
1K-HB139 27.9 [0.5'] 15.6 [2']
1K-SD111 50.5 [0.5'] 43.8 [2']
5A-SD115 54.6 [0.5'] 47.2 [2']
1K5A-SB03 15.7 [0.5'] 16.3 [2']
1K5A-SB06 15 [0.5'] 22.7 [2']
1K-SD112 66.7 [0.5'] 49.7 [2']
1K5A-SB05 18.5 [0.5'] 15.4 [2']
1K5A-SB07 35.4 [0.5'] 15.7 Dup [2']
1K5A-SB01 10.2 [0.5'] 7.76 [2'] 14.2 [5']
1K5A-SB13 10 [0.5'] 10.9 [2'] 13.7 [5']
1K5A-SB02 10.4 [0.5'] 12.3 [2'] 15 [5']
1K5A-SB12 10.1 [0.5'] 28.8 [2']
5A-SD114 45.6 [0.5'] 45.2 [2']
5A-SD116 45.7 [0.5'] 38.8 [2']
5A-SD117 11.3 Dup [0.5'] 16.5 [2']
1K5A-SB04 21.6 [0.5'] 22.7 [2']
5A-SD119 33.7 [0.5'] 46.3 [2']
1K5A-SB11 13.8 Dup [0.5'] 11.7 [2']
1K5A-SB10 16.6 [0.5'] *36.6* [2']
5A-SD118 32.7 Dup [0.5'] 19.3 [2']
5A-SB141 17.3 [0.5'] 19.5 [2']
5A-SB140 15.9 [0.5'] 18.2 [2']
5A-SD120 27.4 [0.5'] 10.2 [2']
5A-SD121 9.95 [0.5'] 18.9 [2']
1K5A-SB09 16.9 [0.5'] 9.11 [2']
1K5A-SB08 19.2 [0.5'] 28.5 [2']
1K5A-SB17 10.4 [0.5'] 8.01 [2']
1K5A-SB15 15.1 [0.5'] 21.2 [2']
1K5A-SB16 29.2 [0.5'] *227* [2']
1K5A-SB14 11.3 [0.5'] 8.59 [2']
5A-SD113 36.3 [0.5'] 31.9 [2']

LAGOON ROAD
ATKINSON ROAD
MAGNOLIA ROAD
K STREET NORTH
N STREET
WILLIAMS ROAD
FLEMING ROAD
JUNKIN ROAD
JESSUP ROAD
ROADLEY ROAD
STOCKES ROAD
35TH STREET
36TH STREET
37TH STREET
39TH STREET
40TH STREET
41ST STREET
42ND STREET
46TH STREET
West Branch Canal Creek
Canal Creek
East Branch Canal Creek

Legend

- 2016/2017 Surface and Subsurface Soil Sample
- 2016/2017 Sediment Sample
- Historical Sediment Sample
- Historical Surface Water Sample
- Storm Sewer Line Outfall
- Former Chemical Sewer Line Outfall
- Groundwater Seep

Chromium in Soil and Sediment (mg/kg)

- 2.9 - 26
- 26 - 63
- 63 - 117
- 117 - 348
- 348 - 861

WBCC Reaches

- Reach A
- Reach B
- Reach C
- Reach D
- Drainage Ditch
- Wetland
- Topographic Contour (2 ft interval)
- Existing Building
- Former Building
- Landfill Area

N

0 240 480 Feet

1 inch = 480 feet

NOTES & SOURCES

Map Coordinates: NAD 83, State Plane, Maryland in US Feet
Map Size: 11"x17" (B-size)

Figure 19-5

Sites EACC1K/EACC5A Canal Creek Marsh and Landfill West and Canal Creek Sediments Chromium Sampling Results

Aberdeen Proving Ground
Maryland

ECC GIS Server F:\Projects\Aberdeen\MapDocuments\CanalCreekWestIRI Report\Fig19-05 EACC1K5A Chromium.mxd

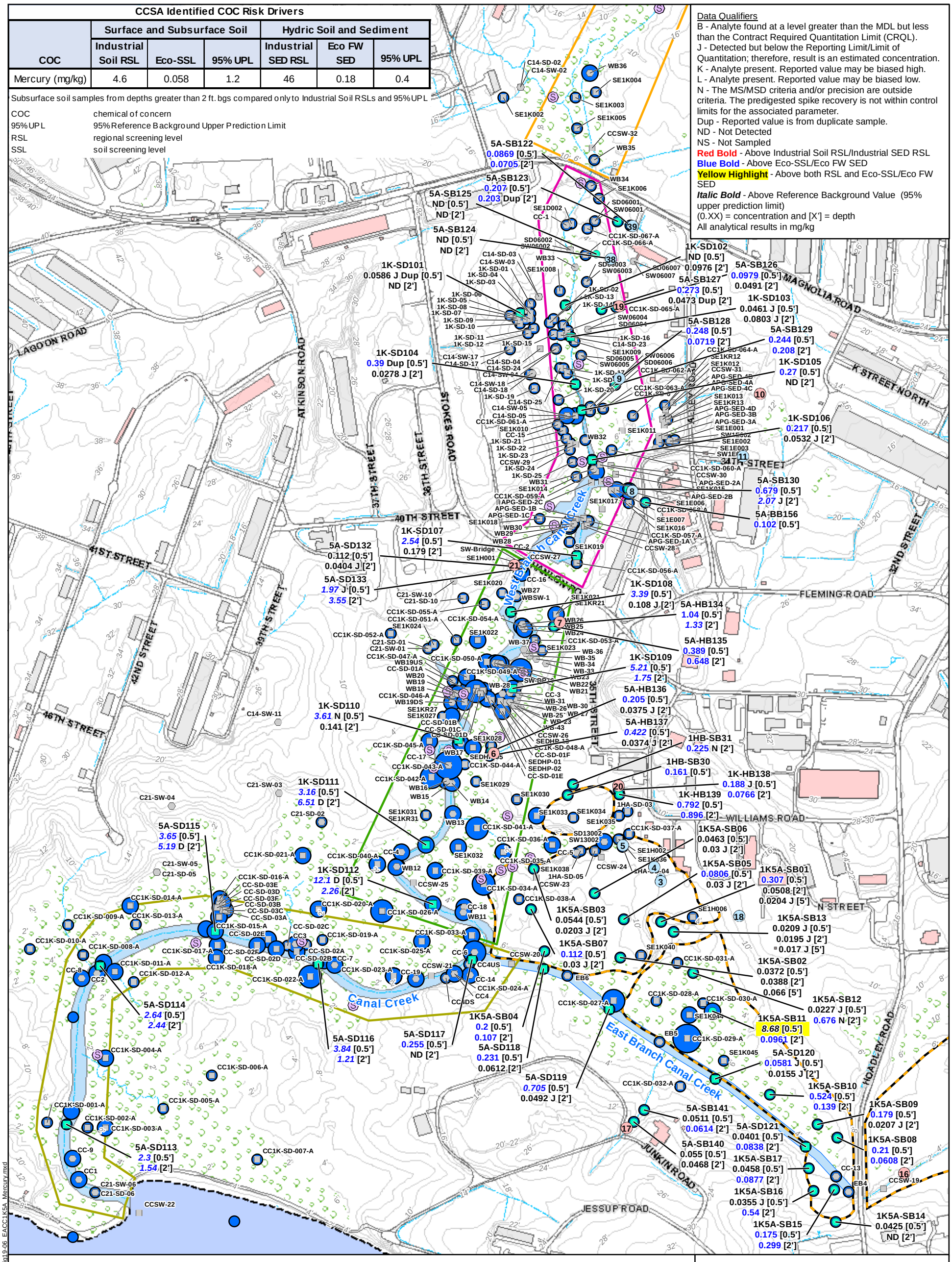
CCSA Identified COC Risk Drivers

COC	Surface and Subsurface Soil			Hydric Soil and Sediment		
	Industrial Soil RSL	Eco-SSL	95% UPL	Industrial SED RSL	Eco FW SED	95% UPL
Mercury (mg/kg)	4.6	0.058	1.2	46	0.18	0.4

Subsurface soil samples from depths greater than 2 ft. bgs compared only to Industrial Soil RSLs and 95% UPL

COC	chemical of concern
95% UPL	95% Reference Background Upper Prediction Limit
RSL	regional screening level
SSL	soil screening level

Data Qualifiers
B - Analyte found at a level greater than the MDL but less than the Contract Required Quantitation Limit (CRQL).
J - Detected but below the Reporting Limit/Limit of Quantitation; therefore, result is an estimated concentration.
K - Analyte present. Reported value may be biased high.
L - Analyte present. Reported value may be biased low.
N - The MS/MSD criteria and/or precision are outside criteria. The predigested spike recovery is not within control limits for the associated parameter.
Dup - Reported value is from duplicate sample.
ND - Not Detected
NS - Not Sampled
Red Bold - Above Industrial Soil RSL/Industrial SED RSL
Blue Bold - Above Eco-SSL/Eco FW SED
Yellow Highlight - Above both RSL and Eco-SSL/Eco FW SED
Italic Bold - Above Reference Background Value (95% upper prediction limit)
(0.XX) = concentration and [X'] = depth
All analytical results in mg/kg



Legend

- 2016/2017 Surface and Subsurface Soil Sample
- 2016/2017 Sediment Sample
- Historical Sediment Sample
- Historical Surface Water Sample
- Storm Sewer Line Outfall
- Former Chemical Sewer Line Outfall
- Groundwater Seep

Mercury in Soil and Sediment (mg/kg)

- Non-detect
- 0 - 4.0
- 4 - 20
- 20 - 50
- 50 - 149

WBCC Reaches

- Reach A
- Reach B
- Reach C
- Reach D
- Drainage Ditch
- Wetland
- Topographic Contour (2 ft interval)
- Existing Building
- Former Building
- Landfill Area

N

0 240 480 Feet

1 inch = 480 feet

NOTES & SOURCES

Map Coordinates: NAD 83, State Plane, Maryland in US Feet
Map Size: 11"x17" (B-size)

Figure 19-6

Sites EACC1K/EACC5A Canal Creek Marsh and Landfill West and Canal Creek Sediments Mercury Sampling Results

Aberdeen Proving Ground
Maryland

ECC GIS Server:F:\Projects\Aberdeen\MapDocuments\CanalCreekWestRI Report\Fig19-06_EACC1K5A_Mercury.mxd

CCSA Identified COC Risk Drivers

COC	Surface and Subsurface Soil			Hydric Soil and Sediment		
	Industrial Soil RSL	Eco-SSL	95% UPL	Industrial SED RSL	Eco FW SED	95% UPL
Lead (mg/kg)	800	11	60	8000	35.8	95

Subsurface soil samples from depths greater than 2 ft. bgs compared only to Industrial Soil RSLs and 95% UPL

COC	chemical of concern
95% UPL	95% Reference Background Upper Prediction Limit
RSL	regional screening level
SSL	soil screening level

Data Qualifiers
B - Analyte found at a level greater than the MDL but less than the Contract Required Quantitation Limit (CRQL).
J - Detected but below the Reporting Limit/Limit of Quantitation; therefore, result is an estimated concentration.
K - Analyte present. Reported value may be biased high.
L - Analyte present. Reported value may be biased low.
N - The MS/MSD criteria and/or precision are outside criteria. The predigested spike recovery is not within control limits for the associated parameter.
Dup - Reported value is from duplicate sample.
ND - Not Detected
NS - Not Sampled
Red Bold - Above Industrial Soil RSL/Industrial SED RSL
Blue Bold - Above Eco-SSL/Eco FW SED
Yellow Highlight - Above both RSL and Eco-SSL/Eco FW SED
Italic Bold - Above Reference Background Value (95% upper prediction limit)
(0.XX) = concentration and [X'] = depth
All analytical results in mg/kg

5A-SB122 86.1 B [0.5'] 63.4 B [2']
5A-SB123 105 B [0.5'] 126 B Dup [2']
5A-SB125 7.26 B [0.5'] 7.16 B [2']
5A-SB124 6.45 B [0.5'] 7.08 B [2']
1K-SD101 14.5 Dup [0.5'] 2.49 [2']
1K-SD102 11.6 [0.5'] 24.5 [2']
1K-SD103 6.8 [0.5'] 12.3 [2']
5A-SB126 31.8 [0.5'] 33.8 [2']
5A-SB127 33.8 [0.5'] 15.4 Dup [2']
5A-SB128 38.1 B [0.5'] 9.17 B [2']
5A-SB129 33.6 B [0.5'] 44.3 B [2']
1K-SD104 77.7 Dup [0.5'] 9.95 [2']
1K-SD105 27.6 [0.5'] 17.6 [2']
1K-SD106 53.7 [0.5'] 22.7 [2']
5A-SB130 46 [0.5'] 245 Dup [2']
5A-BB156 27.5 [0.5']
1K-SD107 94.8 [0.5'] 16.5 [2']
5A-SD132 46.6 J [0.5'] 12.9 J [2']
5A-SD133 188 J [0.5'] 209 J [2']
1K-SD108 235 [0.5'] 49 [2']
5A-HB134 170 B [0.5'] 198 B [2']
5A-HB135 50.1 B [0.5'] 91.2 B [2']
1K-SD109 305 [0.5'] 75.5 [2']
5A-HB136 25.7 B [0.5'] 12.9 B [2']
1K-SD110 132 [0.5'] 24 [2']
5A-HB137 52.9 B [0.5'] 12.8 B [2']
1HB-SB31 120000 DN [2']
1HB-SB30 82.3 [0.5']
1K-HB138 129 J [0.5'] 348 [2']
1K-HB139 144 [0.5'] 123 [2']
1K-SD111 177 Dup [0.5'] 225 [2']
1K-SD112 400 [0.5'] 348 [2']
1K5A-SB06 21 [0.5'] 13.5 [2']
1K5A-SB05 28.1 [0.5'] 16.8 [2']
1K5A-SB01 44.6 B Dup [0.5'] 10.5 B [2'] 8.99 B [5']
1K5A-SB13 10.8 [0.5'] T 5.78 [2'] 7.35 [5']
1K5A-SB03 16.4 [0.5'] 16.3 N [2']
1K5A-SB02 21.5 [0.5'] 28.4 [2'] 45.7 [5']
1K5A-SB07 29.4 [0.5'] 12.5 Dup [2']
1K5A-SB12 18.3 [0.5'] 2760 [2']
1K5A-SB11 23.3 [0.5'] 13.6 [2']
5A-SD120 14.6 [0.5'] 5.85 [2']
5A-SD114 133 [0.5'] 142 [2']
5A-SD115 148 [0.5'] 188 [2']
5A-SD116 240 [0.5'] 25.5 [2']
5A-SD117 12.1 [0.5'] 5.35 [2']
1K5A-SB04 61.7 [0.5'] 9.21 [2']
5A-SD118 15.6 Dup [0.5'] 10.4 [2']
5A-SD119 22.9 [0.5'] 19.5 [2']
1K5A-SB10 17.8 [0.5'] 73.5 [2']
1K5A-SB09 40.7 [0.5'] 1.84 [2']
1K5A-SB08 40 [0.5'] 14 [2']
5A-SB141 41 [0.5'] 56.5 [2']
5A-SD121 32.1 [0.5'] 37.2 [2']
5A-SB140 46 [0.5'] 44.8 [2']
1K5A-SB17 65.7 [0.5'] 11.8 [2']
1K5A-SB16 14.8 [0.5'] 116 [2']
1K5A-SB15 45.4 Dup [0.5'] 66.9 [2']
1K5A-SB14 22.1 [0.5'] 6.12 [2']
5A-SD113 81.7 [0.5'] 83.9 [2']

LAGOON ROAD
ATKINSON ROAD
STOKES ROAD
MAGNOLIA ROAD
K STREET NORTH
FLEMING ROAD
WILLIAMS ROAD
JUNKIN ROAD
JESSUP ROAD
35TH STREET
36TH STREET
37TH STREET
38TH STREET
40TH STREET
41ST STREET
42ND STREET
46TH STREET
West Branch Canal Creek
Canal Creek
East Branch Canal Creek

Legend

- 2016/2017 Surface and Subsurface Soil Sample
- 2016/2017 Sediment Sample
- Historical Sediment Sample
- Historical Surface Water Sample
- Storm Sewer Line Outfall
- Former Chemical Sewer Line Outfall
- Groundwater Seep

Lead in Soil and Sediment (mg/kg)
- 0.07 - 60
- 60 - 500
- 500 - 2,500
- 2,500 - 5,500
- 5,500 - 120,000

WBCC Reaches
- Reach A
- Reach B
- Reach C
- Reach D
- Drainage Ditch
- Wetland
- Topographic Contour (2 ft interval)
- Existing Building
- Former Building
- Landfill Area

N

0 240 480 Feet

1 inch = 480 feet

NOTES & SOURCES

Map Coordinates: NAD 83, State Plane, Maryland in US Feet
Map Size: 11"x17" (B-size)

Figure 19-7

Sites EACC1K/EACC5A Canal Creek Marsh and Landfill West and Canal Creek Sediments Lead Sampling Results

Aberdeen Proving Ground
Maryland

ECC GIS Server F:\Projects\Aberdeen\MapDocuments\CanalCreekWest\RI_Report\Fig19-07_EACC1K5A_Lead.mxd

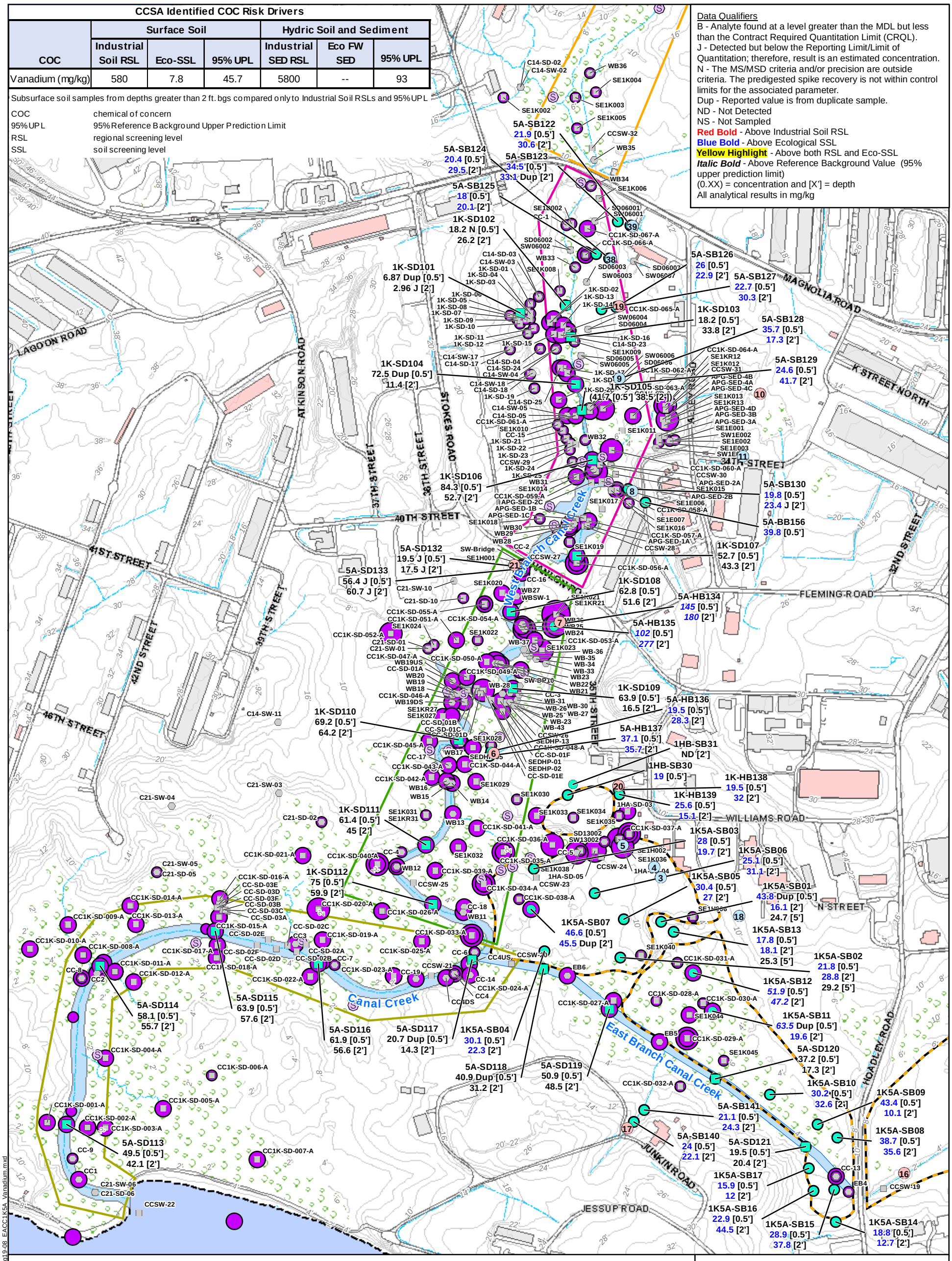
CCSA Identified COC Risk Drivers

COC	Surface Soil			Hydric Soil and Sediment		
	Industrial Soil RSL	Eco-SSL	95% UPL	Industrial SED RSL	Eco FW SED	95% UPL
Vanadium (mg/kg)	580	7.8	45.7	5800	--	93

Subsurface soil samples from depths greater than 2 ft. bgs compared only to Industrial Soil RSLs and 95% UPL

COC	chemical of concern
95% UPL	95% Reference Background Upper Prediction Limit
RSL	regional screening level
SSL	soil screening level

Data Qualifiers
B - Analyte found at a level greater than the MDL but less than the Contract Required Quantitation Limit (CRQL).
J - Detected but below the Reporting Limit/Limit of Quantitation; therefore, result is an estimated concentration.
N - The MS/MSD criteria and/or precision are outside criteria. The predigested spike recovery is not within control limits for the associated parameter.
Dup - Reported value is from duplicate sample.
ND - Not Detected
NS - Not Sampled
Red Bold - Above Industrial Soil RSL
Blue Bold - Above Ecological SSL
Yellow Highlight - Above both RSL and Eco-SSL
Italic Bold - Above Reference Background Value (95% upper prediction limit)
(0.XX) = concentration and [X'] = depth
All analytical results in mg/kg



Legend

- 2016/2017 Surface and Subsurface Soil Sample
- 2016/2017 Sediment Sample
- Historical Sediment Sample
- Historical Surface Water Sample
- Storm Sewer Line Outfall
- Former Chemical Sewer Line Outfall
- Groundwater Seep

Vanadium in Soil and Sediment (mg/kg)

- 3.4 - 7.8
- 7.8 - 45.7
- 45.7 - 93
- 93 - 580
- 580 - 1,900

WBCC Reaches

- Reach A
- Reach B
- Reach C
- Reach D
- Landfill Area
- Existing Building
- Former Building
- Drainage Ditch
- Wetland
- Topographic Contour (2 ft interval)

N

0 240 480 Feet

1 inch = 480 feet

NOTES & SOURCES

Map Coordinates: NAD 83, State Plane, Maryland in US Feet
Map Size: 11"x17" (B-size)

Figure 19-8

Sites EACC1K/EACC5A Canal Creek Marsh and Landfill West and Canal Creek Sediments Vanadium Sampling Results

Aberdeen Proving Ground
Maryland

ECC GIS Server F:\Projects\Aberdeen\MapDocuments\CanalCreekWestIR1 Report\Fig19-08 EACC1K5A Vanadium.mxd

CCSA Identified COC Risk Drivers

COC	Surface and Subsurface Soil			Hydric Soil and Sediment		
	Industrial Soil RSL	Eco-SSL	95% UPL	Industrial SED RSL	Eco FW SED	95% UPL
Zinc (mg/kg)	35000	46	82	350000	121	284

Subsurface soil samples from depths greater than 2 ft. bgs compared only to Industrial Soil RSLs and 95% UPL

COC	chemical of concern
95% UPL	95% Reference Background Upper Prediction Limit
RSL	regional screening level
SSL	soil screening level

Data Qualifiers
J - Detected but below the Reporting Limit/Limit of Quantitation; therefore, result is an estimated concentration.
N - The MS/MSD criteria and/or precision are outside criteria. The predigested spike recovery is not within control limits for the associated parameter.
X - The parameter shows a potential positive bias on a reported concentration due to an ICV or CCV exceeding the upper control limit on the high side.
Dup - Reported value is from duplicate sample.
ND - Not Detected
NS - Not Sampled
Red Bold - Above Industrial Soil RSL
Blue Bold - Above Ecological SSL
Yellow Highlight - Above both RSL and Eco-SSL
Italic Bold - Above Reference Background Value (95% upper prediction limit)
(0.XX) = concentration and [X'] = depth
All analytical results in mg/kg

5A-SB122 220 [0.5'] 218 [2']
5A-SB123 205 [0.5'] 166 Dup [2']
5A-SB125 20 [0.5'] 17.3 [2']
1K-SD102 42.9 N [0.5'] 105 [2']
1K-SD101 16.8 Dup [0.5'] 4.35 J [2']
1K-SD103 (20.2 [0.5'] 33.6 [2'])
1K-SD104 388 Dup [0.5'] 46.6 [2']
1K-SD105 206 [0.5'] 104 [2']
5A-SB124 21.5 [0.5'] 17.8 [2']
5A-SB126 107 [0.5'] 49.5 [2']
5A-SB127 40.6 [0.5'] 29.7 Dup [2']
5A-SB128 24.9 [0.5'] 15.7 [2']
5A-SB129 73.7 [0.5'] 115 [2']
1K-SD106 565 [0.5'] 740 [2']
5A-SB130 87.4 [0.5'] 166 Dup [2']
5A-BB156 276 [0.5']
1K-SD107 521 [0.5'] 64.1 [2']
1K-SD108 1060 [0.5'] 233 [2']
5A-HB134 156 [0.5'] 193 [2']
5A-HB135 82.1 [0.5'] 157 [2']
1K-SD109 2140 [0.5'] 337 [2']
5A-HB136 321 [0.5'] 31 [2']
5A-HB137 327 [0.5'] 128 [2']
1HB-SB31 620 N [2']
1HB-SB30 63.1 [0.5']
1K-HB138 111 J [0.5'] 112 [2']
1K-HB139 238 [0.5'] 190 [2']
1K5A-SB06 37.9 [0.5'] 52.9 [2']
1K5A-SB05 43.4 [0.5'] 33.7 [2']
1K5A-SB01 55.7 [0.5'] 17.1 [2'] 24.3 [5']
1K5A-SB13 18.9 [0.5'] 18.6 [2'] 24 [5']
1K5A-SB02 39.5 [0.5'] 43.1 [2'] 53.4 [5']
1K5A-SB12 35.1 [0.5'] 164 [2']
1K5A-SB11 60.4 [0.5'] 20.6 [2']
5A-SD120 73.6 X [0.5'] 19 X [2']
1K5A-SB10 40.8 [0.5'] 46.1 [2']
1K5A-SB09 61 [0.5'] 2.53 J [2']
1K5A-SB08 71 [0.5'] 69.5 [2']
1K5A-SB15 59.3 Dup [0.5'] 111 [2']
1K5A-SB16 26.4 [0.5'] 351 [2']
1K5A-SB14 34.8 [0.5'] 7.22 [2']
5A-SD132 332 [0.5'] 36.8 J [2']
5A-SD133 913 J [0.5'] 1280 J [2']
1K-SD110 710 N [0.5'] 114 [2']
1K-SD111 970 Dup [0.5'] 1180 [2']
1K-SD112 1610 [0.5'] 904 [2']
5A-SD114 648 X [0.5'] 695 X [2']
5A-SD115 727 X [0.5'] 941 X [2']
5A-SD116 593 X [0.5'] 101 X [2']
5A-SD117 39.6 X [0.5'] 3.35 JX [2']
5A-SD118 80.4 X Dup [0.5'] 32.1 X [2']
5A-SD119 302 X [0.5'] 115 X [2']
1K5A-SB04 52.7 [0.5'] 40 [2']
1K5A-SB03 28.8 [0.5'] 13.8 [2']
1K5A-SB07 41.9 [0.5'] 28.6 Dup [2']
5A-SD121 155 NX [0.5'] 125 X [2']
5A-SB141 117 [0.5'] 110 [2']
5A-SB140 221 [0.5'] 80.8 [2']
1K5A-SB17 31.4 [0.5'] 20.8 [2']
5A-SD113 441 X [0.5'] 454 X [2']

MAGNOLIA ROAD
LAGOON ROAD
ATKINSON ROAD
STONES ROAD
K STREET NORTH
N STREET
FLEMING ROAD
WILLIAMS ROAD
JESSUP ROAD
JUNKIN ROAD
ROADLEY ROAD
35TH STREET
36TH STREET
37TH STREET
39TH STREET
40TH STREET
41ST STREET
42ND STREET
46TH STREET
West Branch Canal Creek
East Branch Canal Creek
Canal Creek

Legend

- 2016/2017 Surface and Subsurface Soil Sample
- 2016/2017 Sediment Sample
- Historical Sediment Sample
- Historical Surface Water Sample
- Storm Sewer Line Outfall
- Former Chemical Sewer Line Outfall
- Groundwater Seep

Zinc in Soil and Sediment (mg/kg)
- 8 - 46
- 46 - 82
- 82 - 600
- 600 - 1,500
- 1,500 - 27,700

WBCC Reaches
- Reach A
- Reach B
- Reach C
- Reach D
- Landfill Area
- Existing Building
- Former Building
- Drainage Ditch
- Wetland
- Topographic Contour (2 ft interval)

N

0 240 480 Feet

1 inch = 480 feet

NOTES & SOURCES

Map Coordinates: NAD 83, State Plane, Maryland in US Feet
Map Size: 11"x17" (B-size)

Figure 19-9

Sites EACC1K/EACC5A Canal Creek Marsh and Landfill West and Canal Creek Sediments Zinc Sampling Results

Aberdeen Proving Ground
Maryland

ECC GIS Server F:\Projects\Aberdeen\MapDocuments\CanalCreekWest\RI Report\Fig19-09 EACC1K5A Zinc.mxd

Table 19-3. Site EACC1K/5A Phase IV Detected Compounds in Hydric Soil and Sediment

ANALYTE	Industrial SED RSL	Eco FW SED	Reference Background	Unit	Sample Location	1K-SD109-SS0.5	1K-SD109-SO02	1K-SD110-SS0.5	1K-SD110-SO02	1K-SD111-SS0.5	1K-SD111-SS0.5X1	1K-SD111-SO02	1K-SD112-SS0.5	1K-SD112-SO02
					Date Sampled	11/18/2017	11/18/2017	11/18/2017	11/18/2017	11/18/2017	11/18/2017	11/18/2017	11/18/2017	11/18/2017
Metals														
Aluminum	1100000	--	31900	mg/kg		25100	7040	**37500 N**	**35500**	23900	22300	17400	30200	**34200**
Antimony	470	2	10.5	mg/kg		ND	ND	ND	ND	ND	ND	ND	ND	2.8 J
Arsenic	30	9.8	14.6	mg/kg		**36.4**	4.82	**57.8**	8.49	**25.1**	**25.4**	***40.2***	***78.2***	***125***
Barium	220000	--	107	mg/kg		**154 X**	**112 X**	**143 X**	131 X	117 X	112 X	**108 X**	**140 X**	**135 X**
Beryllium	2300	--	2.59	mg/kg		2.17 J	0.614 J	2.42 J	2.27	1.99 J	1.87 J	1.54 J	2.12 J	2.44
Cadmium	980	0.99	3.42	mg/kg		**5.64 X**	0.899 JX	1.02 JX	ND	**3.5 JX**	**3.5 JX**	**3.48 X**	**4.55 X**	1.75 JX
Calcium	--	--	9590	mg/kg		**11900**	**107000**	2990	2160	2920 J	2930 J	9060	**10900**	3660
Chromium	63	43.4	117	mg/kg		*69.1*	25	47.9	44.1	50.5	48.3	43.8	*66.7*	49.7
Cobalt	350	50	35.1	mg/kg		**38.9**	8.19	22.7	20.2	28.4	30.6	23.8	30.4	25.6
Copper	47000	31.6	78.7	mg/kg		**169**	37.3	76.1	28.5	**107**	**112**	**125**	**210**	**101**
Iron	820000	20000	54300	mg/kg		47200	13200	29600 N	27500	36100	31700	26700	41500	39400
Lead	8000	35.8	95.0	mg/kg		**305**	75.5	**132**	24	**176**	**177**	**225**	**400**	**348**
Magnesium	--	--	6510	mg/kg		**17500**	**50500**	5600 N	5480	4860 J	5040 J	**10000**	**7030**	5310
Manganese	26000	460	1590	mg/kg		1250 X	441 X	384 NX	309 X	508 X	468 X	497 X	911 X	386 X
Mercury	46	0.18	0.398	mg/kg		**5.21**	**1.75**	**3.61 N**	0.141	**3.16**	**2.95**	**6.51 D**	**12.1 D**	**2.26**
Nickel	22000	22.7	70.1	mg/kg		**71.7**	**81.2**	38.5	31.6	42.8	43.3	46.1	69.9	39.1
Potassium	--	--	3730	mg/kg		2070 J	578 J	2800 N	2820	2210 J	2180 J	1410 J	2230 J	2480
Selenium	5800	2	4	mg/kg		ND	ND	ND	ND	ND	ND	ND	ND	ND
Silver	5800	1	1.75	mg/kg		0.725 J	ND	ND	ND	ND	ND	0.639 J	**1.47 J**	**1.77 J**
Sodium	--	--	6310	mg/kg		2100 J	1830 J	2120 J	1210 J	5950	**7220**	1560 J	2270 J	1760 J
Thallium	12	--	7	mg/kg		ND	ND	ND	ND	ND	ND	ND	ND	ND
Vanadium	5800	--	93	mg/kg		63.9	16.5	69.2	64.2	61.4	58.4	45	75	59.9
Zinc	350000	121	284	mg/kg		**2140**	**337**	**710 N**	114	**916**	**970**	**1180**	**1610**	**904**
Volatile Organic Compounds (VOCs)														
Acetone	670000000	--	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
Benzene	51000	--	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
2-Butanone	--	--	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
Carbon Disulfide	3500000	0.851	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
Chlorobenzene	--	--	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
Cyclohexane	--	--	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
1,4-Dichlorobenzene	110000	599	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
1,1-Dichloroethene	1000000	31	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
1,2-Dichloroethane	20000	--	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
cis-1,2-Dichloroethene	2300000	--	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
trans-1,2-Dichloroethene	23000000	1050	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
total 1,2-Dichloroethene	--	--	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
Methyl Acetate	1200000	--	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
Naphthalene	170000	176	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
1,1,2,2-Tetrachloroethane	27000	1360	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
Tetrachloroethene	390000	468	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
Toluene	47000000	--	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
1,1,2-Trichloroethane	6300	1240	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
Trichloroethene	19000	96.9	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
Vinyl chloride	17000	--	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
m,p-Xylene	2400000	25.2	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
Total xylenes	2500000	--	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
Herbicide														
Silvex	--	--	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
Polychlorinated Biphenyls (PCBs)														
Aroclor-1242	9500	59.8	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
Aroclor-1254	9700	59.8	79.4	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
Aroclor-1260	9900	59.8	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS

Table 19-3. Site EACC1K/5A Phase IV Detected Compounds in Hydric Soil and Sediment

ANALYTE	Industrial SED RSL	Eco FW SED	Reference Background	Unit	Sample Location	1K-SD109-SS0.5	1K-SD109-SO02	1K-SD110-SS0.5	1K-SD110-SO02	1K-SD111-SS0.5	1K-SD111-SS0.5X1	1K-SD111-SO02	1K-SD112-SS0.5	1K-SD112-SO02
					Date Sampled	11/18/2017	11/18/2017	11/18/2017	11/18/2017	11/18/2017	11/18/2017	11/18/2017	11/18/2017	11/18/2017
Explosives														
1,3-Dinitrobenzene	82000	--	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
2,4-Dinitrotoluene	74000	41.6	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)	57000000	--	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
Nitrobenzene	220000	--	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
Nitroglycerin	82000	--	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
2-Nitrotoluene	150000	--	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
1,3,5-Trinitrobenzene	32000000	--	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
2,4,6-Trinitrotoluene	510000	92	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
Pesticides														
Aldrin	--	--	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
alpha-BHC	--	6	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
beta-BHC	--	5	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
delta-BHC	--	6400	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
gamma-BHC	--	2.37	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
alpha-Chlordane	--	3.24	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
gamma-Chlordane	--	3.24	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
4,4-DDD	96000	4.88	55	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
4,4-DDE	93000	3.16	55	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
4,4-DDT	85000	4.16	265	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
Dieldrin	1400	1.9	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
Endosulfan I	--	2.9	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
Endosulfan II	--	14	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
Endosulfan Sulfate	--	5.4	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
Endrin	25000	2.22	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
Endrin Aldehyde	--	--	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
Endrin Ketone	--	--	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
Heptachlor	6300	68	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
Heptachlor epoxide	3300	2.47	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
Methoxychlor	--	--	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
Dioxins and Furans														
Total Heptachlorodibenzo-p-dioxin	--	--	--	µg/kg		0.139	0.067	0.281	0.479	0.619	2.53	1.32	8.21	2.63
1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin	--	--	--	µg/kg		0.0622	0.0221	0.128	0.188	0.254	1.07	0.615	3.68	0.902
Total Heptachlorodibenzofuran	--	--	--	µg/kg		0.0541	0.0083	0.0651	0.00446 J	0.132	0.552	0.668	2.28	0.0691
1,2,3,4,6,7,8-Heptachlorodibenzofuran	--	--	--	µg/kg		0.0307	0.0057	0.0345	0.00267 J	0.0726	0.287	0.337	1.22	0.0396
Total Hexachlorodibenzo-p-dioxin	--	--	--	µg/kg		0.401	0.107	0.393	0.108	0.935	3.36	2.93 E	16.8 E	1.12
1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin	4.7	--	--	µg/kg		0.0089	0.00204	0.0118	0.00413	0.023	0.09	0.0799	0.348	0.0683
1,2,3,7,8,9-Hexachlorodibenzo-p-dioxin	4.7	--	--	µg/kg		0.00317 J	ND	0.00551 J	0.00367 J	0.0114	0.0388	0.0257	0.117	0.0312
1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin	4.7	--	--	µg/kg		0.00345 J	ND	0.00362 J	ND	0.00778 J	0.0298	0.0247	0.105	0.00535
Total Hexachlorodibenzofuran	--	--	--	µg/kg		0.602	0.103	0.458	0.0408	1.13	3.84	3.96 E	17.6	0.56
1,2,3,4,7,8-Hexachlorodibenzofuran	--	--	--	µg/kg		0.0166	0.00368 J	0.0158	ND	0.033	0.123	0.216	0.553	0.029
1,2,3,6,7,8-Hexachlorodibenzofuran	--	--	--	µg/kg		0.00353	ND	0.00399 J	ND	0.00835 J	0.0277	0.048	0.116	0.00637
1,2,3,7,8,9-Hexachlorodibenzofuran	--	--	--	µg/kg		0.00818	0.002 J	0.00693	ND	0.0153	0.0568	0.0779	0.282	0.0112
2,3,4,6,7,8-Hexachlorodibenzofuran	--	--	--	µg/kg		0.0229	0.0079	0.0196	ND	0.0401	0.149	0.207	0.743	0.0268
1,2,3,4,6,7,8,9-Octachlorodibenzo-p-dioxin	--	--	--	µg/kg		0.401	0.242	1.39	4.49 E	3.73	15.1 E	4.11 E	25.8 E	13.1 E
1,2,3,4,6,7,8,9-Octachlorodibenzofuran	--	--	--	µg/kg		0.017	0.00478 J	0.0443	ND	0.0948	0.355	0.608	1.35	0.0328
Total Pentachlorodibenzo-p-dioxin	--	--	--	µg/kg		0.206	0.0602	0.184	0.0296	0.445	1.51	1.34	7.87	0.368
Total Pentachlorodibenzofuran	--	--	--	µg/kg		2.15	0.693	1.52	0.137	3.75	11.1 E	12.1 E	67.4 E	2.38 E
1,2,3,7,8-Pentachlorodibenzofuran	--	--	--	µg/kg		0.00504	0.0019 J	0.00493 J	ND	0.0103 JK	0.0389	0.0607	0.172	0.017
2,3,4,7,8-Pentachlorodibenzofuran	--	--	--	µg/kg		0.0521	0.0176	0.038	0.00477 J	0.0926	0.312	0.322	1.45	0.0533
Total Tetrachlorodibenzo-p-dioxin	--	--	--	µg/kg		0.0813	0.0225	0.069	0.0126	0.156	0.541	0.512	2.54	0.123
Total Tetrachlorodibenzofuran	--	--	--	µg/kg		1.69 E	1.64 E	1.31	0.18	2.99 E	9.17 E	9.48 E	72.4 E	2.43 E
2,3,7,8-Tetrachlorodibenzofuran	--	--	--	µg/kg		0.0116	0.00352	0.0138	0.0012	0.0249	0.0856	0.143	0.279	0.0561
2,3,7,8-Tetrachlorodibenzo-p-dioxin	--	0.00085	--	µg/kg		ND	ND	ND	ND	ND	0.0027	0.00178	0.012	0.000613 J

Table 19-3. Site EACC1K/5A Phase IV Detected Compounds in Hydric Soil and Sediment

ANALYTE	Industrial SED RSL	Eco FW SED	Reference Background	Unit	Sample Location	1K-SD109-SS0.5	1K-SD109-SO02	1K-SD110-SS0.5	1K-SD110-SO02	1K-SD111-SS0.5	1K-SD111-SS0.5X1	1K-SD111-SO02	1K-SD112-SS0.5	1K-SD112-SO02
					Date Sampled	11/18/2017	11/18/2017	11/18/2017	11/18/2017	11/18/2017	11/18/2017	11/18/2017	11/18/2017	11/18/2017
Semi-Volatile Organic Compounds (SVOCs) and Polycyclic Aromatic Hydrocarbons (PAHs)														
Acenaphthene	45000000	6.7	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
Acenaphthylene	--	5.9	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
Antrhacene	230000000	57.2	550	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
Benzaldehyde	8200000	--	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
Benzo(a)anthracene	210000	108	550	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
Benzo(a)pyrene	21000	150	550	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
Benzo(b)fluoranthene	210000	27.2	550	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
Benzo(g,h,i)perylene	--	170	550	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
Benzo(k)fluoranthene	2100000	240	550	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
Benzoic acid	3300000000	--	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
Benzyl alcohol	8200000000	--	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
Bis(2-ethylhexyl)phthalate	--	1800	9300	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
4-Chloroaniline	--	--	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
Carbazole	--	--	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
Chrysene	21000000	166	550	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
Dibenz(a,h)anthracene	21000	33	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
1,4-Dichlorobenzene	110000	599	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
Di-n-butylphthalate	--	6470	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
Fluoranthene	30000000	423	600	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
Fluorene	30000000	77.4	550	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
Indeno(1,2,3-cd)pyrene	210000	17	550	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
1-Methylnaphthalene	730000	--	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
2-Methylnaphthalene	3000000	20.2	--	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
Naphthalene	170000	176	550	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
Phenanthrene	--	204	600	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS
Pyrene	23000000	195	550	µg/kg		NS	NS	NS	NS	NS	NS	NS	NS	NS

Qualifier	Definition
B	Analyte is found in the associated blank as well as in the sample.
D	Data reported from a dilution.
H	The result was analyzed, extracted, or received outside of the EPA recommended holding time.
J	Detected but below the Reporting Limit/Limit of Quantitation; therefore, result is an estimated concentration.
M	Indicates that the sample matrix interfered with the quantitation of the analyte. In dual column analysis the result is reported from the column with the lower concentration. In inorganics, it indicates that the parameters DL/LOD/LOQ has been raised.
N	The MS/MSD criteria and/or precision are outside criteria. The predigested spike recovery is not within control limits for the associated parameter.
P	The associated numerical value is an estimated quantity. There is greater than 40% difference between the two GC columns for the detected concentrations. The higher of the two values is reported unless matrix interference is obvious or for HPLC analysis where the primary column is reported.
Q	The relative percent difference (RPD) and/or percent recovery exceeded limits in the associated Blank Spike and/or Blank Spike Duplicate.
X	The parameter shows a potential positive bias on a reported concentration due to an ICV or CCV exceeding the upper control limit on the high side.
Y	The parameter shows a potential negative bias on a reported concentration due to an ICV or CCV exceeding the lower control limit on the low side.
RSL	Above Industrial Sediment Regional Screening Level
Eco FW SED	Above Ecological Freshwater Sediment Screening Level. (Most conservative value used.)
Bold	Above Reference Background Value (95% upper prediction limit)
RSL & Eco FW SED	Above both RSL and Eco FW SED
--	No screening criteria available
NS	Not Sampled
ND	Not Detected

APPENDIX C TEXAS TECH STANDARD OPERATING PROCEDURES

Standard Operating Procedure for using High Resolution Passive Profilers (HRPP)

Texas Tech University (TTU)

1. SCOPE AND APPLICATION

1.1. This method is an operating procedure for the use of sediment high resolution passive profilers (HRPP).

1.2. The method involves the deployment of HRPP in shallow sediments (<1 to 4m) for the evaluation of the transport and fate of chlorinated solvents, heavy metals, hydrophobic organic compounds (HOC), geochemical species, and other dissolved pore water constituents and contaminants.

1.3. The method generates water samples that can be analyzed by standard methods, SPME fibers that can be extracted and analyzed for adsorbed species, and Biosep beads that can be commercially analyzed for microbial community abundances or CSIA of appropriate species.

1.4. The method also allows for estimation of pore velocity.

2. SUMMARY OF METHOD

2.1. Precleaned stainless steel or polycarbonate HRPP samplers are prepared for deployment.

2.2. HRPP are driven into the sediment.

2.3. HRPP are allowed to equilibrate for 3-4 weeks.

2.4. HRPP are removed from the sediment.

2.5. At the site, water from equilibration cells is removed by syringe and placed in appropriate field containers or immediately used for analysis of unstable geochemical indicators (e.g. Fe^{+2} and S^{-2}).

2.6. SPME fibers are removed and placed in containers with an appropriate solvent.

2.7. Biosep beads are removed washed with sterile buffered solution and placed in sterile containers for shipping.

2.8. All samples are shipped to appropriate labs for sample analysis.

3. APPARATUS AND MATERIALS

3.1. HRPP samplers stainless or polycarbonate (Figure 1 and Figure 2).

3.2. Viton gaskets for sealing equilibrium and velocity cells.

3.3. 0.45 um Nylon membrane or other appropriate membrane.

3.4. 10 µm nylon mesh or 100 µm 316 stainless steel mesh for protection of membrane.

3.5. 100 µm 316 stainless steel mesh for support and protection of SPME fibers.
3.6. Stainless steel (316) mesh with opening <1000 µm for protection of Bio-Sep beads.
3.7. SPME fibers ~8cm pre-equilibrated with appropriate PRCs (see Standard Operating Procedure for the Preparation, Extraction, and Analysis of Solid Phase Micro-extraction Polydimethylsiloxane Fibers used as a Passive Sampling Technique in Sediment and Surface Waters). Note that SPME fibers are only required for applications where evaluation of hydrophobic organic compounds is required.
3.8. Biosep beads which can be acquired from Microbial Insights.
3.9. Quick drying silicone 100% water proof for attachment of fibers to steel mesh.
3.10. Clean container to assemble samplers.
3.11. Distilled and or deionized water of appropriate quality containing bromide (Br^-) at a concentration 100 X background (e.g. typically 100-300 mg/l except in cases where seawater is present).
3.12. Screw guns for attaching cover plates.

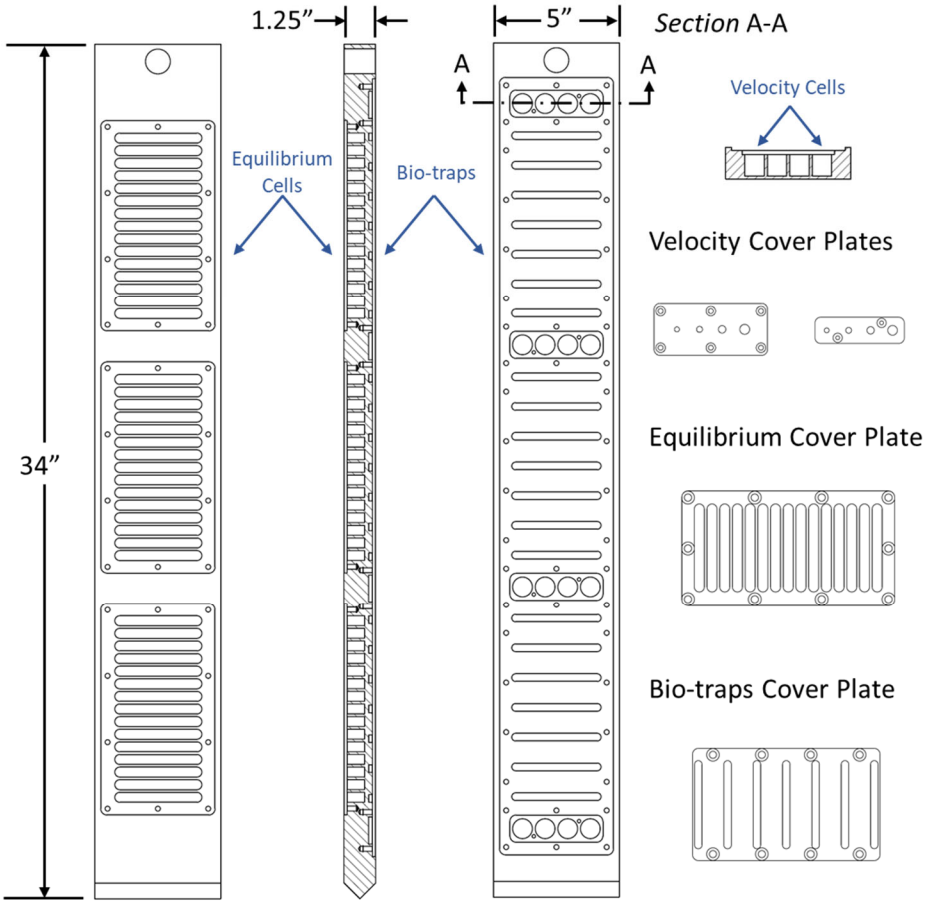


Figure 1. Schematic of the HRPP flat sampler.

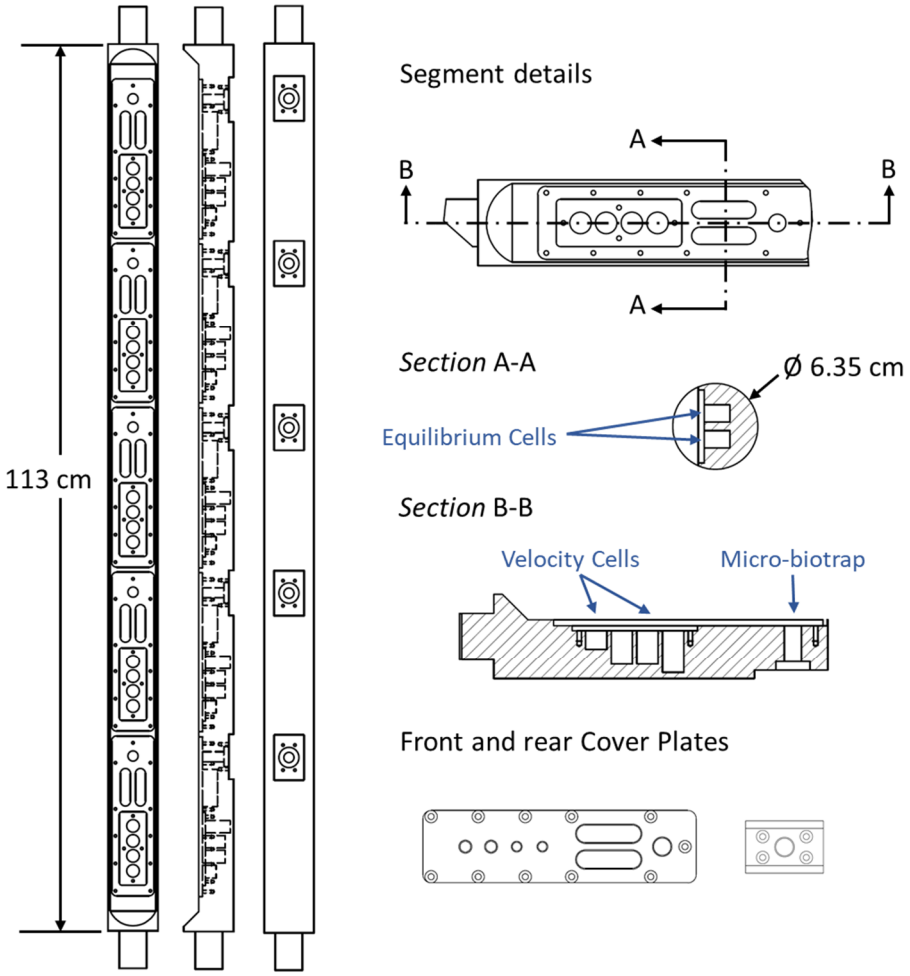


Figure 2. Schematic of the HRPP round sampler.

4. HRPP Cleaning Prior to Deployment

4.1. Stainless HRPP should be cleaned prior to use using laboratory grade detergent and brushes. All visible particles should be removed, and any rust spots removed by abrasion. Screw holes should be irrigated using a 50 ml syringe and large diameter needle. After thoroughly washing the samplers they should be rinsed excessively with tap water (irrigating screw holes). Samplers should then be rinsed with lab quality water, (deionized water), including screw holes. Finally, samplers should be rinsed with methanol to remove residual water. After drying, the samplers should be wrapped in plastic to protect form contamination prior to use.

4.2. FHRPP intended for evaluation of heavy metals (polycarbonate samplers only) after cleaning with soap and water and rinsing with tap water as described above, the sampler should be soaked in 0.1 M HCl for 24 hours. HRPP can then be drained and rinsed with deionized water as described above.

4.3. Cover plates must be washed in the same way as samplers' bodies depending on the construction material.

5. HRPP Preparation for Deployment

5.1. HRPP can be prepared prior to deployment but should be stored in the bromide solution used to prepare the samplers.

5.2. To prepare the samplers for deployment, the cleaned samplers should be submerged in a Br^- solution. The Br^- solution concentration can range from 100- 300 mg/l for fresh water applications. If the deployment will be near sea water, higher concentrations can be used (300-1,000 mg/l). The Br^- concentration is not critical as long as: a) the concentration is known and b) the concentration is not greater than 300 mg/l for fresh water systems or a 1000 mg/l for salt water systems.

5.3. During HRPP assembly, the water in the assembling container should be sampled in order to establish the initial Br^- concentration.

5.4. If sampling requires the use of Biosep beads, bio-traps must be assembled first while the sampler is dry. Biosep beads are placed in the bio-traps with the use of a spatula. Then, a layer of stainless steel mesh and the respective cover plate are placed to keep the beads in the cells. The stainless steel mesh must be clean and cut to size with all the perforations for the screws.

5.5. The HRPP sampler must be kept submerged during the whole assembling process of equilibrium and velocity cells.

5.6. Remove any air bubbles from samplers and irrigate screw holes using syringe to remove trapped air.

5.7. Place in the following order Viton gasket, nylon membrane and protective meshes (nylon for metals analysis, stainless for HOC analysis) over the equilibrium cells. Place the cover plate over the materials. While holding the cover plate in place, use a metal punch to poke holes through the membrane covering each screw hole. This prevents the screw from dislodging the membrane. Secure the cover plates with screws. It is recommended to hand tighten the screws to prevent stripping but a screw gun can be used to initially tighten.

5.8. If SPME analysis is performed, pre-equilibrated fiber segments should be affixed to the stainless mesh prior to assembly and a second layer of stainless mesh should be used to keep the fibers protected. Fibers can be attached with silicone dispensed with a syringe and needle. A very small drop of silicone is applied to each end of the SPME fiber. Finally, the two layers of steel mesh with the fibers are placed under the cover plate for equilibrium cells and assembled under the bromide solution.

6. HRPP deployment

6.1. HRPP can be driven into the sediment using any appropriate drive tool such as a slide hammer, hammer, fence post driver, etc..

6.2. If using polycarbonate HRPP, a protective plate should be placed over the top of the HRPP to prevent cracking.

6.3. A rope and appropriate marker (buoy, stake, etc..) should be attached to allow the HRPP to be located on retrieval.
6.4. HRPP should be deployed for at least 4 weeks if sampling for HOC using SPME. Deployment times greater than 5 weeks will reduce velocity cell sensitivity.

7. HRPP Sampling

Equilibrium Cells

7.1. HRPP equilibrium cells should be sampled as soon as possible after removal.
7.2. After the HRPP has been retrieved, sediment can be removed from the face of the sampler by wiping with a Kimwipes. Do not remove sediment from sample cell indentions until ready to sample.
7.3. Gently dislodge any sediment over the membrane using a Kimwipes or piece of rounded plastic. It is not necessary to remove all sediment but it is useful to have a relatively clean piece of membrane to insert the sample needles. Pierce the membrane with a needle to a depth just below the membrane surface and keep the needle inserted. This will vent the cell while the solution is being extracted.
7.4. With a separate 10 mL or larger syringe coupled to a needle, pierce the membrane and insert to the bottom of the sample cell. The HRPP can be tilted to allow almost complete removal of sample cell water. The cell water should be removed slowly to prevent cavitation and excess vacuum that may cause external water to be sucked into the cell. If not sampling for any organic contaminants using the sample cells (e.g. chlorinated solvents, pesticides, explosives, etc..), a plastic syringe can be used. If any organic contaminants are being measured in the equilibrium cell water, a glass gas tight syringe should be used.
7.5. If filtration is needed for the analysis (Dissolved Organic Carbon, Metals, etc..), once the solution is inside the syringe, exchange the needle for the syringe filter capsule and inject the filtered solution into the appropriate storage vial and/or analyze sample (Fe^{+2} and S^{-2}) on site.
7.6. Sample preservation, pretreatment, storage, and shipping should be conducted according to standard methods for any water sample.

SPME Fibers for HOC Sampling

7.7. Remove screws holding the equilibrium cell cover plates. Gently remove the stainless steel screens and separate the stainless screen with SPME fibers attached from the upper layer.
7.8. Rinse the screen with fibers attached with lab grade water to remove most sediment.
7.9. Using a ceramic SPME fiber cutter, carefully cut the fiber at the point of attachments, be sure to remove any fiber in contact with silicone adhesive). Remove fiber and gently clean with a kimwipe. Place fiber on a clean piece of aluminum foil and cut fiber int to appropriate length segments for storage. If using autosampler vials with low volume

inserts the fibers are usually cut into 1-2 cm lengths. The fibers should be stored in the vials with an appropriate solvent for the extraction method (See SPME SOP).

Velocity Cell Sampling

7.10. Remove sediment from velocity cells and blot dry with a Kimwipe.
7.11. Using two needles as described above (7.4) remove water form velocity cell.
7.12. Remove needle and inject water into a storage vessel.
7.13. Store samples on ice and ship for Br^- analysis.

Biosep bead sampling for Microbial community Analysis

7.14. Remove cover plates covering cells containing Biosep beads.
7.15. Using a sterile spatula, remove beads and place in stainless steel strainer that has been rinsed with methanol and sterile water.
7.16. Using either a squirt bottle filled with sterile buffered water (see Appendix 1 for preparation of solution) or a 50 ml syringe, gently wash beads of all sediment.
7.17. Transfer beads to a sterile storage container and store on ice. Follow sample storage and shipping guidelines for commercial analysis.
7.18. If only CSIA will be conducted NOT microbial analysis there is no need to use sterile water, or tools.

8. HRPP demobilization

8.1. HRPP should be cleaned in the field to remove bulk sediment.
8.2. Remove any remaining screws and cover plates.
8.3. Using a brush and bucket of water, remove sediment and rinse all HRPP parts.
8.4. HRPP can then be shipped in an appropriate container for a detailed cleaning in the laboratory (section 4).

Appendix 1. Preparation of Phosphate-buffered saline (PBS)

Ingredients for 1 L of solution:

- 8 g of sodium chloride (NaCl)
- 0.2 g of potassium chloride (KCl)
- 1.44 g of sodium phosphate dibasic (Na_2HPO_4)
- 0.24 g of potassium phosphate monobasic (KH_2PO_4)

Procedure

Dissolve the reagents listed before in 800 mL of distilled deionized water. Adjust the pH to 7.4 with HCl 1 M and then add water to complete 1000 mL.
Sterilize the solution by autoclaving for 20 minutes at 15 psi.
Store PBS solution at room temperature.

Standard Operating Procedure for the Use, Extraction, and Analysis of Solid Phase Microextraction Polydimethylsiloxane Fibers used as a Passive Sampling Technique in Sediment and Surface Waters

1. SCOPE AND APPLICATION

1.1. This method is an operating procedure for measurement of sediment pore water concentrations with solid phase microextraction (SPME) using polydimethylsiloxane (PDMS) as the polymer sorbent.

1.2. The method is applicable to hydrophobic organic contaminants (HOCs) and the focus herein is on polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and DDx.

1.3. This procedure generates extracts suitable for High Performance Liquid Chromatography (HPLC) and GC-MS analysis for priority and alkyl PAHs (PAH-38) and GC-MS/MS and GC-ECD for PCBs.

1.4. This extraction procedure is applicable to lab or field exposed PDMS fibers.

2. SUMMARY OF METHOD

2.1. The method can be applied *in situ* (field) or *ex-situ* (laboratory) but both approaches entail exposing PDMS fibers to the sediments by direct insertion into the sediment for a period of time followed by extraction and chemical analysis.

2.2. A specific length of PDMS is cleaned by consecutive extraction with dichloromethane, hexane, methanol and ultrapure water.

2.3. Performance reference compounds (PRCs) are loaded onto cleaned PDMS fiber in water-methanol (80:20%) solution.

2.4. A shaker table is required to facilitate well-mixing of the PRC spiking solution and contact with the PDMS fibers.

2.5. The PDMS fibers are kept in the PRC solution until preparation for deployment.

2.6. PDMS fibers are inserted to the sediment or water column and exposed for 21-28 days.

2.7. Upon retrieval from a field location or from laboratory sediment, any adhering material is removed from the PDMS fiber with a lint-free damp tissue before segmentation into appropriate lengths along the PDMS fiber to acquire a concentration depth profile into the sediment or in the water column. The PDMS fibers are extracted with an appropriate solvent (i.e. acetonitrile or hexane) overnight. The PDMS fibers are removed from the extract before analysis via HPLC or GC methods.

3. INTERFERENCES

3.1. In general, the use of PDMS as an extracting phase limits the amount of extraneous compounds from the sample and provides a phase that is easily extracted. This limits the

amount of sample cleanup necessary as well as the need for surrogates to test extraction efficiency. However, both may be necessary under some conditions.

3.2. PDMS fibers can become contaminated from the atmosphere and surfaces, and therefore techniques to limit the amount of undesired exposure must be followed.

3.3. Biofilms, adhering sediment, or chemical residues like NAPL residues can be removed by wiping the PDMS fiber with a MiliQ water wetted Kimwipe®

3.4. Method detection limits are related to compound hydrophobicity and therefore the method must be used with caution when analyzing relatively volatile constituents which exhibit greater losses and relatively poor detection limits.

3.5. Sediments that are contaminated with oil or other nonaqueous phase liquid (NAPL) will greatly complicate the interpretation of the results. The NAPL can absorb directly onto the PDMS and will also affect the partitioning into water. Use of the technique in NAPL-contaminated sediments should not be expected to provide quantitation on mobile contaminants

4. APPARATUS AND MATERIALS

4.1. Washing, PRC loading and storage vessel (250 mL, amber/clear glass depending on the analytes of interest) with foil-lined cap. Larger Volumes can be used depending on application.

4.2. Solid phase micro-extraction polydimethylsiloxane fibers – commercially available through suppliers like Polymicro Technologies™ (Molex, Phoenix) and Fiberguide (New Jersey).

4.3. Sampling device/fiber holder –

4.3.1. For *ex situ* use: a septa or mesh bag; Sampling device/fiber holder: a septa or mesh bag; Fibers require neither holder nor protective sheath if used in short lengths in laboratory samples or laboratory slurries although some form of holder (e.g. wire mesh envelope) is useful for locating and retrieving many fibers or smaller fiber sizes (< 500 μm). Their size (< 1 mm diameter) suggests that this can be accomplished with minimal disturbance to the surrounding sediment. Very small fibers may need to be inserted into a septum to aid location and withdrawal.

4.3.2. For *in situ* use: A sheath or holder is typically necessary to both protect the PDMS and to locate the sampler after sediment exposure. Three types of holders have been employed in our laboratory

4.3.2.1. Henry sampler (manufactured by M.H.E. Products) that has been modified. Modifications included 4 mm diameter perforations in the outer sheath, a 2 mm groove in the inner rod of the sampler, and the attachment of a washer that rests at the sediment–water interface during deployments. The groove length of the inner rod dictates the sampling length of the sampler (i.e. 60 or 90 cm). The outer sheath facilitates fiber-porewater contact while protecting the fiber. The inner rod secures the fiber from movement during deployment and retrieval.

4.3.2.2. 30 cm T-bars without the outer sheath attached to a triangle frame (for triplicate measurements, spaced 1 foot apart) can be used for deployment in soft sediments. In this configuration, two 2 mm grooves in the T-rod can accommodate more PDMS for improvement of detection limits especially for monitoring sites after activated carbon addition.

4.3.2.3. sHRPP which can accommodate 45 5cmfibers oriented horizontally at ~1-2 cm spacing. The fibers are placed between an outer mesh (pore size >100um) and inner 0.2um membrane. Samplers can be inserted into any sediment matrix in which they can be driven by hammering.

4.4. Extraction vessels – 2 mL amber (for PAHs) or clear glass (for PCBs) autosampler vials.

4.5. 300 µL glass inserts with springs for ultra-low solvent volumes.

4.6. PTFE/Silicone/PTFE screw caps for short-term storage and PTFE lined solid tops for long-term storage.

4.7. Kimwipes®

4.8. Food-grade aluminum foil

4.9. Tweezers

4.10. Single-edge razor

4.11. Ceramic Cutter

4.12. Syringe needle

4.13. Glass tubes

4.14. Shaker table or overhead tumbler

5. REAGENTS

5.1. Sodium azide (NaN_3)

5.2. Dichloromethane (methylene chloride, CH_2Cl_2)

5.3. Hexane

5.4. Acetonitrile

5.5. Methanol

5.6. MiliQ Water (Barnstead, GenPure Pro)

5.7. Research grade deuterated or C^{13} labeled compounds as performance reference compounds (PRCs): d-Fluoranthene, d-Chrysene, d-Benzo(b)Fluoranthene, d-Dibenzo(ah)anthracene and C^{13} mix containing PCBs 28/52/101/153/138/180/209 (Ultra Scientific and Cambridge Isotope Laboratories).

5.8. Research grade deuterated or C^{13} labeled compounds as surrogates or internal standards for GC-MS or GC-TQMS analysis: d-acenapthene, d-phenanthrene and d-perylene for PAHs (working standard concentration of 1000 µg/L in hexane) and C^{13} mix containing PCBs 9/118/188 (working standard concentration of 1000 µg/L in hexane).

Table 1. PRCs and internal standards used for spiking and analysis of PDMS.

Analysis	PRC	Internal Standard
Method 1668	^{13}C-28, 52, 101,153,138, 180, 209	^{13}C- 9, 118, 188
Method 8081A	^{13}C- 2,4'DDT, 4,4'-DDE, and 4,4'-DDD	^{13}C-, d-perylene

6. HANDLING AND PRESERVATION

6.1. All personnel should wear nitrile or powder-free gloves when handling the sampling devices and the PDMS fiber.

6.2. Clean PDMS should be stored in clean, sealed, glass vessels.

6.3. Solvent rinsed tweezers should be used when handling the PDMS.

6.4. The loaded PDMS fibers should be stored in the PRC solution until further use.

7. PROCEDURE

7.1. PDMS fiber is purchased from Polymicro Technologies™ on a spool with a nominal PDMS coating of 35 µm. Other thickness can be used depending on application. The fiber is cut into desired lengths, for example 5 cm, which can be easily inserted in small vials with sediment. The 5 cm lengths can be easily cut into smaller segments (i.e. 2+2+1 cm) for extraction and processing and may also provide replication and/or contingency in situations when 2 cm lengths are used for analysis and data interpretation. Details on the quantity of fiber per sampling exercise are provided in Appendix 1.

7.2. PDMS washing

7.2.1. The cut PDMS fibers are placed in the 250 ml glass vessel and cleaned by washing consecutively with three solvents i.e. dichloromethane (2x), hexane (2x) and methanol (2x) for 30 minutes each on a shaking table. Care should be taken to avoid PDMS breakage during washing with solvents. Therefore, gentle shaking is recommended or unobstructed movement of the PDMS in the washing vessel. After the methanol solvent wash, the fibers are rinsed with MiliQwater at least three times. The rinsed PDMS fibers are then blotted dry with lint-free tissues.

7.2.2. A portion of the cleaned fibers should be checked for residual contamination by pipetting 1 mL of clean hexane or equivalent solvent down the fiber length, collecting the solvent at the bottom of the PDMS fiber, and analytically checking for

contamination. The cleaning process is repeated until any analytes of concern are not detected in the test solvent.

7.2.3. The loaded PDMS fibers should be stored in the PRC solution until further use.

7.3. Loading of PDMS with performance reference compounds:

7.3.1. PRCs should be chosen to assess kinetic dissipation/uptake rates during field deployments. PRCs are loaded onto the PDMS before deployment.

7.3.2. 200 mL of spiking solution (water and 20% methanol) is placed in the glass vessel with cleaned PDMS. Deuterated/C^{13} labeled versions of the analytes of interest (**Table 1)** at working concentration of 2500 ng/ml in methanol or acetone are added to the water-20% methanol solution. Higher concentrations of working standards are available for d-PAHs. The levels of PRCs on PDMS should be similar to the target analytes and can be predetermined by using PDMS-water partition coefficients corrected for loading efficiency in the water-20% methanol solution (see PRC spiking calculation in **Appendix 1**). The total volume of water-methanol solution should result in minimum headspace and ensure effective mixing and transfer of PRCs to PDMS. To avoid losses via volatilization during mixing, the outer side of the caps should be covered with parafilm. Note, after exposure of the loaded PDMS with sediment or overlying water, part of the PRCs will leave the fiber resulting in lower concentrations for analysis. Therefore, one may design the loading calculation in such way that the initial concentration of PRCs in the extract and thus fiber is a factor of 2-3 higher to meet the requirements for detection after PRCs exposure.

7.3.3. The spiking solution with PDMS is agitated (approximately 130 strokes per minute) using a shaker table for a minimum of 8 days with deuterated PAHs and a minimum of three weeks with C^{13} labeled PCBs before using the PRC loaded PDMS. Longer equilibration times may be required for thicker samplers.

7.3.4. The loaded PDMS fibers should be stored in the PRC solution until further use.

7.3.5. PRC loaded PDMS fibers should be used for exposure into sediments and a subset of the simultaneously prepared fibers should be analyzed for initial PRC concentrations in the fibers. At least 6 PRC loaded PDMS fibers should be analyzed for initial PRC concentrations.

7.4. All sampling devices are disassembled and washed with detergent and hot water. Following being washed with detergent and hot water, the sampling devices are sequentially soaked in dichloromethane, hexane, methanol or equivalent solvent based upon analytes of interest, and MiliQ water for at least an hour each. The sampling devices are then dried under the fume hood on clean tissues overnight.

7.4.1. After the process is complete, 3 mL of clean hexane or equivalent solvent is introduced to the inner rod of the sampling device, collected at the bottom of the sampler, and analytically checked for contamination. The cleaning process is repeated until any analytes of concern are not detected in the test solvent.

7.5. Deployment of PDMS in sediment samples

7.5.1. All personnel should wear nitrile or powder-free gloves when handling the sampling devices and the PDMS fiber.

7.5.2. Solvent rinsed tweezers should be used when handling the PDMS.

7.5.3. For *ex situ* deployment: Prior to exposure *ex situ*, all sediment samples (in jars) should be homogenized for 12 hours on a roller-bank. Approximately 22-25 g of wet sediment samples from each sampled location (in triplicate) are weighed into 20 mL amber or clear vials (depending on compounds of interest). The sediment samples should be fully saturated with native water or not exceed 50% dry weight sediment. In case sediment does not appear saturated, a subsample of sediment from original jar should be transferred into a secondary container followed by addition of MiliQ water to ensure saturation and homogenized for 1 hour or a roller-bank.

7.5.4. Sediment samples in 20 mL vials are dosed with sodium azide (NaN_3) to prevent biological activity and homogenized gently with a stainless steel spatula. The addition of NaN_3 should yield a concentration of 100 mg/L in the 20 mL vial.

7.5.5. The loaded PDMS fibers are withdrawn from the PRC solution using clean tweezers, rinsed with MiliQ water and blotted on Kimwipes® to remove any residual methanol.

7.5.6. The loaded PDMS fibers are then inserted into a septa/envelope or placed directly in the 20 ml vials with sediment. Vertical placement is recommended. The vials with sediment and PDMS are closed with an aluminum lined cap and allowed to equilibrate for 21-28 days with gentle shaking on a shaking table at 20ºC.

7.5.7. For *in situ* deployment: the cleaned PDMS fibers are laid into the groove of the sampling device's inner rod and attached with 1 cm or less of waterproof caulk (hydrocarbon free silicon) at both ends of the groove. Care should be taken to avoid any placement of silicon on the active measurement portion of the sampling device or placement of too much silicon so that the cured silicon will hinder insertion or removal of the sampling device's inner rod from its outer sheath. Once the caulk is cured, the sampling device's inner rod is inserted into the outer sheath. The handles of the inner rod and outer sheath are then wrapped together to maintain orientation of the fiber to the screened section of the outer sheath. The sampling devices with PDMS are wrapped in foil and covered with ice for transport.

7.5.8. For *in situ* deployment: before sampling device insertion, buoys are attached via nylon cord to the sampling device to serve as markers for retrieval.

7.5.9. For *in situ* deployment: The sampling devices should be labelled with a waterproof marker on the tape wrapped around the inner rod and outer sheath handles or with an equivalent label that will not be disturbed during deployment.

7.6. Retrieval

7.6.1. All surfaces that the PDMS fiber will come into contact with must be covered with clean food grade aluminum foil.

7.6.2. Hexane or equivalent (other solvents can be selected based upon analytes of interest) rinsed tweezers and ceramic column cutters are used for segmentation of the PDMS fiber.

7.6.3. All laboratory and field personnel must wear nitrile or powder-free gloves when handling the PDMS fiber holder and the PDMS fiber. It is recommended to have two people in the field, one to handle the removal of the PDMS fiber from the holder and cleaning of the PDMS fiber and the other to handle segmentation and extraction. If only one person is available for completing retrieval activities, than the nitrile or latex gloves must be exchanged between the removal/cleaning step and the segmentation/extraction step.

7.6.4. Upon retrieval, the PDMS fiber should be removed from the fiber holder and any biofilms, adhering sediment/particles, or chemical residues should be wiped from its surface using a DI water wetted Kimwipe®. After cleaning, the fiber should be blotted dry prior to segmentation and extraction.

7.6.5. Segmentation of the PDMS fiber should be done as efficiently as possible to minimize volatilization of more volatile analytes of concern.

8. **PROCEDURE**

8.1. *Ex situ* Retrieval

8.1.1. After 28 d the vials are removed from the shaker table and the PDMS fiber is carefully withdrawn from the sediment. Any adhering sediment, particles, biofilm, or residue is removed from the PDMS fiber using a MiliQ water wetted Kimwipe®. PDMS fibers are then blotted dry before segmentation.

8.1.2. PDMS fibers are segmented using a ceramic column cutter into smaller lengths, for example a 5 cm segment can be cut into 2+2+1 cm lengths.

8.2. Extraction: the 2+2+1 cm fiber segments are then transferred to 2 mL amber vials with glass inserts prefilled with 250 µL of the appropriate solvent depending upon the subsequent analysis. The solvent volume in the insert should be enough for the complete immersion of the PDMS fiber segment. Extraction can also be into a greater volume (e.g. amber vial without insert) if needed, for subsequent processing. The sample can also be reduced in volume by solvent evaporation to concentrate the sample for improvement of detection.

8.2.1. Examples of solvent extract volumes: 250 µL for 5-cm segments of PDMS fiber with a PDMS thickness of greater than or equal to 30 µm and 100 µL for 8 1-cm segments of PDMS fiber with a PDMS thickness of 10 µm

8.2.2. The PDMS fiber segments are left in the solvent overnight and stored at -17°C.

8.2.3. Following overnight extraction vials with inserts containing SPME segments and solvent are sonicated for 1 min.

8.2.4. A portion of the extract should be transferred to a new vial with insert and internal standard (IS) should be added at target concentration before analysis.

8.2.5. Priority pollutant PAHs can be analyzed by EPA Method 8310 or 8270 and PCB congeners by EPA Method 8082/8270 or modified Method 1668.

8.3. *In-situ* retrieval: After removal from the field for in-situ deployments, the sampling device's inner rod is separated from the outer sheath or the outer mesh is removed fro sHRPP. The PDMS fiber is carefully removed from the inner rod or membrane using a single edge razor and any adhering sediment, particles, biofilm, or residue is removed from the PDMS fiber using a MiliQ water wetted Kimwipe®. PDMS fibers are then blotted dry before segmentation. PDMS fibers are segmented using a ceramic column cutter into predetermined lengths at predetermined locations along the PDMS fiber, which correspond to specific depths of interest from the sediment-water interface.

8.4. The SPME PDMS fiber segments are left in the solvent overnight and stored at -17°C. During transportation from a field site, the samples are kept at 4°C until receipt at the laboratory.

8.5. Following overnight extraction vials with inserts containing PDMS segments and solvent are sonicated or vortexed for 1 min (depending on the amount of PDMS in vial or insert).

8.6. If the extracts will be analyzed by another laboratory, the vials will be shipped while maintained at 4°C. The volume of the vials and PRC compounds can be tailored to meet requirements of the receiving laboratory for the analyses planned.

8.7. Priority pollutant PAHs can be analyzed by EPA Method 8310 or 8270 and PCB congeners by EPA Method 8082/8270 or modified Method 1668. Although, these standard methods are more frequently used by research and commercial labs, any method appropriate for the contaminants of concern capable of analyzing a concentrated sample of extract can also be successfully employed.

9. QUALITY CONTROL & METHOD PERFORMANCE

9.1. PRC loading before deployment i.e. @ t=0: 6 samples of loaded PDMS must be collected from different parts of the PDMS fiber, extracted, and analyzed prior to field deployment.

9.2. Blanks

9.2.1. Deployment Blank: For *in situ* deployments, a deployment blank is a sampler that is shipped together with the other samplers to the field, but is shipped back without deployment and processed in the laboratory in the exact same fashion as samplers deployed in the field.

9.2.2. Solvent Blanks: Solvent blanks will be analyzed at the time of filling the vials for shipment i.e. one at the start of filling at one at the end where the same solvent source has been used. If these contain significant levels of contamination, new vials will be filled with a separate source and the process will be repeated. Additional

solvent blanks should be shipped with the samples at a frequency of one per 20 samples.

9.2.3. Field Control Samples: For in situ deployments, field control samples are used to track the solvent volume change or contamination during transition if on site processing samplers are needed. The field control samples can be calibration standards or other solutions with known concentrations. The field control samples are treated identically with the other samples. At least five field control samples are needed for each deployment. The average of the concentration change for all compounds and in all field control samples should be within 5% to avoid solvent volume adjustment.

9.3. Chemical Analysis: The QAQC samples for chemical analysis include initial calibration, second source standard checks, and continuous calibration verification checks; all should meet the acceptance criterion set in the analytical methods. A complete set of appropriate guidelines can be found in Table 2.

Table 2. Quality Guidelines for Organic Analysis by Gas Chromatography and High-Performance Liquid Chromatography (EPA 8310) from DOD QSM Version 4.1.

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Demonstrate acceptable analyst capability	Prior to using any test method and at any time there is a significant change in instrument type, personnel, or test method	QC acceptance criteria published by DoD, if available; otherwise method-specific criteria.	Recalculate results; locate and fix problem, then rerun demonstration for those analytes that did not meet criteria	NA	This is a demonstration of analytical ability to generate acceptable precision and bias per the procedure in Appendix A. No analysis shall be allowed by analyst until successful demonstration of capability is complete
MDL study	At initial set-up and subsequently once per 12-month period; otherwise quarterly	See 40 CFR 136B. MDL verification checks must produce a signal at least 3 times the instrument's noise level.	Run MDL verification check at higher level and set MDL higher or re-conduct MDL study	NA	Samples cannot be analyzed without a valid MDL.

	MDL verification checks shall be performed				
Minimum five-point initial calibration for all analytes (ICAL)	Initial calibration prior to sample analysis	One of the options below: Option 1: RSD for each analyte ≤ 20%; Option 2: linear least squares regression: r ≥ 0.995; Option 3: non-linear regression: coefficient of determination (COD) r2 ≥ 0.99 (6 points shall be used for second order, 7 points shall be used for third order).	Correct problem then repeat initial calibration.	NA	Problem must be corrected. No samples may be run until ICAL has passed.

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Continuing calibration verification (CCV)	Prior to sample analysis, after every 10 field samples, and at the end of the analysis sequence.	All project analytes within established retention time windows. All project analytes within ± 15% of expected value from the ICAL	Correct problem, then rerun calibration verification. If that fails, then repeat ICAL. Reanalyze all samples since the last successful calibration verification.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to all results for the specific analyte(s) in all samples since the last acceptable calibration verification.	Problem must be corrected. Results may not be reported without a valid CCV. Flagging is only appropriate in cases where the samples cannot be reanalyzed. Retention time windows are updated per the method.
Second source calibration verification (ICV)	Once after each initial calibration	All project analytes within established retention time windows. Value of second source for all analytes within ± 15% of expected value (ICAL)	Correct problem and verify second source standard. Rerun second source verification. If that fails, correct problem and repeat ICAL	NA	Problem must be corrected. No samples may be run until calibration has been verified.
Evaluation of relative retention times (RRT)	With each sample	RRT of each target analyte in each calibration standard within ± 0.06 RRT units.	Correct problem, then rerun ICAL.	NA	

Internal standards verification	In all field samples and standards	Retention time ± 30 seconds from retention time of the midpoint standard in the ICAL EICP area within - 50% to + 100% of ICAL midpoint standard	Reanalysis of samples analyzed while system was malfunctioning is mandatory.	If corrective action fails in field samples, apply Q-flag to analytes associated with the non-compliant IS. Flagging criteria are not appropriate for failed standards.	Sample results are not acceptable without a valid IS verification.
QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Method blank	One per preparatory batch	No analytes detected > ½ RL. and > 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater). Blank result must not otherwise affect sample results	Correct problem, then, If required, re-prep and reanalyze method blank and all samples processed with the contaminated blank.	Apply B-flag to all results for the specific analyte(s) in all samples in the associated preparatory batch.	Problem must be corrected. Results may not be reported without a valid method blank. Flagging is only appropriate in cases where the samples cannot be reanalyzed.

Retention time window position establishment for each analyte	Once per ICAL and at the beginning of the analytical shift	Position shall be set using the midpoint standard of the ICAL curve when ICAL is performed. On days when ICAL is not performed, the initial CCV is used.	NA	NA	
Results reported between MDL and MRL	NA	NA	NA	Apply J-flag to all results between MDL and MRL.	

9. DETERMINATION OF PORE WATER CONCENTRATIONS

The freely-dissolved pore water concentrations can be calculated from the accumulated uptake in the fiber and the fiber-water partition coefficients as shown in the following equation:

$$Cw = \frac{C_{PDMS}}{K_{PDMS-W}} = \frac{A*RSF*V_{solvent}}{L_{fiber}*V_{fiber}*K_{PDMS}*f_{ss}}$$

where:

A = Areas of chromatography peaks
RSF = response factor from calibration curve unique to each HOCs
$V_{solvent}$ = volume of solvent used to extract fiber
L_{fiber} = length of fiber sample
V_{fiber} = specific volume of fiber
K_{PDMS-W} = fiber-water partition coefficient unique to each HOCs
f_{ss}= fractional approach to steady state from PRCs

The fiber-water partition coefficient should correlate with the hydrophobicity of the compound and thus can be correlated with K_{ow} as shown in Ghosh et al. 2014. PRCs will be interpreted employing the methods of Lampert et al. (2015) to determine the fractional approach to steady state, f_{ss}. The fiber-water partition coefficients for dioxins can be extrapolated using the regression parameters for PCBs. Table 3 and 4 summarizes typical potential method detection limits by SPME-PDMS for selected PCBs and DDx.

Table 3. Method Detection limits (as indicated in porewater) by SPME-PDMS for selected PCB congeners by GC-TQMS. This assumes 150 µL solvent volume and 6 cm of PDMS fiber with 558 µm outside diameter and 497 µm inside diameter.

PCBs	Log KOW[a]	Log Kpdms[b]	MDL pg/L[c]
PCB-18	5.24	4.94528	562.984
PCB-28	5.67	5.35249	220.438
PCB-52	5.84	5.51348	152.159
PCB-66	6.2	5.8544	69.403
PCB-101	6.38	6.02486	46.872
PCB-77	6.35	5.99645	50.041
PCB-118	6.74	6.36578	21.379
PCB-153	6.92	6.53624	14.439
PCB-138	6.83	6.45101	17.570
PCB-187	7.17	6.77299	8.371
PCB-180	7.36	6.95292	5.532
CB-170	7.27	6.86769	6.731
PCB-209	10.54	9.96438	0.005

[a] PCB log KOW values from Hawker and Connell (1988); PAH log KOW values were calculated using the SPARC program (http://archemcalc.com/sparc-web/calc).

[b] Kpdms from Ghosh et al (2014)

[c] MDL using 6 cm of 31 µm PDMS on a 497 µm core

Table 4. Method Detection limits (as indicated in porewater) by SPME-PDMS for DDx by GC-TQMS. This assumes 150 µL solvent volume and 6 cm of PDMS fiber with 558 µm outside diameter and 497 µm inside diameter.

DDx	Log KOW[a]	Log Kpdms[b]	MDL pg/L[c]
2,4' DDT	6.7	6.3	7.3
4,4 DDT	6.6	6.2	9.1
2,4' DDE	6.7	6.3	7.3
4,4' DDE	6.9	6.5	4.7
2,4' DDD	6.1	5.8	27
4,4 DDD	6.1	5.8	27

[a] DDT log KOW values from Gschwend et al., (2018).

[b] Kpdms from Ghosh et al (2014)

[c] MDL using 5 cm of 31 µm PDMS on a 497 µm core

10. REFERENCES

Ghosh, U., et al., *Passive sampling methods for contaminated sediments: Practical guidance for selection, calibration, and implementation.* Integrated Environmental Assessment and Management, 2014. **10**(2): p.210-223

Lampert, D., C. Thomas, and D. Reible, *Internal and external transport significance for predicting contaminant uptake rates in passive samplers.* Chemosphere, 2015. **119**: p. 910-916.

Hawker, D.W. and D.W. Connell, *Octanol Water Partition-Coefficients of Polychlorinated Biphenyl Congeners.* Environmental Science & Technology, 1988. **22**(4): p. 382-387.

Borrelli et al., 2018. Performance of passive sampling with low-density polyethylene membranes for the estimation of freely dissolved DDx concentrations in lake environments. Chemosphere (200):p. 227-236

Department of Defense (DOD). Quality Systems Manual for Environmental Laboratories, Version 4.1. 2006. http://www.navylabs.navy.mil/QSM%20Version%204.1.pdf

U.S. Environmental Protection Agency. 1986. Test methods for evaluating solid waste physical/chemical methods, 3rd ed. Method 8310. SW-846. Office of Solid Waste and Emergency Response, Washington, DC.

U.S. Environmental Protection Agency. 1986. Test methods for evaluating solid waste physical/chemical methods, 3rd ed. Method 8082. SW-846. Office of Solid Waste and Emergency Response, Washington, DC.

Appendix 1. Example spreadsheet for calculating spiking of Performance Reference Compounds onto PDMS.

Step 1: Indicate the desired concentration of PRCs in extract after analysis to meet the requirements of detection. Here an example with 10 ng/mL (high resolution) and 100 ng/mL (low resolution) is provided. Note, after exposure of the loaded PDMS with sediment or overlying water, part of the PRCs will leave the fiber resulting in lower concentrations for analysis. Therefore, one may design the loading calculation in such way that the initial concentration of PRCs in the extract and thus fiber is a factor of 2-3 higher to meet the requirements for detection after PRCs exposure. For example, if the initial concentration of PCB-28 in the PDMS extract is 10 ng/mL and approximately 70% loss of the compound from the PDMS within exposure timeframe (28 days), the expected concentration in the extract will be 2 ng/mL.

Step 2: Indicate the length of PDMS per sample (extract) and the total amount of PDMS needed for the sampling exercise (here 50 pieces of 5 cm segments are chosen resulting in a total fiber length of 250 cm). Choose a vessel to accommodate the PDMS and water-methanol (80:20) inside without much headspace (here 250 mL amber glass bottle is used). For the PDMS length and extract volume, calculate the concentration in PDMS. Use the PDMS-water partition coefficients (Ghosh et al., 2014) to calculate the concentration in water (only) at equilibrium.

Step 3. Solve for initial spiking solution concentration of PRCs that result in the PRC loadings in the PDMS:

$$C_{initial\ spiking\ solution} = \frac{C_{PDMS} \times L_{fiber} \times V_{fiber} + C_{W,eq} \times V_W}{V_W} \quad (1)$$

Note, initial spiking solution concentration of PRCs will be the same in water-methanol (80:20) or water.

Step 4. Solve for volume of working standard, that needs to be added to the water:methanol solution (W:M) for impregnation of PDMS.

$$V_{working\ stand.} = \frac{C_{initial\ spiking\ solution} \times V_{W:M}}{C_{Working\ stand.}} \quad (2)$$

Fiber	
575	core diameter with PDMS coating (µm)
500	core diameter without PDMS coating (µm)
0.001806416	area (m2)
6.33227E-08	volume (m3)
3.50543E-05	length (m) i.e. coating thickness
35.05	length (µm) i.e. coating thickness

			fiber	
Water:MeOH (80:20) volume:	**200**	ml	5	cm
extract solvent (µl):	**250**	µl	50	No of 5 cm segments
Total fiber spiked:	**250**	cm	250	total fiber spiked cm
PDMS volume (µL/cm):	**0.633**	µL/cm		
Fiber length per sample extract:	**5**	cm		

CALCULATIONS FOR PRC LOADING --> individual compound spiking

log K_{PDMS-W}= 0.947*logKow-0.017 (PCB) ; log K_{PDMS-W}=0.725*logKow+0.479 (PAH)

log K_{ow} - Hawker and Connell, 1988 (PCB) and log Kow (SPARC estimates) PAH

High Res PCBs	logKow (Hawker and Conell 1988)	log K_{PDMS-W} (Ghosh et al., 2014)	Final Concentration in solvent extract ng/mL	mass in solvent µg	Conc on PDMS ng/ml	Conc in water (eq) ng/mL	fraction in PDMS in water only	Initial concentration in solution ng/mL	volume of working standard needed based on log KPDMS-W ml	volume of working standard needed based on log KPDMS-W µl	working standard in acetone ng/mL
C13-28	5.67	5.35	10	0.0025	790	0.00351	0.9944	0.626	0.05	50.1	2500
C13-47	5.85	5.52	10	0.0025	790	0.00237	0.9962	0.625	0.05	50.0	2500
C13-70	6.2	5.85	10	0.0025	790	0.00110	0.9982	0.625	0.05	50.0	2500
C13-80	6.48	6.12	10	0.0025	790	0.00060	0.9990	0.625	0.05	50.0	2500
C13-111	6.76	6.38	10	0.0025	790	0.00033	0.9995	0.625	0.05	50.0	2500
C13-141	6.82	6.44	10	0.0025	790	0.00029	0.9995	0.625	0.05	50.0	2500
C13-182	7.2	6.80	10	0.0025	790	0.00012	0.9998	0.625	0.05	50.0	2500

Standard Operating Procedure for the Analysis of Metals in Water Samples from High Resolution Passive Profilers Using ICP-MS

Texas Tech University (TTU)

1. SCOPE AND APPLICATION

1.1. This method is an operating procedure for the analysis of metal concentrations in water samples from high resolution passive profilers (HRPP).

1.2. The method involves the extraction and filtration of water samples from the HRPP cells.

1.3. The method involves the preservation of the samples with Nitric acid (HNO_3).

2. This procedure generates samples that can be analyzed metals following the EPA Method 220.8: D*etermination of Trace Metals in Waters and Wastes by Inductively Coupled Plasma-Mass Spectrometry*.

3. SUMMARY OF METHOD

3.1. A 4 to 10 mL sample is extracted from the HRPP cells with the use of clean, pretested syringes and stainless steel needles.

3.2. The sample is filtered through a 0.45µm syringe filter before being added to the storage vial.

3.3. The sample is preserved by addition of HNO_3.

3.4. The sample is then analyzed for selected trace metals according to EPA method 200.8.

4. METHOD DETECTION LIMITS, INTERFERENCES AND SAFETY

4.1. The method detection limit (MDL) for each metal of interest is will be determined prior to analysis based on the method. Method estimated DL for metals of interest are 0.02, 0.04, 0.015, 0.006, and 0.07 ug/l for As, Cr, Pb, V, and Zn, respectively. The MDL should be determined when a new operator begins to use the instrument or whenever, in the judgement of the laboratory, it is necessary to reevaluate the instrument capability and should be established annually. For MDL determination, follow guidelines in EPA 200.8.:

4.1.1. Select a spiking level between 2 to 5 times the expected MDL.

4.1.2. Process a minimum of seven spiked samples and seven method blank samples through all the steps of the method. The samples for MDL must be prepared in at least 3 batches on three separate calendar dates and analyzed on three separate calendar dates.

4.1.3. Calculate the sample standard deviation of the 7 MDL samples. Compute the MDL (based on spiked samples) as follows:

$$MDL = t_{6,0.99} * S$$

Where $t_{6,0.99}$=3.14 is the Student's t value for a 99% confidence level with 6 degrees of freedom. *S* is the sample standard deviation (n-1).

4.2. Always work accurately and neat, because of safety and quality assurance.

4.3. Always wear a laboratory coat, gloves and safety glasses; some chemicals are very toxic and corrosive.

4.4. Use a permanent fume hood when working with concentrated acids and powerful oxidants.

5. APPARATUS AND MATERIALS

5.1. Syringe and needle for extraction of water sample from HRPP cells — 10 mL Polyproylene or polyethylene and 20 gauge stainless steel needles.

5.2. Syringe Filter — 0.45µm opening.

6. REAGENTS and STANDARDS

6.1. All chemicals will be reagent grade or better. All acids will be trace metal grade.

6.2. Reagent grade water (purity~18 MΩ.cm).

6.3. Concentrated HNO_3

6.4. Certified Metal Standards

6.5. Nitrogen—Grade 5.0 (ultra high-purity, GC grade) nitrogen.

6.6. Argon—Grade 5.0 (ultra high-purity, GC grade) argon.

7. PREPARATION AND HANDLING

Sample extraction and filtration

7.1. After the HRPP has been retrieved, rinse the surface of the membrane covering the sampling cell.

7.2. With 10 mL syringe coupled to a needle, pierce the membrane and extract the content of the cell.

7.3. Once the solution is inside the syringe, exchange the needle for the syringe filter and inject the filtered solution into the storage vial.

7.4. The sample must be preserved within 48 hours of collection with either 0.5 % V/V of concentrated HNO_3 One option is to have the storage vial preloaded with the amount of concentrated HNO_3 to reach a concentration 0.5 % V/V.

7.5. Sample preparation for analysis

Analysis

7.6. Analyze the prepared sample in the ICP-MS ELAN DRC-e (Perkin Elmer-SCIEX) following the EPA method 200.8.

8. ANALYTICAL CALIBRATION

8.1. Precalibration Routine-Allow instrument tto warm up for >30 min. Conduct mass calibration and resolution checks using tuning solution. Adjust spectrometer resolution to produce a peak width of approximately 0.75AMU at 5% peak height. Adjust mass calibration if shifted > 0.1amu.

8.2. Instrument stability demonstrated by running tuning solution >5 times with <5% relative standard deviation.

8.3. Add Internal standards using either Method A or Method B.

8.4. Calibrate instrument using Calibration Standards A and B and calibration blanks.

8.5. Analyze the standards beginning with the lowest concentration and proceeding to the highest.

8.6. Prepare and analyze a minimum of 3 system blanks and tabulate the peak areas. Calculate the mean peak area for the system blank.

9. QUALITY CONTROL & METHOD PERFORMANCE

9.1. Chemical Analysis: The quality control (QC) samples for chemical analysis include initial calibration, second source standard checks, continuous calibration verification checks, matrix spike and matrix spike duplicates; all should meet the acceptance criterion set in the analytical methods. A complete set of appropriate guidelines can be found in Table 1.

9.1.1. Matrix spike percent recovery:

$$\%\ R = 100*(A-B)/T$$

Where:

A = Measured amount of Metal after spiking

B = Measured amount of Metal before spiking

T = True concentration of the spike. The spiking level shall be 1-5 times the background concentration.

9.1.2. Relative percent difference of matrix spike duplicates:

$$\%\ \mathrm{RPD} = 200*(|D1-D2|)/(D1+D2)$$

Where:

D1 = concentration of Metal in the matrix spike sample.

D2 = concentration of Metal in the matrix spike duplicate sample.

9.2. For every batch of 20 samples there must be at least one reagent blank, one laboratory fortified blank, one continuing calibration check, and two matrix spikes.

9.3. There must be at least 5 equipment blanks. Equipment blanks are generated by sampling a HRPP that is prepared in the same way and at the same time as deployed samplers. It is brought to the field with deployed samplers but not deployed. When the samplers are retrieved the non-deployed sampler is also sampled identically to the deployed using the same needles, syringes, filters, and acid as the rest of the profilers.

9.4. Field blanks: At least five blank samples are to be collected per sampling event. Field blanks are samples of reagent grade water collected using the same type of syringes, needles, filters and vials that are being used for the rest of the samples.

Table 1. Quality Guidelines for Metals by EPA 200.8 method.

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
MDL study	At initial set-up and subsequently once per 12-month period. Whenever a new operator begins to use the instrument.	< 0.5 µg/L	Run MDL verification check at higher level and set MDL higher or re-conduct MDL study	NA	Samples cannot be analyzed without a valid MDL.
Minimum five-point initial calibration for all analytes (ICAL)	Initial calibration prior to sample analysis	See EAP 200.8 for crtiria.	Correct problem then repeat initial calibration.	NA	Problem must be corrected. No samples may be run until ICAL has passed.
Continuing calibration verification (CCV)	Prior to sample analysis, after every 10 field samples, and at the end of	Hg result within ± 15% of expected value from the ICAL	Correct problem, then rerun calibration verification. If that fails, then repeat ICAL. Reanalyze all	If reanalysis cannot be performed, data must be qualified and explained in the case narrative.	Problem must be corrected. Results may not be reported without a valid CCV. Flagging is only appropriate in cases where

	the analysis sequence.		samples since the last successful calibration verification.	Apply Q-flag to all results for the specific analyte(s) in all samples since the last acceptable calibration verification.	the samples cannot be reanalyzed. Retention time windows are updated per the method.
Second source calibration verification (ICV)	Once after each initial calibration	Metal result within ± 15% of expected value (ICAL)	Correct problem and verify second source standard. Rerun second source verification. If that fails, correct problem and repeat ICAL	NA	Problem must be corrected. No samples may be run until calibration has been verified.
Method blank	Two per batch of 20 samples.	The mean result for the two system blanks must be < 2XMDL or 10% of a sample. If not the system is out of control.	Correct problem. Then, if required, prepare and reanalyze method blank and all samples processed with the contaminated blank.	Apply B-flag to all results for the specific analyte(s) in all samples in the associated preparatory batch.	Problem must be corrected. Results may not be reported without a valid method blank. Flagging is only appropriate in cases where the samples cannot be reanalyzed.

Matrix Spike (MS)	One each per every batch of 20 samples.	The recovery must be between 70 and 130 %.	If results of the MS/MSD are similar and fail the acceptance criteria, an interference is present and the results may not be reported or otherwise used for permitting or regulatory compliance purposes.	NA	Interferences must be corrected. Sample and its MS/MSD must be re-analyzed.
Results reported between MDL and MRL	NA	NA	NA	Apply J-flag to all results between MDL and MRL (minimum reporting limit).	

Table 2: Sequence & QA/QC for Metal Analysis.

Sl No	Sample ID	Description	Preparation	No of samples	QA/QC criteria
1	Calibration standards	A solution prepared from the dilution of stock standard solutions. Used to calibrate the instrument response with respect to analyte concentration.	certified standards	≥ 5 point	Linear fit $R^2 \geq 0.995$ (or) % RSD of Relative concentration factor (RCF) ≤ 15 % % RSD of individual calibration standard ≤ 15 %
4	Reagent Blank	Used to determine sample/standard carry over, and determine the contribution of reagents	Ultra-pure water containing IS	1	<2X MDL
5	ICV/VER	Initial calibration verification - used to verify that a calibration is accurate. Typically prepared from source other than the one used for calibration standard. (e.g., ICP-MS 1 ppm standard stock)	Standard in Ultra-pure water containing IS	1	85-115% Recovery
6	Reagent Blank	Same as above	Same as above	1	Same as above
7	Unknown samples	Unknown	With IS	16	Values fall within the calibration range
10	Matrix Spike	One of the unknown samples that is spiked with a known amount of Hg from the stock standard. See section 9.2.1 of this document.	Unknown sample plus spike. They are prepared in BrCl, HH and $SnCl_2$	1	Recovery of spike between 71-125 %.
11	Sample Duplicate	One of the 10 samples run above	With IS	1	Relative percent difference between MS and MSD must be less or equal to 24%.
13	Reagent Blank	Same as above	Same as above	1	Same as above
17	CCV	A solution with a known concentration of metal prepared from the dilution of stock standard solutions.	Standard in Ultra-pure water containing BrCl, HH and $SnCl_2$	1	Concentration of 5 pg/mL. 77-123% Recovery

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10. REFERENCES

Department of Defense (DOD). Quality Systems Manual for Environmental Laboratories, Version 4.1. 2006. http://www.navylabs.navy.mil/QSM%20Version%204.1.pdf.

Clarisse and Hintelmann (2006), Journal of Environmental Monitoring, 8, 1242-1247.

U.S. Environmental Protection Agency (2002): Method 1631, Revision E: Mercury in water by oxidation, purge and trap, and cold vapor atomic fluorescence spectrometry.

Standard Operating Procedure for the Analysis of Total Mercury in Water Samples from High Resolution Passive Profilers Using Cold Vapor Atomic Fluorescence Spectrometry

Texas Tech University (TTU)

1. SCOPE AND APPLICATION

1.1. This method is an operating procedure for the analysis of total mercury concentration in water samples from high resolution passive profilers (HRPP).

1.2. The method involves the extraction and filtration of water samples from the HRPP cells.

1.3. The method involves the preservation of the samples with hydrochloric acid (HCl) followed by bromine monochloride (BrCl) oxidation.

1.4. This procedure generates samples that can be analyzed for total mercury following the EPA Method 1631E: *Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry* using the MERX Total Hg system of Brooks Rand™.

2. SUMMARY OF METHOD

2.1. A 4 to 10 mL sample is extracted from the HRPP cells with the use of clean, pretested syringes.

2.2. The sample is filtered through a 0.45µm capsule filter before being added to the storage vial.

2.3. The sample is preserved by addition of either HCl or BrCl.

2.4. All Hg in the preserved sample is oxidized to Hg(II) with BrCl prior to analysis.

2.5. The oxidized sample is then analyzed for total Hg according to EPA method 1631E.

3. METHOD DETECTION LIMITS, INTERFERENCES AND SAFETY

3.1. The method detection limit (MDL) for Hg has been determined to be 0.2 ng/L when no interferences are present. The minimum level of quantification (ML) has been determined to be 1 ng/L. The MDL should be determined when a new operator begins to use the instrument or whenever, in the judgement of the laboratory, it is necessary to reevaluate the instrument capability. For MDL determination, follow the Title 40 of the Code of Federal Regulations part 136, Appendix B:

3.1.1. Select a spiking level between 2 to 10 times the expected MDL.

3.1.2. Process a minimum of seven spiked samples and seven method blank samples through all the steps of the method. The samples for MDL must be prepared in at least 3 batches on three separate calendar dates and analyzed on three separate calendar dates.

3.1.3. Calculate the sample standard deviation of the 7 MDL samples. Compute the MDL (based on spiked samples) as follows:

$$MDL = t_{6,0.99} * S$$

Where $t_{6,0.99}$=3.14 is the Student's t value for a 99% confidence level with 6 degrees of freedom. *S* is the sample standard deviation (n-1).

3.2. Always work accurate and neat, because of safety and quality assurance.

3.3. Always wear a laboratory coat, gloves and safety glasses; some chemicals are very toxic and corrosive.

3.4. Use a permanent fume hood when working with concentrated acids and powerful oxidants.

4. APPARATUS AND MATERIALS

4.1. Syringe and needle for extraction of water sample from HRPP cells — 10 mL Polyproylene or polyethylene.

4.2. Filter capsule — 0.45µm opening.

4.3. Digestion and storage vial — 15 ml polypropylene centrifuge tube or equivalent.

4.4. Autosampler vial— MERX trace metal grade total mercury autosampler vials, 40 mL capacity from Brooks Rand™

4.5. Balance—Analytical, capable of weighing 1.0 mg.

5. REAGENTS and STANDARDS

5.1. All chemicals will be reagent grade or better. If necessary, the chemicals used for extraction and analysis be analyzed to ensure total Hg is < 5 pg/mL. All acids will be trace metal grade.

5.2. Reagent grade water (purity~18 MΩ.cm).

5.3. Concentrated HCl~ 36 % (12 N) - trace metal grade.

5.4. Potassium Bromide (KBr).

5.5. Potassium Bromate ($KBrO_3$).

5.6. Concentrated (0.2 N) Bromide monochloride solution– In a fume hood , dissolve 27 g of KBr in 2.5 L of conc. HCl. Place a clean, teflon magnetic stir bar in the bottle and stir for approximately 1 hour in the fume hood. Slowly add 38 g of $KBrO_3$ to the acid while stirring. When all of the $KBrO_3$ has been added, the solution color should change from yellow to red to orange. Loosely cap the bottle, and allow to stir another hour before tightening the lid.

5.7. Hydroxylamine Hydrochloric Acid Reagent (HH) —Dissolve 300 g of $NH_2OH.HCl$ in reagent water and bring to 1.0 L. This solution may be purified by the addition of 1.0 mL of $SnCl_2$ solution and purging overnight at 500 mL/min with ultra high purity nitrogen gas. Alternative, certified HH reagent from Brooks Rand Instruments (cat no: 03610, Total mercury < 1 ng/L) can be used.

5.8. Stannous Chloride ($SnCl_2$) —Bring 200 g of $SnCl_2.2H_2O$ and 100 mL concentrated HCl to 1.0 L with reagent water. Purge overnight with ultra high purity nitrogen gas at 500 mL/min to remove all traces of Hg. Store tightly capped. Alternative, certified SnCl reagent from Brooks Rands Instruments (cat no: 03620, Total mercury < 1 ng/L) can be used.

5.9. Stock total mercury standard—certified 1 ppm from Brooks Rand Instruments (cat no: 03600). Shelf life is 18 months from time of certification.

5.10. Secondary ICP-MS mercury standard— 1 ppm Hg(II) in 2% Nitric Acid (NO_3).

5.11. Working Hg Standard A — Dilute 0.100 mL of the stock Hg standard to 10 mL in an autosampler vial with reagent water containing 1% by volume BrCl solution. This solution contains 10 ng/mL and should be replaced weekly, or longer if extended stability is demonstrated.

5.12. Working Hg Standard B—Dilute 0.100 mL of working Hg Standard A to 10mL in an autosampler vial with reagent water containing 1% by volume BrCl solution. This solution contains 100 pg / mL and should be replaced every analysis.

5.13. Nitrogen—Grade 5.0 (ultra high-purity, GC grade) nitrogen.

5.14. Argon—Grade 5.0 (ultra high-purity, GC grade) argon.

6. PREPARATION AND HANDLING

Sample extraction and filtration

6.1. After the HRPP has been retrieved, rinse the surface of the membrane covering the sampling cell.

6.2. Pierce the membrane with a needle and keep the needle inserted. This is going to vent the cell while the solution is being extracted.

6.3. With a separate 10 mL syringe coupled to a needle, pierce the membrane and extract the content of the cell. Do it slowly so you don't bring outer solution into the cell.

6.4. Once the solution is inside the syringe, exchange the needle for the filter capsule and inject the filtered solution into the storage vial.

6.5. The sample must be preserved within 48 hours of collection with either 0.5 % V/V of concentrated HCl or 0.5 % V/V of BrCl. One option is to have the storage vial preloaded with the amount of concentrated HCl to reach a concentration 0.5 % V/V. Don't preload vials with BrCl due to its high volatility.

Sample preparation for analysis

6.6. At least 48 h before analysis, in a permanent fume hood, add 1% V/V of BrCl to the sample for oxidation of all forms of mercury into Hg(II).

Analysis

6.7. Analyze the prepared sample in the MERX Total Hg system of Brooks Rand™ following the EPA method 1631E.

7. ANALYTICAL CALIBRATION

7.1. Place 20 mL of reagent water and 200 µL of concentrated BrCl (1% V/V BrCl, same concentration as the samples) solution in each of 6 40-mL autosampler vials. Prepare the lower end calibration by using Working Hg Standard B. Begin with an aliquout of 250 µL and 1000 µL. Next, using Working Hg Standard A, finish the calibration with sequential aliquots of 25, 50, 250 and 1000 µL.

7.2. Add 100 µL of HH solution. Pick up the vial and gently mix the solution allow until the yellow color disappears.

7.3. Add 100 µL of $SnCl_2$ solution to the individual vials and immediately cap the vial tightly.

7.4. Place into the analysis rack of the THg MERX System.

7.5. Analyze the standards beginning with the lowest concentration and proceeding to the highest. Tabulate the area for the Hg peak.

7.6. Prepare and analyze a minimum of 3 system blanks and tabulate the peak areas. Calculate the mean peak area for the system blanks.

7.7. For each calibration point, subtract the mean peak area of the Calibration/Bubbler Blanks from the peak area of each standard. Calculate the calibration factor (CF_x) for Hg in each of the five standards using the mean bubbler-blank-subtracted peak area and the following equation:

$$CF_x = \frac{(A_x - \bar{A}_{BB})}{C_X}$$

Where:

A_x = peak area for Hg in standard

$\bar{A}_{BB}$ = mean peak area for Hg in calibration blanks

Cx = Amount of mercury in the standard (pg)

7.8. Calculate the mean calibration factor (CFm), the standard deviation of the calibration factor (SD; n-1), and the relative standard deviation (RSD) of the calibration factor, where RSD = 100 x SD/CFm.

7.9. If RSD ≤ 15%, calculate the recovery for the lowest standard using CFm. If the RSD ≤ 15% and the recovery of the lowest standard is in the range of 75-125%, the calibration is acceptable and CFm may be used to calculate the concentration of Hg in samples. If RSD > 15% or if the recovery of the lowest standard is not in the range of 75-125%, recalibrate the analytical system and repeat the test.

7.10. Bubbler blanks—Bubbler blanks are analyzed to demonstrate that bubbler systems are free from contamination at levels that could affect data quality. At least three bubbler blanks must be run during calibration and with each analytical batch. Bubbler blanks consist of reagent water, BrCl, HH, and $SnCl_2$.

7.11. Calculate the concentration of Hg in the bubbler blanks using CFm. The bubbler blanks must meet the criteria in Section 9.4.1 of EPA 1631E; otherwise, mercury in the system must be reduced and the calibration repeated until the bubbler blanks meet the criteria.

8. DATA ANALYSIS and CALCULATIONS

8.1. Calculate the mean peak area for Hg in the bubbler blanks measured during system calibration or with the analytical batch (A_{BB}; n = 3 minimum).

8.2. Calculate the concentration of Hg in ng/L (parts-per-trillion; ppt) in each diluted sample according to the following equation:

$$[Hg](ng/L) = \frac{(A_s - \bar{A}_{BB})}{CF_m \times V}$$

Where:

A_s = peak area for Hg in sample.

$\bar{A}_{BB}$ = mean peak area for Hg in bubbler blanks.

CF_m = mean calibration factor (as calculated from Section 7).

V = volume of sample added to the autosampler vial (mL).

9. QUALITY CONTROL & METHOD PERFORMANCE

9.1. The MDL should be determined as it was mentioned in section 3.1 of this document.

9.2. Chemical Analysis: The quality control (QC) samples for chemical analysis include initial calibration, second source standard checks, continuous calibration verification checks, matrix spike and matrix spike duplicates; all should meet the acceptance criterion set in the analytical methods. A complete set of appropriate guidelines can be found in Table 1.

9.2.1. Matrix spike percent recovery:

$$\%\ R = 100*(A-B)/T$$

Where:

A = Measured amount of Hg after spiking

B = Measured amount of Hg before spiking

T = True concentration of the spike. The spiking level shall be 1-5 times the background concentration or between 0.5 - 2.5 pg/mL.

9.2.2. Relative percent difference of matrix spike duplicates:

$$\%\ RPD = 200*(|D1-D2|)/(D1+D2)$$

Where:

D1 = concentration of Hg in the matrix spike sample.

D2 = concentration of Hg in the matrix spike duplicate sample.

9.3. For every batch of 10 samples there must be at least two reagent blanks, one on-going precision and recovery, one matrix spike and one matrix spike duplicate. See Table 2 for a sequence of THg MERX analysis.

9.4. There must be at least 5 reference blanks. Reference blanks are generated by sampling a HRPP that is prepared in the same way and at the same time as deployed samplers. It is brought to the field with deployed samplers but not deployed. When the samplers are retrieved the non-deployed sampler is also sampled identically to the deployed using the same needles, syringes, filters, and acid as the rest of the profilers.

9.5. Field blanks: At least five blank samples are to be collected per sampling event. Field blanks are samples of reagent grade water collected using the same type of syringes, needles, filters and vials that are being used for the rest of the samples.

Table 1. Quality Guidelines for total Hg by CVAFS as derived from EPA 1631B method.

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
MDL study	At initial set-up and subsequently once per 12-month period. Whenever a new operator begins to use the instrument.	< 0.2 pg/mL	Run MDL verification check at higher level and set MDL higher or re-conduct MDL study	NA	Samples cannot be analyzed without a valid MDL.
Minimum five-point initial calibration for all analytes (ICAL)	Initial calibration prior to sample analysis	See section 7 of this document for criteria.	Correct problem then repeat initial calibration.	NA	Problem must be corrected. No samples may be run until ICAL has passed.
Continuing calibration verification (CCV)	Prior to sample analysis, after every 10 field samples, and at the end of	Hg peak within established retention time windows. Hg result within ± 23% of	Correct problem, then rerun calibration verification. If that fails, then repeat ICAL. Reanalyze all samples since	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag	Problem must be corrected. Results may not be reported without a valid CCV. Flagging is only appropriate in cases where the samples

	the analysis sequence.	expected value from the ICAL	the last successful calibration verification.	to all results for the specific analyte(s) in all samples since the last acceptable calibration verification.	cannot be reanalyzed. Retention time windows are updated per the method.
Second source calibration verification (ICV)	Once after each initial calibration	Hg peak within established retention time windows. Hg result within ± 21% of expected value (ICAL)	Correct problem and verify second source standard. Rerun second source verification. If that fails, correct problem and repeat ICAL	NA	Problem must be corrected. No samples may be run until calibration has been verified.
Method blank	Two per batch of 10 samples.	The mean result for the three system blanks must be < 0.5 pg/mL with a standard deviation (n-1) of 0.1 pg/mL. If system blank is found to contain ≥ 0.5 pg/mL Hg, the system is out of control.	Correct problem. Then, if required, prepare and reanalyze method blank and all samples processed with the contaminated blank.	Apply B-flag to all results for the specific analyte(s) in all samples in the associated preparatory batch.	Problem must be corrected. Results may not be reported without a valid method blank. Flagging is only appropriate in cases where the samples cannot be reanalyzed.

Matrix Spike (MS) and Matrix Spike Duplicate (MSD)	One of each per every batch of 10 samples.	The recovery must be between 71 and 125 %. The relative percent difference between MS and MSD must be less or equal to 24%	If results of the MS/MSD are similar and fail the acceptance criteria, an interference is present and the results may not be reported or otherwise used for permitting or regulatory compliance purposes.	NA	Interferences must be corrected. Sample and its MS/MSD must be re-analyzed.
Results reported between MDL and MRL	NA	NA	NA	Report as < MDL	

Table 2: Sequence & QA/QC for THg MERX Analysis.

SI No	Sample ID	Description	Preparation	No of samples	QA/QC criteria (EPA 1631 Criteria)
1	Equipment Blanks	For analytical system rinse.	Ultra-pure reagent water	2-4	
2	Calibration Bubbler Blank	A sample of analyte-free media which is used to establish the low range of a calibration. Used to check for reagent contamination and used in internal calculations for background subtraction from the samples.	Ultra-pure reagent water containing BrCl, HH and $SnCl_2$	2	≤ 20 % of the lowest calibration standard (or) ≤ 0.5 pg/mL
3	Calibration standards	A solution prepared from the dilution of stock standard solutions. Used to calibrate the instrument response with respect to analyte concentration.	THg standard prepared from 1 ppm stock Brooks Rand (or other certified) standards	≥ 5 point	Linear fit $R^2 \geq 0.995$ (or) % RSD of Relative concentration factor (RCF) ≤ 15 % % RSD of individual calibration standard ≤ 15 %
4	Reagent Blank	Used to determine sample/standard carry over, and determine the contribution of reagents	Ultra-pure water containing BrCl, HH and $SnCl_2$	1	0.1% of the highest standard used (or) ≤ 0.5 pg/mL
5	ICV/VER	Initial calibration verification - used to verify that a calibration is accurate. Typically prepared from source other than the one used for calibration standard. (e.g., ICP-MS 1 ppm standard stock)	Standard in Ultra-pure water containing BrCl, HH and $SnCl_2$	1	Typical ICV used = 250 pg; 79-121% Recovery
6	Equipment Blanks	Same as above	Same as above	2	
7	Reagent Blank	Same as above	Same as above	1	Same as above
8	Unknown samples	Unknown	Prepared in BrCl, HH and $SnCl_2$	10	Values fall within the calibration range
9	Matrix Spike	One of the unknown samples that is spiked with a known amount of Hg from the stock standard. See section 9.2.1 of this document.	Unknown sample plus spike. They are prepared in BrCl, HH and $SnCl_2$	1	Recovery of spike between 71-125 %.

10	Matrix Spike Duplicate	Prepared in the same way as the matrix spike.	Same as matrix spike.	1	Relative percent difference between MS and MSD must be less or equal to 24%.
11	Reagent Blank	Same as above	Same as above	1	Same as above
12	CCV	A solution with a known concentration of Hg prepared from the dilution of stock standard solutions.	Standard in Ultra-pure water containing BrCl, HH and $SnCl_2$	1	Concentration of 5 pg/mL. 77-123% Recovery
13	Equipment Blanks	Same as above	Same as above	2	

After the first batch of 10 samples that follows the instrument calibration, the next batch starts in the point number 7.

10. REFERENCES

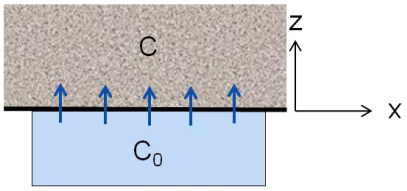
Department of Defense (DoD), Department of Energy (DOE). Consolidated Quality Systems Manual (QSM) for Environmental Laboratories Version 5.1 (2017). https://www.denix.osd.mil/edqw/documents/documents/qsm-version-5-1-final/

U.S. Environmental Protection Agency (2002): Method 1631, Revision E: Mercury in water by oxidation, purge and trap, and cold vapor atomic fluorescence spectrometry.

APPENDIX D ANALYTICAL MODEL OF A CONSERVATIVE TRACER

Section 3. Analytical Model of a Conservative Tracer equilibrating with a pore fluid incorporating the impact of pore velocity on the mass transfer coefficient.

An analytical model was used to predict how k_m should correlate to velocity using the following equation and boundary conditions for a two-dimensional quasi steady state system (see below) (Choy and Reible, 2000):



$$U\frac{dC}{dz} = D_z\frac{d^2C}{dz^2} \qquad \text{Eqn. E2-1}$$

$$C_0 - C = C_0\ ,\ z = 0 \to \infty,\ x = 0 \qquad \text{Eqn. E2-2}$$

$$D_z\frac{dC}{dz} = \frac{D_m}{\delta}(C_0 - C)\ ,\ z = 0 \to \infty,\ x > 0 \qquad \text{Eqn. E2-3}$$

which results in

$$k_m = \frac{D_m}{\delta}e^{\left(\frac{\left(\frac{D_m}{\delta}\right)^2 x}{UD_z}\right)}erfc\left(\frac{D_m}{\delta}\sqrt{\frac{x}{UD_z}}\right) \qquad \text{Eqn. E2-4}$$

where U is the velocity, D_z is the diffusivity through porous media in the z direction D_m is the membrane diffusivity, δ is the thickness of the membrane boundary layer, x is the length of the cell opening in the x direction. D_z is defined by the following equation:

$$D_z = \frac{D_w\emptyset}{\tau} + \alpha U \qquad \text{Eqn. E2-5}$$

$$\frac{\emptyset}{\tau} = \emptyset^{4/3} \qquad \text{Eqn. E2-6}$$

$$\alpha = \frac{d_p}{10} \qquad \text{Eqn. E2-7}$$

where D_w is the open water diffusivity of bromide, ϕ, τ, and α are the porosity, tortuosity, and transverse dispersivity of the porous media, and d_p is the average particle diameter.

APPENDIX E PHOTOS OF FIELD ACTIVITIES

APPENDIX E1: CANAL CREEK; ABERDEEN PROVING GROUND, MD

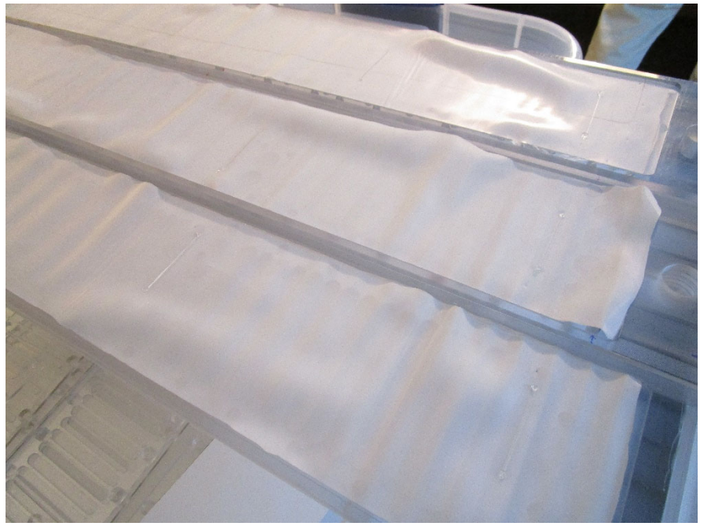


Photo 1: SPME attached to underside of membranes with silicone

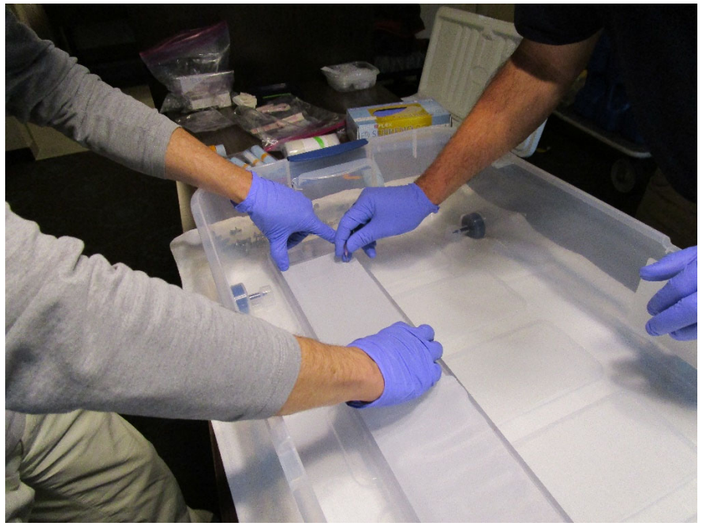


Photo 2: Membranes being installed on sHRPP in 100 ppm Br^- water

Photo 3: SPME preparation with Biosep beads installed

Photo 4: Canal Creek at Aberdeen Proving Ground (MD)

Photo 5: Prepared sHRPP ready for deployment

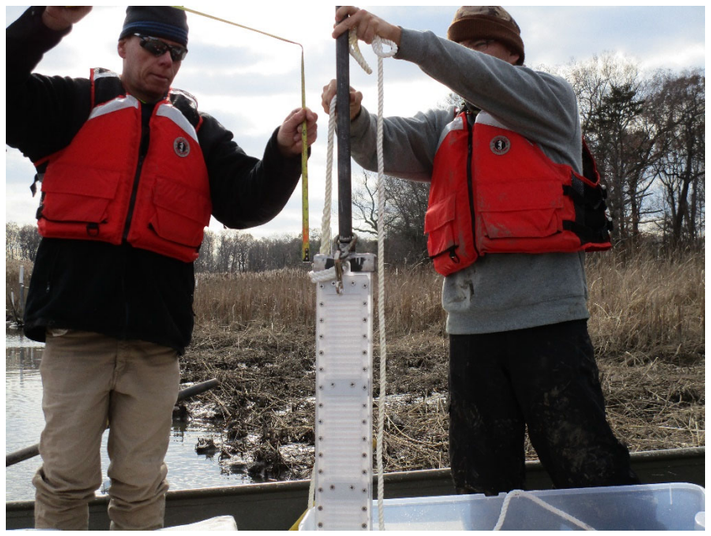


Photo 6: Setup to deploy sHRPP in creek bottom sediments

Photo 7: Deployment of sHRPP in creek bottom sediments

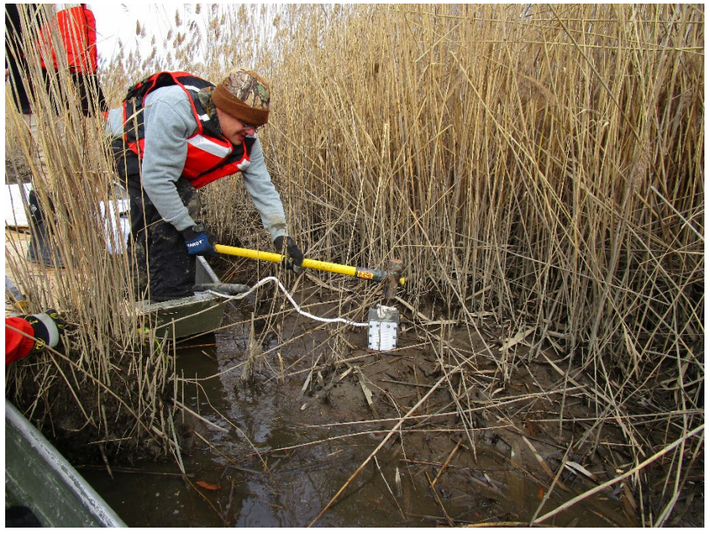


Photo 8: Deployment of sHRPP in marsh sediments

Photo 9: sHRPP deployed in marsh sediments

Photo 10: sHRPP retrieval from creek bottom sediments

Photo 11: sHRPP being transported in boat to sampling van

Photo 12: sHRPP ready for processing/sampling

Photo 13: Van outfitted with tables, sampling supplies and equipment

Photo 14: Interior of sampling van

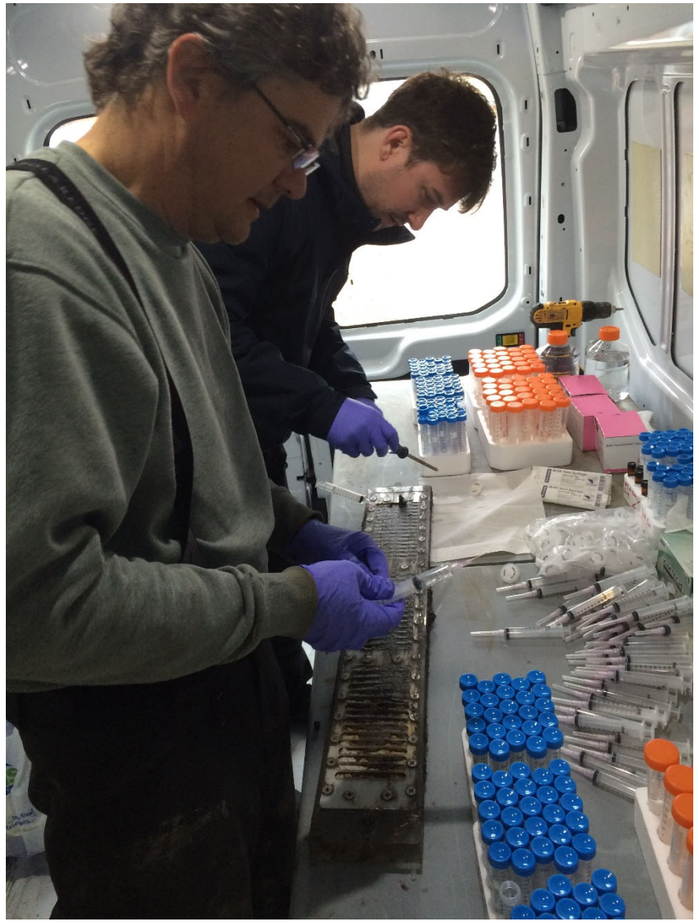


Photo 15: sHRPP processing/sampling

APPENDIX E2: ABRAHAM'S CREEK; MCB QUANTICO, VA

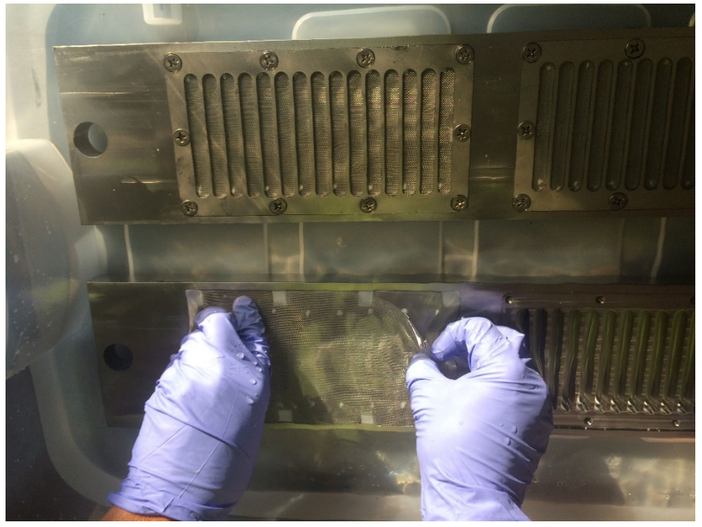


Photo 1: Installing stainless steel mesh over cells in 100 ppm Br^- water

Photo 2: Membrane cover-plates installed in 100 ppm Br^- water

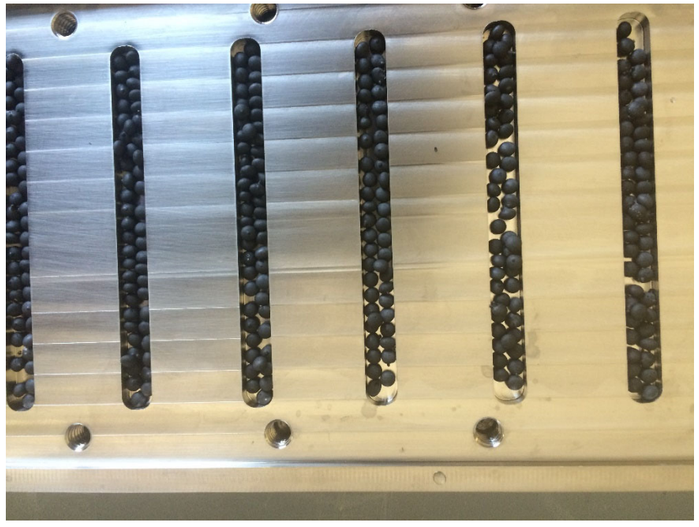


Photo 3: Biosep beads installed in sHRPP

Photo 4: Abraham's Creek at MCB-Quantico (VA)

Photo 5: Equipment and crew ready for deployment activities

Photo 6: sHRPP ready for deployment

Photo 7: sHRPP deployment tooling (marker buoy on tag end of rope)

Photo 8: Deployment of sHRPP in creek sediments

Photo 9: SPME fiber T-Bar sampler

Photo 10: Van outfitted with tables, sampling supplies and equipment

Photo 11: sHRPP processing/sampling

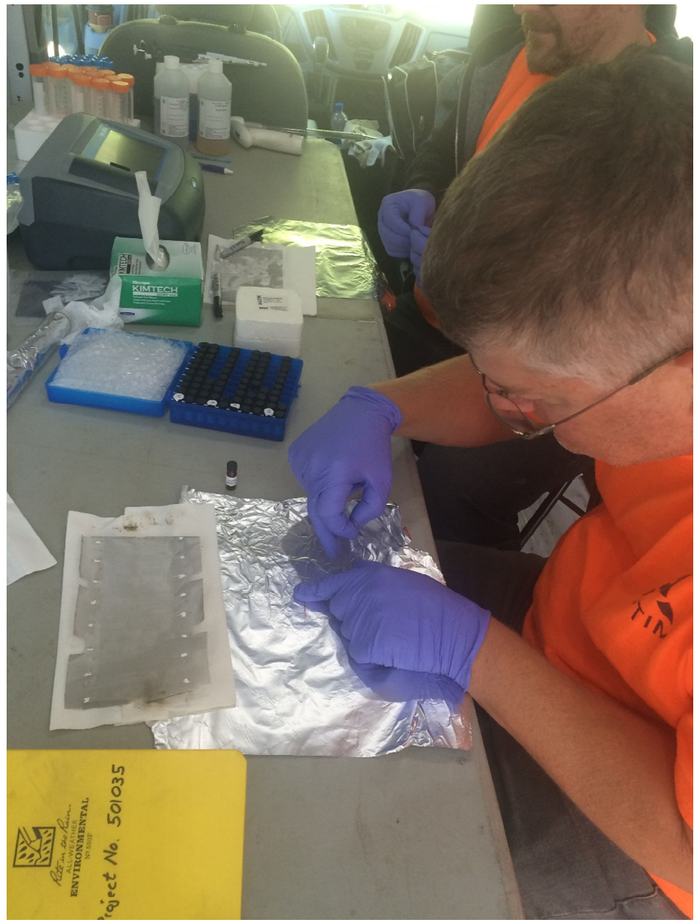


Photo 12: SPME fiber processing/sampling

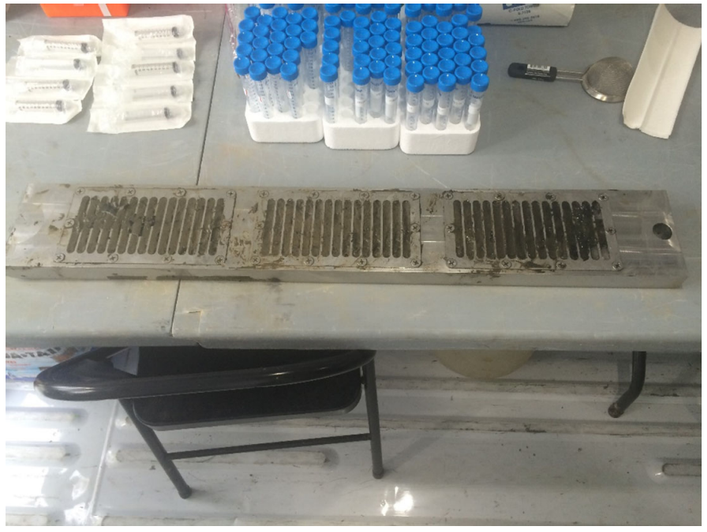


Photo 13: sHRPP ready for processing/sampling

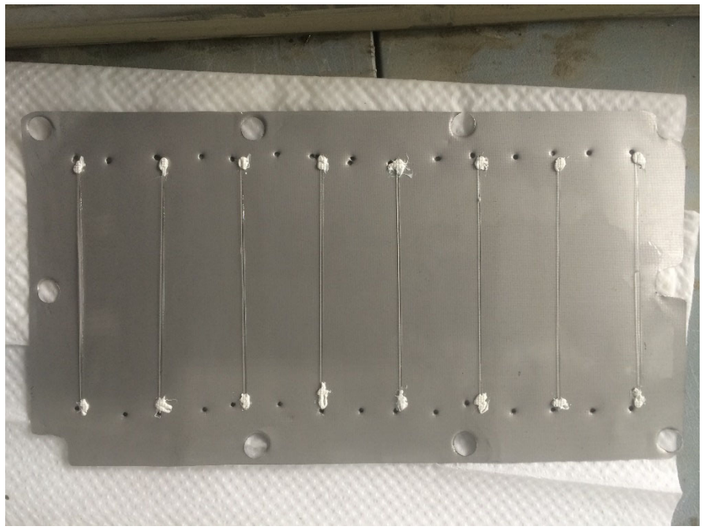


Photo 14: SPME fibers removed from sHRPP and ready for processing

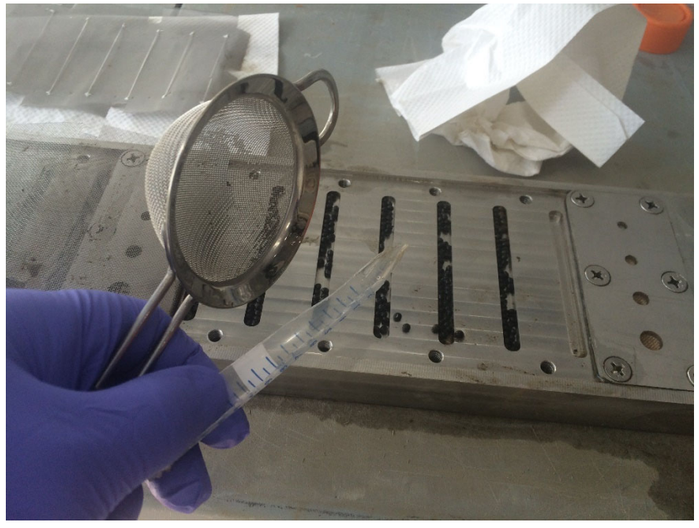


Photo 15: Biosep beads ready for processing/sampling

Photo 16: Creek sediment core collection

Photo 17: Sediment core retrieval

Photo 18: SPME T-Bar sampler ready for processing/sampling

APPENDIX E3: QUANTICO EMBAYMENT; MCB QUANTICO, VA

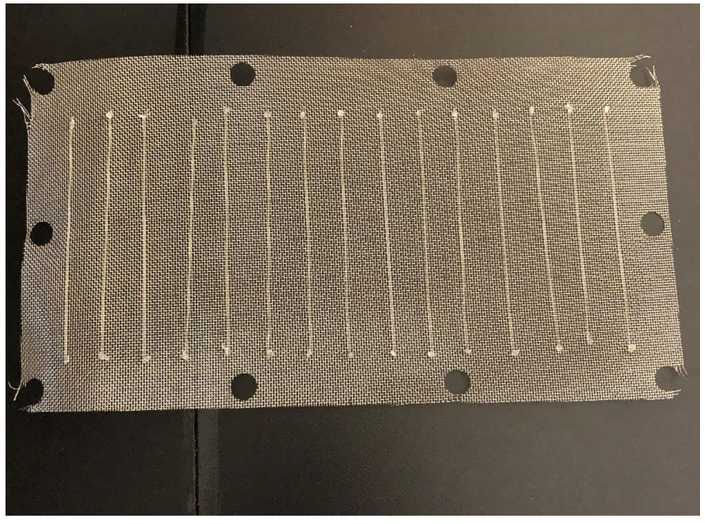


Photo 1: SPME fibers on stainless steel mesh ready for install on sHRPP

Photo 2: SPME fibers installed on sHRPP

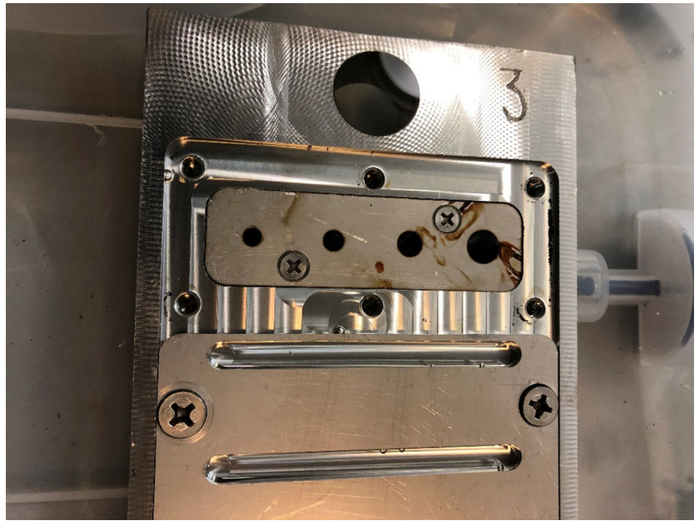


Photo 3: Velocity cells prepared in 100 ppm Br^- water

Photo 4: Quantico Embayment at MCB-Quantico (VA)

Photo 5: Wastewater treatment plant outfall entering the embayment

Photo 6: Equipment and crew ready for sHRPP deployment activities

Photo 7: sHRPP deployment into embayment sediments

Photo 8: sHRPP transect nearing low tide

Photo 9: sHRPP Location #3 and Location #4

Photo 10: sHRPP just removed from embayment sediments

Photo 11: Oxidation indicating sediment-surface water interface

Photo 12: sHRPP cell sampling

Photo 13: SPME fiber processing

Photo 14: sHRPP velocity cell sampling

Photo 15: Quantico Embayment at low tide

Photo 16: Sediment core collection

Photo 17: Intact sediment core

Photo 18: sHRPP transect at low tide (Location #2 already retrieved)

APPENDIX E4: GREAT LAKES GRAND CALUMET RIVER AOC EAST CHICAGO, IN

Photo 1: sHRPP being prepared in 100 ppm Br^- water

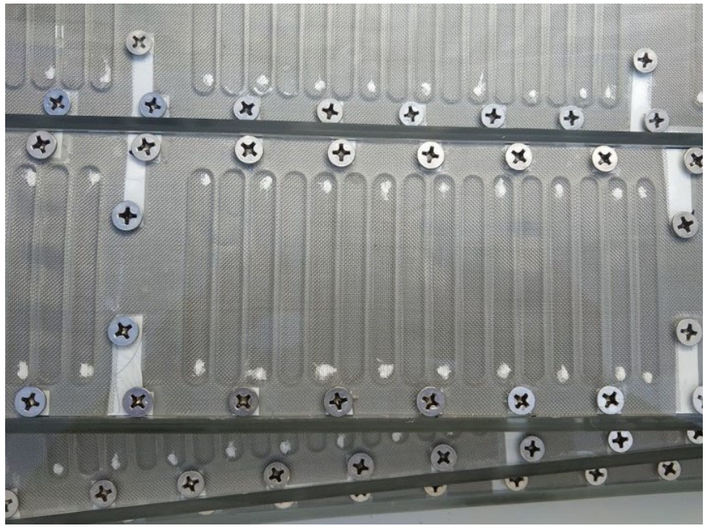


Photo 2: SPME fibers installed on sHRPP

Photo 3: Great Lakes Grand Calumet River AOC (IN)

Photo 4: Great Lakes Grand Calumet River AOC (IN)

Photo 5: Equipment and crew heading out for sHRPP deployment

Photo 6: sHRPP being readied for deployment

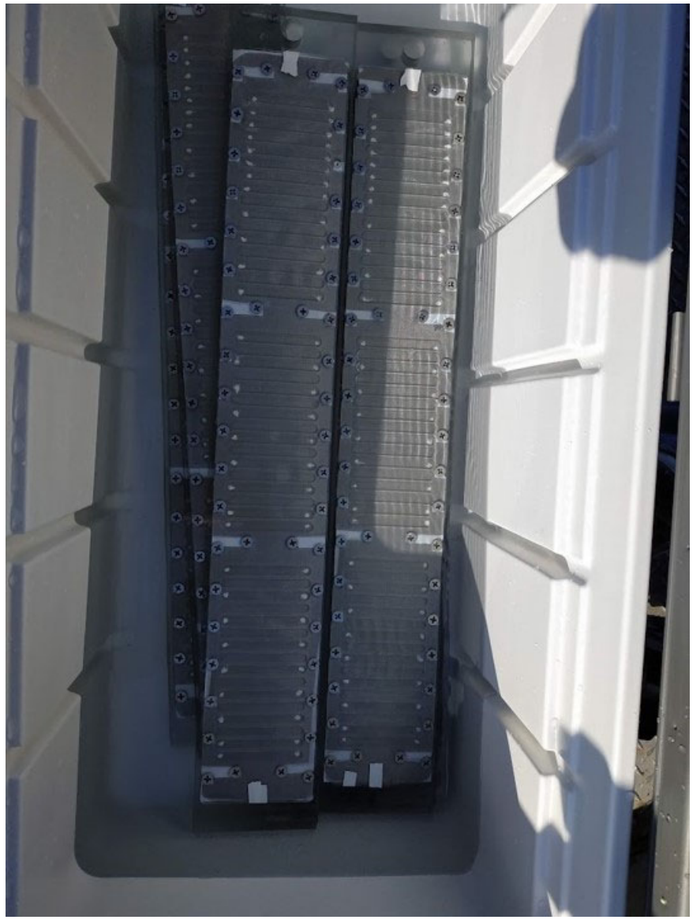


Photo 7: sHRPPs transferred to field site in 100 ppm Br^- water

Photo 8: T Bar sampler being prepared for deployment

Photo 9: sHRPP processing

Photo 10: sHRPP just removed from river sediments

Photo 11: SPME fibers ready for sampling after sHRPP retrieval

Photo 12: sHRPP and T Bar sampler ready for sampling

APPENDIX F ANALYTICAL RESULTS TABLES

APPENDIX F1. CANAL CREEK

Canal Creek Insitu Results

Sample ID	Depth (cm)	Depth Common Datum (cm)	fss	Cl- (mg/L)	NO3- (mg/L of N)	SO4-- (mg/L)	Hg (ng/L)	S-- (ug/L)	DOC (mg/L of C)	As (ug/L)	Zn (ug/L)	Pb (ug/L)	Iron (mg/L)	Depth U (cm)	U (cm/d)	U-95% (cm/d)	U+95% (cm/d)
PQL =				**0.3**	**0.25**	**1.50**	**1.14**	**25.0**	**2.0**	**0.13**	**0.26**	**0.04**	**0.18**				
p 0	0.0		1.00	41	0.38	17.50	4.95	<25		0.77	11.48	0.70	<0.18				
p 1-1	1.9	73.1	1.00	131	<0.25	4.44	1.60	40.2		11.12	16.37	1.02	9.03	-0.4	>100	13	>100
p 1-3	4.4	70.6	1.00	167	<0.25	1.57	2.42	80.4		7.96	3.40	0.17	21.10	22.9	9	1	34
p 1-5	6.9	68.1	0.99	187	<0.25	1.62	21.35	90.7		5.32	3.21	0.16	17.14	46.1	4	0	11
p 1-7	9.4	65.6	0.98	206	<0.25	<1.5	2.08	30.7	33.4	6.14	2.68	0.17	12.79	69.3	3	0	7
p 1-9	11.9	63.1	0.95	217	<0.25	1.55	2.87	42.1		6.69	3.26	0.20	16.05				
p 1-11	14.4	60.6	0.91	235	<0.25	1.53	2.61	32.9		5.84	3.62	0.17	16.45				
p 1-13	16.9	58.1	0.89	263	<0.25	1.51	2.59	<25		6.08	3.60	0.25	18.60				
p 1-15	19.4	55.6	0.88	310	<0.25	1.95	5.31	<25	28.8	6.23	6.47	0.31	15.55				
p 1-17	25.1	49.9	0.87	417	<0.25	2.20	2.66	<25		4.43	4.43	0.29	6.92				
p 1-19	27.6	47.4	0.82	447	<0.25	2.01	2.04	266.9		4.70	4.02	0.19	13.04				
p 1-21	30.1	44.9	0.81	489	<0.25	2.21	2.58	86.5		4.92	3.75	0.19	10.19				
p 1-23	32.6	42.4	0.82	507	<0.25	2.26	6.84	73.6	35.9	4.74	5.68	0.43	13.80				
p 1-25	35.1	39.9	0.82	526	<0.25	2.32	1.77	171.5		4.43	4.28	0.15	17.76				
p 1-27	37.6	37.4	0.82	547	<0.25	2.41	1.84	85.4		4.54	4.46	0.18	18.92				
p 1-29	40.1	34.9	0.82	559	<0.25	2.60	2.02	97.0		4.79	3.56	0.12	21.52				
p 1-31	42.6	32.4	0.84	559	<0.25	2.83	2.05	106.8	22.3	4.38	4.16	0.18	23.45				
p 1-33	48.3	26.7	0.86	573	<0.25	2.71	1.40	93.3		2.87	4.59	0.11	17.78				
p 1-35	50.8	24.2	0.84	557	<0.25	2.18	2.19	59.8		4.64	5.70	0.20	28.71				
p 1-37	53.3	21.7	0.83	544	<0.25	1.72	2.78	132.3		3.18	2.66	0.13	25.85				
p 1-39	55.8	19.2	0.83	538	<0.25	2.20	1.70	48.4		4.17	4.02	0.12	36.00				
p 1-41	58.3	16.7	0.83	519	<0.25	2.20	1.53	48.3	33.3	4.01	3.69	0.13	34.39				
p 1-43	60.8	14.2	0.83	506	<0.25	1.97	2.00	157.0		5.54	5.19	0.18	36.54				
p 1-45	63.3	11.7	0.84	487	<0.25	2.47	2.09	59.7		3.66	4.36	0.12	35.23				
p 1-47	65.8	9.2	0.86	483	<0.25	2.39	<1.14	93.6		3.50	4.59	0.13	30.12				

Sample ID	Depth (cm)	Depth Common Datum (cm)	fss	Cl- (mg/L)	NO3- (mg/L of N)	SO4-- (mg/L)	Hg (ng/L)	S-- (ug/L)	DOC (mg/L of C)	As (ug/L)	Zn (ug/L)	Pb (ug/L)	Iron (mg/L)	Depth U (cm)	U (cm/d)	U-95% (cm/d)	U+95% (cm/d)
p 0	0.0		1.00	41	0.38	17.50	4.95	<25		0.77	11.48	0.70	<0.18				
p 2-1	1.4	73.6	1.00	121	<0.25	8.88	1.91	<25		5.04	28.83	0.21	5.78	-0.9	>100	20	>100
p 2-3	3.9	71.1	0.99	148	<0.25	6.55	1.47	<25		5.85	20.33	0.14	20.87	22.4	56	7	>100
p 2-5	6.4	68.6	0.99	151	<0.25	11.07	1.72	<25		4.89	11.02	0.13	27.97	45.6	49	8	>100
p 2-7	8.9	66.1	0.99	159	<0.25	5.61	1.78	30.4	34.5	3.55	7.17	0.21	23.29	68.8	38	12	>100
p 2-9	11.4	63.6	0.98	162	<0.25	5.45	1.49	30.5		3.17	6.41	0.09	21.89				
p 2-11	13.9	61.1	0.98	164	<0.25	5.29	2.65	41.0		2.85	5.63	0.10	17.42				
p 2-13	16.4	58.6	0.97	178	<0.25	5.40	1.47	31.0		2.96	5.73	0.12	16.79				
p 2-15	18.9	56.1	0.95	256	<0.25	4.27	<1.14	31.5	20.3	3.28	5.22	0.17	19.96				
p 2-17	24.6	50.4	0.90	381	<0.25	2.58	1.38	33.4		3.91	6.51	0.18	28.41				
p 2-19	27.1	47.9	0.89	380	<0.25	2.76	2.08	45.2		3.73	6.43	0.12	35.29				
p 2-21	29.6	45.4	0.89	370	<0.25	2.27	4.40	44.7		4.37	6.69	0.12	38.00				
p 2-23	32.1	42.9	0.90	384	<0.25	1.76	1.74	44.4	33.8	4.61	5.23	0.40	38.86				
p 2-25	34.6	40.4	0.90	359	<0.25	1.73	6.63	44.3		4.23	4.52	0.15	36.24				
p 2-27	37.1	37.9	0.90	363	<0.25	<1.5	1.44	33.2		4.85	5.05	0.08	55.01				
p 2-29	39.6	35.4	0.90	340	<0.25	<1.5	2.43	33.3		5.11	3.61	0.11	64.32				
p 2-31	42.1	32.9	0.90	326	<0.25	<1.5	1.52	33.4	24.9	4.83	3.98	0.11	35.91				
p 2-33	47.8	27.2	0.88	279	<0.25	1.60	1.20	34.3		3.51	4.06	0.09	37.97				
p 2-35	50.3	24.7	0.88	254	<0.25	2.60	1.55	56.9		4.37	5.97	0.11	27.90				
p 2-37	52.8	22.2	0.89	230	<0.25	<1.5	1.72	<25		5.62	11.74	0.14	36.70				
p 2-39	55.3	19.7	0.89	201	<0.25	<1.5	1.74	168.7		6.10	11.27	0.14	39.64				
p 2-41	57.8	17.2	0.90	179	<0.25	<1.5	1.88	<25	31.6	6.23	11.23	0.16	42.77				
p 2-43	60.3	14.7	0.92	157	<0.25	<1.5	1.79	<25		7.34	11.55	0.14	41.83				
p 2-45	62.8	12.2	0.94	143	<0.25	<1.5	2.38	<25		4.41	5.02	0.11	35.20				
p 2-47	65.3	9.7	0.96	123	<0.25	<1.5	1.63	31.2		2.96	10.40	0.17	23.64				

Sample ID	Depth (cm)	Depth Common Datum (cm)	fss	Cl- (mg/L)	NO3- (mg/L of N)	SO4-- (mg/L)	Hg (ng/L)	S-- (ug/L)	DOC (mg/L of C)	As (ug/L)	Zn (ug/L)	Pb (ug/L)	Iron (mg/L)	Depth U (cm)	U (cm/d)	U-95% (cm/d)	U+95% (cm/d)
p 0	0.0		1.00	41	0.38	17.50	4.95	<25		0.77	11.48	0.70	<0.18				
p 3-1	-0.1	115.1	0.99	43	0.51	39.85	2.28	<25		0.46	85.77	0.18	<0.18	-2.4	65	16	>100
p 3-3	2.4	112.6	0.92	56	<0.25	39.76	1.37	<25		0.32	109.79	0.06	<0.18	20.9	12	0	>100
p 3-5	4.9	110.1	0.87	75	<0.25	22.38	2.27	<25		1.51	22.62	0.15	2.59	44.1	14	0	>100
p 3-7	7.4	107.6	0.83	107	<0.25	2.89	6.45	<25	35.1	5.11	8.27	0.19	25.75	67.3	5	0	16
p 3-9	9.9	105.1	0.76	146	<0.25	2.64	2.66	26.4		2.10	19.29	0.32	4.96				
p 3-11	12.4	102.6	0.75	187	<0.25	2.31	2.60	<25		3.41	12.24	0.19	18.00				
p 3-13	14.9	100.1	0.80	201	<0.25	1.55	3.52	<25		4.82	6.75	0.13	28.26				
p 3-15	17.4	97.6	0.85	227	<0.25	<1.5	1.20	<25	29.0	6.07	7.17	0.12	28.07				
p 3-17	23.1	91.9	0.86	344	<0.25	<1.5	2.30	<25		6.50	6.18	0.66	37.52				
p 3-19	25.6	89.4	0.82	427	<0.25	1.93	5.03	<25		4.26	6.23	0.14	22.92				
p 3-21	28.1	86.9	0.80	495	<0.25	3.14	9.46	<25		3.61	7.67	0.30	19.31				
p 3-23	30.6	84.4	0.79	570	<0.25	3.80	3.01	25.2	35.2	3.37	10.29	0.16	19.85				
p 3-25	33.1	81.9	0.80	608	<0.25	5.16	5.23	<25		3.16	14.65	0.23	14.94				
p 3-27	35.6	79.4	0.82	669	<0.25	2.67	2.06	<25		4.35	11.69	0.37	38.57				
p 3-29	38.1	76.9	0.82	684	<0.25	3.18	1.29	73.3		4.15	13.51	0.11	24.75				
p 3-31	40.6	74.4	0.84	735	<0.25	1.69	1.58	<25	26.4	8.84	5.94	0.19	31.73				
p 3-33	46.3	68.7	0.89	750	<0.25	2.01	1.21	<25		3.12	6.79	0.13	17.44				
p 3-35	48.8	66.2	0.87	758	<0.25	2.38	<1.14	<25		3.68	6.00	0.08	20.14				
p 3-37	51.3	63.7	0.86	783	<0.25	1.71	1.22	<25		3.68	6.17	0.10	24.12				
p 3-39	53.8	61.2	0.86	783	<0.25	2.07	<1.14	<25		3.38	7.90	0.09	17.54				
p 3-41	56.3	58.7	0.86	805	<0.25	2.23	1.67	<25	34.0	4.19	5.28	0.09	29.23				
p 3-43	58.8	56.2	0.86	799	<0.25	<1.5	1.46	<25		5.95	5.63	0.09	35.71				
p 3-45	61.3	53.7	0.87	816	<0.25	<1.5	1.68	46.0		6.00	6.28	0.09	37.67				
p 3-47	63.8	51.2	0.88	827	<0.25	<1.5	2.76	<25		6.09	6.82	0.14	45.78				

Sample ID	Depth (cm)	Depth Common Datum (cm)	fss	Cl- (mg/L)	NO3- (mg/L of N)	SO4-- (mg/L)	Hg (ng/L)	S-- (ug/L)	DOC (mg/L of C)	As (ug/L)	Zn (ug/L)	Pb (ug/L)	Iron (mg/L)	Depth U (cm)	U (cm/d)	U-95% (cm/d)	U+95% (cm/d)
p 0	0.0		1.00	41	0.38	17.50	4.95	<25		0.77	11.48	0.70	<0.18				
p 4-1	-18.0	18.0	1.00	45	0.41	16.06	3.48	<25		0.77	11.59	0.19	0.25	-20.2	>100	80	>100
p 4-3	-15.5	15.5	1.00	44	0.38	16.23	2.95	<25		0.81	10.90	0.25	<0.18	3.0	12	6	23
p 4-5	-13.0	13.0	1.00	46	0.39	16.30	3.99	<25		0.84	13.73	0.25	<0.18	26.2	1	0	3
p 4-7	-10.5	10.5	1.00	45	0.40	16.54	3.43	70.1	23.3	0.83	11.31	0.26	0.75	49.5	1	0	3
p 4-9	-8.0	8.0	1.00	44	0.40	16.23	4.59	60.1		0.88	11.62	0.26	0.75				
p 4-11	-5.5	5.5	1.00	44	0.41	16.41	3.12	<25		0.99	11.75	0.31	<0.18				
p 4-13	-3.0	3.0	1.00	45	0.41	16.56	3.41	<25		1.12	12.67	0.34	0.50				
p 4-15	-0.5	0.5	1.00	45	0.40	16.75	2.93	<25	17.1	1.43	13.05	0.19	0.50				

p 4-17	5.2	-5.2	0.99	53	<0.25		4.53	3.20	<25			4.78	9.97	0.22	8.38
p 4-19	7.7	-7.7	0.99	50	<0.25		6.93	2.80		81.0		5.65	4.25	0.15	8.86
p 4-21	10.2	-10.2	0.98	53	<0.25		6.93	2.58		50.9		5.30	3.24	0.08	8.66
p 4-23	12.7	-12.7	0.95	64	<0.25		3.78	2.52		52.5	42.8	5.51	3.78	0.11	18.65
p 4-25	15.2	-15.2	0.91	86	<0.25		1.85	2.54		55.2		5.66	3.64	0.09	21.25
p 4-27	17.7	-17.7	0.87	107	<0.25	<1.5		3.52		57.2		8.91	3.34	0.08	37.77
p 4-29	20.2	-20.2	0.85	128	<0.25	<1.5		3.03		47.0		5.06	2.62	0.09	30.25
p 4-31	22.7	-22.7	0.86	142	<0.25		1.63	2.49		46.8	19.7	3.73	5.65	0.15	15.78
p 4-33	28.5	-28.5	0.86	163	<0.25	<1.5		1.85		46.6		2.39	4.98	0.14	5.83
p 4-35	31.0	-31.0	0.84	165	<0.25		1.61	1.72		47.6		2.26	5.65	0.12	6.25
p 4-37	33.5	-33.5	0.83	167	<0.25		1.93	2.50	<25			2.00	7.62	0.12	6.91
p 4-39	36.0	-36.0	0.83	162	<0.25		2.24	1.91	<25			1.89	5.22	0.10	11.75
p 4-41	38.5	-38.5	0.84	157	<0.25		2.31	2.59	<25		27.0	2.64	6.18	0.10	17.95
p 4-43	41.0	-41.0	0.84	150	<0.25		2.30	3.28	<25			2.18	5.56	0.15	13.91
p 4-45	43.5	-43.5	0.85	147	<0.25		2.16	2.41	<25			2.60	4.57	0.11	17.93
p 4-47	46.0	-46.0	0.87	141	<0.25		2.02	1.99	<25			1.55	8.41	0.07	8.90

Sample ID	Depth (cm)	Depth Common Datum (cm)	fss	Cl- (mg/L)	NO3- (mg/L of N)	SO4-- (mg/L)	Hg (ng/L)	S-- (ug/L)		DOC (mg/L of C)	As (ug/L)	Zn (ug/L)	Pb (ug/L)	Iron (mg/L)
p 0	0.0		1.00	41	0.38	17.50	4.95	<25			0.77	11.48	0.70	<0.18
p 6-1	-0.1	72.9	1.00	48	0.28	39.88	2.94	<25			0.81	31.90	0.23	0.50
p 6-3	2.4	70.4	1.00	58	0.28	45.54	2.22	<25			0.75	49.48	0.09	0.50
p 6-5	4.9	67.9	1.00	59	<0.25	51.22	2.27	<25			0.70	45.20	0.08	0.25
p 6-7	7.4	65.4	1.00	64	<0.25	69.73	2.82	<25		21.3	0.78	44.34	0.07	<0.18
p 6-9	9.9	62.9	1.00	75	<0.25	92.79	2.38	<25			1.04	33.65	0.06	0.25
p 6-11	12.4	60.4	1.00	81	<0.25	104.35	2.79		110.5		2.95	10.18	0.05	3.01
p 6-13	14.9	57.9	0.99	83	<0.25	103.65	4.24		100.5		2.24	4.46	0.07	5.03
p 6-15	17.4	55.4	0.98	91	<0.25	71.21	6.93		325.2	21.1	2.44	3.00	0.05	2.03
p 6-17	23.1	49.7	0.89	133	<0.25	3.41	4.28		56.3		6.32	1.65	0.06	22.80
p 6-19	25.6	47.2	0.86	153	<0.25	3.54	4.39	<25			5.17	2.96	0.06	33.48
p 6-21	28.1	44.7	0.85	173	<0.25	3.00	4.86		141.8		4.83	3.64	0.13	36.05
p 6-23	30.6	42.2	0.84	200	<0.25	2.85	5.41		35.6	216.8	4.72	8.01	0.11	23.74
p 6-25	33.1	39.7	0.83	219	<0.25	2.57	7.33		84.4		4.32	2.20	0.08	42.19
p 6-27	35.6	37.2	0.82	248	<0.25	1.66	9.01		196.1		4.33	2.08	0.21	31.86
p 6-29	38.1	34.7	0.81	276	<0.25	1.86	8.60		222.0		4.34	1.96	0.07	25.60
p 6-31	40.6	32.2	0.83	279	<0.25	1.66	7.04		84.0	212.6	3.21	1.93	0.07	23.40
p 6-33	46.3	26.4	0.85	287	<0.25	2.11	4.23		93.8		1.27	1.86	0.09	6.16
p 6-35	48.8	23.9	0.83	279	<0.25	1.83	5.38		36.2		1.90	2.86	0.12	9.94
p 6-37	51.3	21.4	0.81	255	<0.25	1.65	5.60		61.4		2.02	2.01	0.09	15.65
p 6-39	53.8	18.9	0.81	250	<0.25	1.64	10.00	<25			1.98	2.02	0.12	13.97
p 6-41	56.3	16.4	0.81	232	<0.25	1.75	5.35		74.5	62.7	1.99	2.97	0.14	13.66
p 6-43	58.8	13.9	0.81	222	<0.25	<1.5	19.77		62.0		2.56	3.47	0.18	14.88
p 6-45	61.3	11.4	0.82	207	<0.25	1.54	10.79		85.5		2.21	2.61	0.17	16.18
p 6-47	63.8	8.9	0.85	193	<0.25	1.79	8.41		82.4		1.65	2.75	0.20	11.18

Depth U (cm)	U (cm/d)	U-95% (cm/d)	U+95% (cm/d)
-2.4	78	17	>100
20.9	5	2	9
44.1	2	0	7
67.3	2	0	6

Sample ID	Depth (cm)	Depth Common Datum (cm)	fss	Cl- (mg/L)	NO3- (mg/L of N)	SO4-- (mg/L)	Hg (ng/L)	S-- (ug/L)		DOC (mg/L of C)	As (ug/L)	Zn (ug/L)	Pb (ug/L)	Iron (mg/L)
p 0	0.0		1.00	41	0.38	17.50	4.95	<25			0.77	11.48	0.70	<0.18
p 7-1	6.9	60.6	0.99	54	0.26	36.53	2.36	<25			0.58	114.51	0.11	<0.18
p 7-3	9.4	58.1	0.97	57	<0.25	43.92	2.73	<25			0.59	237.61	0.13	<0.18
p 7-5	11.9	55.6	0.90	68	<0.25	55.49	4.89	<25			0.52	185.39	0.09	0.28
p 7-7	14.4	53.1	0.88	73	<0.25	30.39	18.04	<25		24.0	3.29	18.40	1.62	<0.18
p 7-9	16.9	50.6	0.84	81	<0.25	14.22	2.80	<25			4.37	8.19	0.13	6.23
p 7-11	19.4	48.1	0.83	84	<0.25	7.61	3.03	<25			5.12	7.72	0.26	6.05
p 7-13	21.9	45.6	0.84	87	<0.25	10.10	3.33	<25			3.75	10.31	0.21	9.58
p 7-15	24.4	43.1	0.88	87	<0.25	12.66	2.93	<25		15.1	2.82	9.44	0.15	2.26
p 7-17	30.1	37.4	0.90	127	<0.25	<1.5	2.46	<25			16.56	7.01	0.45	19.92
p 7-19	32.6	34.9	0.89	159	<0.25	1.55	4.17	<25			8.68	5.37	0.34	21.75
p 7-21	35.1	32.4	0.89	227	<0.25	<1.5	19.37	<25			11.69	4.09	0.17	10.98
p 7-23	37.6	29.9	0.88	205	<0.25	<1.5	4.09	<25		44.2	15.53	5.95	0.98	7.63
p 7-25	40.1	27.4	0.89	215	<0.25	<1.5	8.06	<25			15.70	4.67	0.41	10.45
p 7-27	42.6	24.9	0.89	238	<0.25	<1.5	12.86	<25			9.02	5.21	0.72	16.10
p 7-29	45.1	22.4	0.88	268	<0.25	<1.5	3.26	<25			9.41	2.73	0.12	11.38
p 7-31	47.6	19.9	0.88	295	<0.25	<1.5	2.51		68.2	46.5	12.44	4.52	0.17	13.35
p 7-33	53.3	14.2	0.88	299	<0.25	<1.5	2.92		113.9		3.22	6.39	0.32	2.28
p 7-35	55.8	11.7	0.85	281	<0.25	<1.5	2.03		82.2		4.68	5.79	0.17	2.94
p 7-37	58.3	9.2	0.84	263	<0.25	<1.5	2.65		47.5		3.92	5.86	0.18	4.16
p 7-39	60.8	6.7	0.84	229	<0.25	<1.5	2.45		142.7		4.32	6.14	0.84	3.57
p 7-41	63.3	4.2	0.87	182	<0.25	<1.5	1.88		161.4	29.8	3.36	4.72	0.13	2.59
p 7-43	65.8	1.7	0.90	157	<0.25	3.96	1.92		88.5		3.43	6.28	0.13	2.49
p 7-45	68.3	-0.8	0.94	148	<0.25	4.41	53.28		84.9		2.51	4.65	0.16	2.39
p 7-47	70.8	-3.3	0.93	160	<0.25	1.95	1.72		74.9		1.90	5.61	0.13	1.34

Depth U (cm)	U (cm/d)	U-95% (cm/d)	U+95% (cm/d)
4.6	18	3	67
27.9	38	1	>100
51.1	6	1	18
74.3	2	0	5

Canal Creek Exsitu

Sample ID	Depth (cm)	Cl- (mg/L)	Br- (mg/L)	SO4-- (mg/L)	Hg (ng/L) DGT	Hg (mg/kg)	As (mg/kg)	Cr (mg/kg)	Zn (mg/kg)	Pb (mg/kg)	TOC (mg of C/mg)
PQL =		**0.3**	**1.0**	**1.5**	**2.0**	**0.009**	**0.08**	**0.08**	**0.1**	**0.08**	
c 1-12	3	189	1.4	789	<2	2.07	16	45	9671	132	0.11
c 1-11	8	197	<1	730	4.3	2.64	21	50	2922	176	0.12
c 1-10	14	205	<1	725	4.0	3.25	22	55	4857	208	0.11
c 1-9	19	212	<1	641	6.6	2.62	28	49	4208	185	0.12
c 1-8	25	254	<1	522	41.5	2.93	20	39	3794	144	0.12
c 1-7	30	310	1.0	634	6.5	2.26	15	28	1896	67	0.08
c 1-6	36	385	1.4	798	3.1	0.08	16	32	2496	32	0.10
c 1-5	41	449	1.6	539	<2	0.11	8	32	4548	30	0.09
c 1-4	47	541	1.9	296	<2	0.07	6	32	4212	24	0.08
c 1-3	52	584	2.1	133	2.1	0.06	5	31	3568	20	0.09
c 1-2	58	596	1.6	90	<2	0.06	5	31	2889	19	0.10
c 1-1	63	475	1.6	223	<2	0.05	5	26	2626	14	0.08
Sample ID	Depth (cm)	Cl- (mg/L)	Br- (mg/L)	SO4-- (mg/L)	Hg (ng/L) DGT	Hg (mg/kg)	As (mg/kg)	Cr (mg/kg)	Zn (mg/kg)	Pb (mg/kg)	TOC (mg of C/mg)
c 2-10	3	298	1.6	592	15.9	4.44	29	50	3599	256	0.08
c 2-9	10	301	1.6	570	7.9	4.54	31	54	4957	273	0.08
c 2-8	16	311	1.8	542	13.5	3.73	31	52	3772	250	0.09
c 2-7	23	303	2.1	362	12.8	3.17	29	56	3890	249	0.09
c 2-6	29	286	2.0	296	11.3	3.68	26	53	3688	220	0.08
c 2-5	36	264	1.8	251	6.3	2.89	23	49	4023	195	0.08
c 2-4	42	249	1.7	204	2.7	2.77	26	50	4061	195	0.10
c 2-3	49	250	1.9	99	5.6	3.09	25	47	3855	178	0.09
c 2-2	55	290	2.4	152	10.8	3.09	25	52	3615	194	0.09
c 2-1	62	245	2.4	114	3.6	3.06	24	54	3516	193	0.09
Sample ID	Depth (cm)	Cl- (mg/L)	Br- (mg/L)	SO4-- (mg/L)	Hg (ng/L) DGT	Hg (mg/kg)	As (mg/kg)	Cr (mg/kg)	Zn (mg/kg)	Pb (mg/kg)	TOC (mg of C/mg)
c 3-12	3	218	<1	34	24.7	3.47	22	48	3195	233	0.08
c 3-11	8	170	<1	44	20.4	2.75	17	40	4964	163	0.08
c 3-10	14	199	<1	28	24.7	2.99	25	44	3488	188	0.08
c 3-9	19	250	<1	67	17.0	3.94	23	46	2872	227	0.07
c 3-8	24	291	1.1	147	20.8	3.40	25	50	5601	220	0.06
c 3-7	30	303	1.0	353	14.6	3.56	27	52	3992	236	0.07
c 3-6	35	322	1.1	506	18.9	4.04	27	53	2512	240	0.06
c 3-5	41	414	<1	1190	80.0	4.31	36	56	2093	300	0.06
c 3-4	46	394	1.2	1066	13.8	4.65	33	58	3052	369	0.06
c 3-3	51	424	<1	1329	6.5	4.64	33	57	2423	311	0.07
c 3-2	57	465	1.1	1669	37.2	3.94	36	62	3113	317	0.07
c 3-1	62	432	<1	1372	79.7	5.26	30	62	3497	341	0.06
Sample ID	Depth (cm)	Cl- (mg/L)	Br- (mg/L)	SO4-- (mg/L)	Hg (ng/L) DGT	Hg (mg/kg)	As (mg/kg)	Cr (mg/kg)	Zn (mg/kg)	Pb (mg/kg)	TOC (mg of C/mg)
c 6-1	3	136	<1	19	171.4	2.52	23	49	5346	183	0.10
c 6-2	8	113	<1	11	161.1	2.13	20	49	4793	174	0.12
c 6-3	14	117	<1	13	122.6	2.59	22	48	2835	183	0.12
c 6-4	19	132	<1	36	86.6	2.51	27	50	4742	210	0.08
c 6-5	24	130	<1	52	32.7	2.90	32	48	4520	209	0.10
c 6-6	30	108	<1	51	9.2	2.53	29	48	2402	202	0.08
c 6-7	35	125	<1	37	12.4	1.55	20	48	1452	141	0.07
c 6-8	41	187	<1	19	9.1	0.45	12	76	1943	68	0.07
c 6-9	46	222	<1	24	4.3	0.22	7	38	3495	76	0.07
c 6-10	51	277	<1	60	3.8	0.06	5	31	2228	19	0.07
c 6-11	57	289	<1	40	2.0	0.29	5	29	2697	20	0.08
c 6-12	62	244	<1	322	2.0	0.09	5	28	2686	20	0.07
Sample ID	Depth (cm)	Cl- (mg/L)	Br- (mg/L)	SO4-- (mg/L)	Hg (ng/L) DGT	Hg (mg/kg)	As (mg/kg)	Cr (mg/kg)	Zn (mg/kg)	Pb (mg/kg)	TOC (mg of C/mg)
c 7-1	3	46	<1	3	163.7	2.25	20	52	5000	175	0.11
c 7-2	8	66	<1	4	147.7	2.28	18	51	7340	182	0.09
c 7-3	14	93	<1	4	176.9	2.25	22	57	4543	212	0.08
c 7-4	19	103	<1	3	112.6	2.62	24	54	3808	216	0.10
c 7-5	24	113	<1	5	43.3	2.55	43	54	5836	220	0.07
c 7-6	30	128	<1	<1.5	76.8	2.88	21	54	7184	216	0.07
c 7-7	35	142	<1	<1.5	118.7	2.00	15	41	3588	154	0.07
c 7-8	41	189	<1	<1.5	25.3	0.99	5	30	1076	127	0.03
c 7-9	46	243	<1	<1.5	55.5	0.89	3	23	1311	63	0.04
c 7-10	51	241	<1	<1.5	7.5	2.98	17	47	5753	514	0.07
c 7-11	57	270	<1	49	11.5	3.18	20	35	3431	334	0.03
c 7-12	62	299	<1	177	24.8	2.23	13	29	3255	193	0.03

APPENDIX F2. ABRAHAM'S CREEK

Abraham's Creek PCBs sHRPP

Cw of PCBs (pg/L) (use of average fss)

Sample ID	Depth (cm)	8	5	18	16	32	28	52	44	66	101	110	118	153	132	105	164	138	126	187	183	128+167	174	193	169	170	195	206	209
PQL =		**19.2**	**23.91**	**13.27**	**15.80**	**8.58**	**5.20**	**3.59**	**4.36**	**4.09**	**1.10**	**0.89**	**0.50**	**0.34**	**0.71**	**0.61**	**0.73**	**0.41**	**2.22**	**0.20**	**0.18**	**0.28**	**0.22**	**0.13**	**0.12**	**0.16**	**0.08**	**0.03**	**0.05**
Control - North																													
1	2	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	5.9	<4.36	<4.09	2.5	4.2	3.7	5.7	2.4	1.8	3.2	2.2	<2.22	1.6	0.5	0.8	1.4	0.2	<0.12	0.7	0.2	<0.03	<0.05
5	8	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	5.4	<4.36	<4.09	2.1	4.7	2.3	5.2	2.1	1.5	2.9	2.6	<2.22	1.4	0.4	0.7	1.0	0.2	<0.12	0.5	0.1	<0.03	<0.05
7	10	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	7.2	<4.36	<4.09	2.5	5.0	2.2	4.2	1.9	1.7	2.5	2.0	<2.22	1.2	0.4	0.7	1.0	0.2	<0.12	0.4	0.1	<0.03	<0.05
9	13	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	8.2	4.9	<4.09	2.7	5.6	2.3	5.4	2.4	1.9	3.6	3.3	<2.22	1.4	0.5	0.8	1.3	0.2	<0.12	0.5	0.2	<0.03	<0.05
11	15	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	6.5	<4.36	<4.09	2.7	5.7	3.4	6.0	2.2	1.9	3.2	3.1	<2.22	1.4	0.6	0.9	1.3	0.2	<0.12	0.6	0.2	<0.03	<0.05
13	18	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	7.2	<4.36	<4.09	3.3	7.2	3.6	8.1	3.8	2.3	4.9	4.9	<2.22	2.1	0.8	1.1	1.8	0.2	<0.12	0.8	0.1	0.0	<0.05
15	20	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	6.6	<4.36	<4.09	3.4	9.2	2.6	11.7	4.9	2.4	8.8	5.8	<2.22	2.9	1.2	1.4	2.7	0.3	<0.12	1.1	0.2	0.0	<0.05
16	27	<19.2	<23.91	14.3	<15.80	<8.58	<5.20	8.3	<4.36	<4.09	2.7	7.0	9.6	9.1	3.6	1.9	4.5	5.3	<2.22	2.4	0.9	1.0	2.3	0.3	<0.12	1.0	0.2	0.0	<0.05
18	29	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	9.1	<4.36	<4.09	3.0	14.4	12.0	20.5	9.4	2.1	11.2	12.0	<2.22	4.9	2.2	1.5	4.9	0.4	<0.12	2.2	0.3	0.1	<0.05
20	32	<19.2	<23.91	14.8	<15.80	<8.58	<5.20	10.4	4.7	<4.09	2.5	5.7	2.5	6.3	2.9	1.8	2.7	2.9	<2.22	1.9	0.6	1.0	1.5	0.2	<0.12	0.8	0.2	<0.03	<0.05
22	35	<19.2	<23.91	13.3	<15.80	<8.58	<5.20	11.5	4.7	<4.09	3.5	10.9	6.2	16.2	7.0	2.5	8.9	7.2	<2.22	4.7	1.7	1.8	4.0	0.3	<0.12	1.7	0.3	0.1	<0.05
24	37	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	7.8	<4.36	<4.09	2.9	7.8	3.1	12.3	4.9	2.0	6.1	5.9	<2.22	3.1	1.3	1.2	3.0	0.3	<0.12	1.4	0.2	0.0	<0.05
30	45	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	8.7	<4.36	<4.09	3.2	12.3	10.0	20.0	8.6	2.3	10.0	10.6	<2.22	5.6	2.1	1.9	5.0	0.4	<0.12	1.9	0.3	0.1	<0.05
31	51	23.7	29.5	19.9	<15.80	<8.58	5.9	20.8	7.9	5.8	4.4	24.2	5.6	39.4	17.4	3.1	19.4	22.2	<2.22	8.9	4.3	2.4	9.2	0.7	0.3	4.5	0.6	0.1	<0.05
33	54	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	12.1	5.0	<4.09	3.2	16.1	4.6	24.8	11.3	2.3	11.2	13.7	<2.22	5.8	2.6	1.9	6.4	0.5	<0.12	2.6	0.4	0.0	<0.05
35	56	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	19.7	5.2	5.2	3.2	25.5	5.7	35.0	17.0	2.3	17.6	22.2	<2.22	7.2	3.4	2.1	7.6	0.6	<0.12	3.8	0.5	0.1	<0.05
37	59	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	13.5	<4.36	5.4	4.3	17.6	2.5	29.1	15.4	3.0	14.8	19.5	<2.22	7.0	3.0	1.8	6.9	0.9	<0.12	3.1	0.7	0.1	0.1
39	62	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	18.6	5.6	5.2	3.8	28.5	9.6	44.8	20.5	2.7	18.7	20.9	<2.22	9.6	4.6	2.5	9.9	0.7	<0.12	4.4	0.5	0.1	<0.05
41	64	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	11.8	<4.36	<4.09	3.2	17.6	7.7	29.8	12.8	2.2	13.3	14.4	<2.22	6.8	3.2	2.0	7.0	0.5	<0.12	3.3	0.4	0.1	<0.05
43	67	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	10.4	<4.36	<4.09	3.0	14.4	4.0	23.0	9.8	2.1	12.7	11.4	<2.22	5.7	2.5	2.0	5.8	0.5	<0.12	3.1	0.3	0.0	<0.05
45	69	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	16.0	5.4	<4.09	3.1	17.9	3.7	22.0	9.8	2.2	10.0	11.8	<2.22	4.6	1.8	1.5	4.3	0.4	<0.12	1.5	0.3	0.1	<0.05
Sample ID	Depth (cm)	8	5	18	16	32	28	52	44	66	101	110	118	153	132	105	164	138	126	187	183	128+167	174	193	169	170	195	206	209
Control - Center																													
1	1	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	8.0	<4.36	<4.09	3.9	4.0	4.6	7.2	2.1	1.5	3.4	2.7	<2.22	0.7	0.8	0.7	1.7	0.3	<0.12	0.8	0.2	0.0	<0.05
3	4	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	7.9	<4.36	<4.09	3.1	3.6	2.9	5.1	2.1	2.0	2.9	2.9	<2.22	0.8	0.6	0.6	1.5	0.2	<0.12	0.7	0.2	0.0	<0.05
5	7	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	6.1	<4.36	<4.09	2.8	3.2	2.3	2.5	1.4	1.4	1.7	1.3	<2.22	0.2	0.2	0.4	0.6	0.2	<0.12	0.3	0.1	<0.03	<0.05
7	9	<19.2	<23.91	<13.27	<15.80	<8.58	6.1	7.2	<4.36	<4.09	3.1	3.8	3.4	3.1	1.4	1.6	1.5	2.6	<2.22	0.8	0.3	0.5	0.9	0.2	<0.12	0.4	0.1	<0.03	<0.05
9	12	<19.2	<23.91	17.3	<15.80	<8.58	<5.20	9.4	4.5	<4.09	4.7	6.5	3.5	6.1	2.6	1.9	3.4	2.8	<2.22	0.5	0.4	0.8	1.4	0.2	<0.12	0.7	0.2	<0.03	<0.05
11	14	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	7.1	<4.36	<4.09	4.5	6.1	3.4	7.1	2.9	1.7	3.5	3.1	<2.22	0.3	0.7	0.6	1.5	0.3	<0.12	0.7	0.2	0.0	<0.05
13	17	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	5.9	<4.36	<4.09	3.0	4.3	2.0	5.1	1.8	1.4	2.7	2.9	<2.22	1.0	0.5	0.5	1.3	0.2	<0.12	0.7	0.1	0.0	<0.05
15	19	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	6.0	<4.36	<4.09	3.6	4.0	2.7	6.3	2.3	1.8	3.4	2.4	<2.22	0.3	0.7	0.6	1.8	0.3	<0.12	0.7	0.2	<0.03	<0.05
16	26	<19.2	<23.91	19.2	<15.80	<8.58	6.4	13.2	4.6	<4.09	7.8	11.6	13.1	13.3	6.0	2.5	5.0	5.7	<2.22	0.3	1.4	1.0	3.1	0.3	<0.12	1.5	0.3	0.1	<0.05
18	28	<19.2	<23.91	15.7	17.3	14.0	13.4	11.5	6.6	4.2	4.8	7.2	4.1	8.6	3.5	3.9	3.9	4.9	2.6	1.0	1.1	1.1	2.7	0.6	<0.12	1.4	0.5	0.1	0.1
20	31	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	14.1	4.5	<4.09	8.5	11.5	3.3	13.8	6.5	1.3	5.3	5.5	<2.22	0.3	1.3	0.9	3.0	0.3	<0.12	1.6	0.2	<0.03	<0.05
22	34	<19.2	<23.91	16.3	<15.80	<8.58	5.8	13.7	4.4	<4.09	8.1	10.2	2.9	10.4	4.1	1.6	4.7	3.4	<2.22	0.4	1.2	0.8	2.8	0.3	<0.12	1.4	0.2	0.0	<0.05
24	36	<19.2	<23.91	14.8	<15.80	<8.58	<5.20	12.0	5.3	<4.09	7.8	9.8	3.0	15.8	6.4	2.0	7.3	7.3	<2.22	0.4	1.8	0.9	4.0	0.4	<0.12	2.0	0.3	0.1	<0.05
28	41	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	11.1	4.9	<4.09	6.6	9.3	3.6	16.8	6.3	1.8	7.3	6.6	<2.22	1.0	2.1	0.8	4.7	0.4	<0.12	2.3	0.4	0.1	<0.05
30	44	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	9.7	<4.36	<4.09	7.6	11.0	4.3	20.6	7.9	1.9	10.3	7.6	<2.22	2.4	2.4	1.1	5.4	0.6	<0.12	2.6	0.4	0.1	<0.05
31	50	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	11.7	<4.36	<4.09	9.5	11.6	2.7	16.2	6.7	1.5	7.8	7.3	<2.22	0.7	1.6	0.8	3.6	0.4	<0.12	1.5	0.3	0.0	<0.05
33	53	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	11.8	<4.36	<4.09	15.7	19.2	4.6	41.3	16.2	2.1	22.5	16.5	<2.22	5.5	4.8	1.7	10.1	0.8	<0.12	5.2	0.5	0.1	<0.05
35	55	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	10.1	<4.36	<4.09	7.9	9.7	3.4	15.1	6.5	1.6	7.5	7.0	<2.22	2.3	1.7	0.9	3.8	0.4	<0.12	2.0	0.3	0.1	<0.05
37	58	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	10.8	<4.36	<4.09	10.5	13.0	4.3	22.3	8.6	1.6	9.8	9.9	<2.22	3.1	2.6	1.1	5.4	0.4	<0.12	2.7	0.3	0.1	<0.05
39	61	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	8.2	<4.36	<4.09	7.3	11.3	4.3	17.7	7.5	3.1	11.9	8.6	<2.22	0.8	2.1	1.2	4.5	0.8	<0.12	1.9	0.5	0.1	0.1
41	63	<19.2	<23.91	13.3	<15.80	<8.58	<5.20	12.4	<4.36	<4.09	13.9	17.2	5.2	24.6	11.1	1.8	11.7	10.9	<2.22	0.7	2.5	1.1	5.5	0.5	<0.12	2.5	0.4	0.1	<0.05
43	66	<19.2	<23.91	15.5	<15.80	<8.58	<5.20	14.3	<4.36	<4.09	15.8	20.0	5.1	31.9	13.6	2.0	14.3	14.7	<2.22	4.0	3.5	1.4	7.6	0.6	<0.12	3.5	0.4	0.1	<0.05
45	68	<19.2	<23.91	14.5	<15.80	<8.58	<5.20	12.6	<4.36	<4.09	10.3	12.3	4.1	21.8	9.4	1.9	9.3	10.0	<2.22	2.8	2.3	1.1	5.1	0.5	<0.12	2.5	0.3	0.0	<0.05
Sample ID	Depth (cm)	8	5	18	16	32	28	52	44	66	101	110	118	153	132	105	164	138	126	187	183	128+167	174	193	169	170	195	206	209
Control - South																													
1	-4	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	6.5	<4.36	<4.09	2.0	2.8	4.5	2.4	1.0	1.4	1.2	1.0	<2.22	0.6	<0.18	0.7	0.5	0.2	<0.12	0.2	0.1	0.0	<0.05
3	-1	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	7.7	<4.36	<4.09	2.9	3.9	1.8	4.7	1.4	1.5	1.9	1.8	<2.22	1.1	0.5	0.7	0.9	0.2	<0.12	0.4	0.1	0.0	<0.05
5	2	<19.2	<23.91	13.7	<15.80	<8.58	<5.20	9.0	4.4	<4.09	2.8	4.3	1.8	4.3	1.5	1.5	2.0	1.5	<2.22	1.1	0.4	0.7	1.0	0.2	<0.12	0.5	0.2	0.0	<0.05
7	4	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	8.0	<4.36	<4.09	2.4	3.3	1.2	4.0	1.6	1.5	1.9	1.9	<2.22	1.1	0.4	0.7	1.0	0.2	<0.12	0.5	0.1	0.0	<0.05
9	7	<19.2	<23.91	15.8	<15.80	<8.58	<5.20	9.4	<4.36	<4.09	3.4	4.2	2.4	7.7	2.7	1.7	3.3	3.0	<2.22	2.1	0.8	1.1	1.9	0.2	<0.12	1.0	0.2	0.1	<0.05
11	9	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	7.6	<4.36	<4.09	2.8	3.5	0.7	5.7	1.9	1.3	3.0	2.2	<2.22	1.7	0.6	0.6	1.5	0.2	<0.12	0.8	0.2	0.1	<0.05
13	12	<19.2	<23.91	14.4	<15.80	<8.58	<5.20	9.6	<4.36	<4.09	2.7	3.9	2.2	5.8	1.9	1.5	3.0	2.7	<2.22	1.7	0.6	0.7	1.4	0.2	<0.12	0.8	0.2	0.0	<0.05
15	14	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	6.9	<4.36	<4.09	3.7	4.3	1.5	7.0	2.5	1.4	3.1	3.1	<2.22	2.1	0.8	0.9	1.8	0.3	<0.12	0.9	0.2	0.1	<0.05
16	21	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	8.5	<4.36	<4.09	4.0	4.8	4.6	8.8	3.3	1.6	4.2	3.1	<2.22	2.7	1.0	0.9	2.3	0.3	<0.12	1.0	0.2	0.0	<0.05
18	23	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	<3.59	<4.36	<4.09	2.4	3.4	<0.50	5.1	2.3	2.6	3.0	1.9	<2.22	2.2	0.6	0.9	1.7	0.6	<0.12	0.6	0.4	0.1	0.1
20	26	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	5.0	<4.36	<4.09	2.8	3.4	0.9	5.1	2.0	1.2	2.7	1.8	<2.22	1.5	0.6	0.8	1.5	0.2	<0.12	0.7	0.2	0.0	<0.05
22	29	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	6.3	<4.36	<4.09	3.4	4.2	0.6	6.3	2.0	1.8	3.0	3.3	<2.22	1.8	0.7	0.8	1.8	0.3	<0.12	0.9	0.2	0.1	<0.05
24	31	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	5.1	<4.36	<4.09	2.9	3.7	0.8	5.9	2.1	1.3	2.4	3.3	<2.22	1.8	0.6	0.7	1.6	0.2	<0.12	0.9	0.2	0.1	<0.05
26	34	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	8.3	<4.36	<4.09	3.5	4.3	2.0	6.1	2.2	1.6	3.4	3.2	<2.22	1.7	0.8	0.8	1.7	0.3	<0.12	0.9	0.2	0.1	<0.05
28	36	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	8.2	4.4	<4.09	5.0	6.1	8.0	10.5	4.1	1.7	5.6	5.2	<2.22	3.1	1.2	1.0	3.1	0.4	<0.12	1.3	0.2	0.1	<0.05
30	39	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	6.3	<4.36	<4.09	4.9	5.9	5.4	11.2	4.2	1.8	5.4	5.2	<2.22	3.1	1.4	1.0	2.9	0.3	<0.12	1.7	0.3	0.1	<0.05
31	45	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	6.8	<4.36	<4.09	5.4	6.5	2.8	13.1	5.1	1.3	6.1	6.0	<2.22	3.7	1.5	1.3	3.4	0.4	<0.12	1.7	0.3	0.1	<0.05
33	48	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	7.4	<4.36	<4.09	4.4	5.7	2.3	10.4	3.6	1.4	4.2	4.4	<2.22	2.8	1.1	1.1	2.6	0.3	<0.12	1.2	0.2	0.1	<0.05
35	50	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	10.1	<4.36	<4.09	8.0	8.9	1.7	17.0	6.7	1.7	7.1	6.0	<2.22	4.7	2.0	1.3	4.5	0.4	<0.12	2.1	0.3	0.1	<0.05
39	56	24.3	<23.91	47.3	26.6	17.2	11.8	38.3	15.0	9.2	27.0	35.5	1.4	61.7	22.5	6.7	27.3	23.6	3.5	15.2	6.3	4.3	7.6	1.6	<0.12	7.4	1.1	0.2	0.1
41	58	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	8.8	<4.36	<4.09	5.6	6.5	1.4	11.6	4.4	1.8	6.5	4.3	<2.22	3.1	1.3	1.1	2.9	0.4	<0.12	1.6	0.2	0.1	<0.05
43	61	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	7.5	<4.36	<4.09	5.4	6.8	2.5	11.9	4.7	1.6	5.9	5.4	<2.22	3.1	1.2	1.2	2.9	0.4	<0.12	1.5	0.2	0.1	<0.05
45	63	<19.2	<23.91	13.3	<15.80	<8.58	<5.20	8.5	<4.36	<4.09	5.9	7.5	2.3	11.7	4.7	1.3	6.0	5.2	<2.22	3.2	1.2	0.9	3.2	0.4	<0.12	1.1	0.3	0.1	<0.05
Sample ID	Depth (cm)	8	5	18	16	32	28	52	44	66	101	110	118	153	132	105	164	138	126	187	183	128+167	174	193	169	170	195	206	209
SediMite - North																													
1	1	<19.2	<23.91	<13.27	<15.80	8.8	<5.20	6.2	<4.36	<4.09	2.4	4.2	0.5	3.3	1.4	3.2	1.0	2.3	2.5	1.5	0.4	0.8	1.0	0.7	0.1	0.5	0.4	0.1	0.1
3	4	<19.2	<23.91	<13.27	<15.80	9.4	<5.20	6.4	<4.36	<4.09	2.3	4.0	<0.50	6.4	1.9	2.5	2.6	3.9	<2.22	2.3	0.7	0.7	2.0	0.6	<0.12	0.9	0.3	0.1	0.1
5	7	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	5.6	<4.36	<4.09	2.2	4.4	<0.50	5.6	2.4	2.8	1.9	3.1	<2.22	2.4	0.7	0.7	2.0	0.6	<0.12	1.0	0.4	0.1	0.1
7	9	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	4.8	<4.36	<4.09	1.5	3.2	<0.50	3.2	1.2	2.4	1.1	1.7	<2.22	1.6	0.5	0.7	1.2	0.5	<0.12	0.4	0.3	0.1	0.1
9	12	<19.2	<23.91	<13.27	<15.80	9.9	<5.20	5.4	<4.36	<4.09	3.1	4.1	<0.50	5.6	2.1	2.8	2.0	3.6	<2.22	2.3	0.6	0.7	1.7	0.6	<0.12	0.9	0.4	0.1	0.1
11	14	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	3.9	<4.36	<4.09	1.7	3.8	<0.50	4.4	1.7	2.8	1.9	2.0	<2.22	1.8	0.5	0.8	1.5	0.6	<0.12	0.4	0.4	0.1	0.1
13	17	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	4.9	<4.36	<4.09	3.4	5.8	<0.50	6.4	3.6	2.7	2.6	2.6	<2.22	2.2	0.7	0.8	2.1	0.7	<0.12	0.7	0.4	0.1	0.1
15	19	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	4.5	<4.36	<4.09	2.6	5.0	<0.50	7.2	2.7	2.7	5.0	4.4	<2.22	2.6	0.9	0.8	2.3	0.6	<0.12	0.8	0.4	0.1	0.1
16	26	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	6.7	<4.36	<4.09	3.5	6.4	2.2	6.9	3.3	2.5	4.6	4.9	<2.22	2.3	0.9	0.8	1.8	0.6	<0.12	0.7	0.4	0.1	0.1
18	28	<19.2	<23.91	<13.27	<15.80	10.8	<5.20	8.8	<4.36	<4.09	5.1	7.2	8.2	8.7	4.8	3.0	3.5	4.3	<2.22	3.0	1.0	0.8	2.6	0.7	<0.12	0.9	0.4	0.1	0.1
20	31	<19.2	<23.91	<13.27	<15.80	8.7	<5.20	9.3	<4.36	<4.09	6.1	9.2	1.8	11.5	5.5	2.6	7.4	6.6	2.4	3.5	1.2	1.0	2.9	0.7	<0.12	1.3	0.4	0.1	0.1
22	34	<19.2	<23.91	<13.27	<15.80	8.9	<5.20	5.2	<4.36	<4.09	1.8	4.5	5.3	4.6	2.2	2.5	2.0	2.9	<2.22	2.1	0.6	0.7	1.4	0.6	<0.12	0.7	0.4	0.1	0.1
24	36	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	4.6	<4.36	<4.09	2.7	4.1	7.3	7.1	2.7	1.4	3.7	3.9	<2.22	2.6	0.9	0.5	1.9	0.3	<0.12	0.9	0.2	0.0	<0.05
26	39	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	3.9	<4.36	<4.09	2.0	2.8	1.5	6.0	2.3	1.3	2.7	3.4	<2.22	2.1	0.9	0.4	2.0	0.3	<0.12	1.0	0.2	0.1	<0.05
30	44	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	4.0	<4.36	<4.09	1.8	2.7	0.9	5.4	2.3	1.4	2.5	2.5	<2.22	2.2	0.7	0.4	1.8	0.3	<0.12	0.9	0.2	0.0	<0.05
33	53	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	3.8	<4.36	<4.09	2.3	3.8	0.7	7.1	3.1	1.2	3.8	3.6	<2.22	2.5	1.1	0.5	2.2	0.3	<0.12	1.0	0.3	0.0	<0.05
35	55	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	7.4	<4.36	<4.09	7.3	10.3	6.0	19.2	8.2	1.4	9.6	11.0	<2.22	5.3	2.4	0.9	5.0	0.4	<0.12	2.3	0.4	0.1	<0.05
37	58	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	12.7	5.1	<4.09	14.9	20.1	4.5	44.7	17.6	2.3	20.4	23.2	<2.22	11.6	5.4	2.0	11.4	0.8	<0.12	5.7	0.7	0.1	<0.05
39	61	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	5.9	<4.36	<4.09	5.3	7.9	1.2	17.3	7.5	1.4	7.8	9.9	<2.22	5.0	2.1	0.9	4.7	0.4	<0.12	2.2	0.4	0.1	<0.05
41	63	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	7.8	<4.36	<4.09	9.2	11.8	2.0	27.7	11.3	1.6	16.3	10.2	<2.22	7.2	3.3	1.2	6.9	0.5	<0.12	3.3	0.4	0.1	<0.05
43	66	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	4.9	<4.36	<4.09	4.5	6.8	3.8	14.4	5.2	1.7	7.5	5.1	<2.22	4.1	1.8	0.8	3.8	0.4	<0.12	1.6	0.3	0.0	<0.05
45	68	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	6.8	<4.36	<4.09	5.2	6.1	1.5	8.2	4.8	3.4	3.8	5.4	<2.22	3.1	1.0	0.9	2.3	0.7	<0.12	1.0	0.4	0.1	0.1
Sample ID	Depth (cm)	8	5	18	16	32	28	52	44	66	101	110	118	153	132	105	164	138	126	187	183	128+167	174	193	169	170	195	206	209
SediMite - Center																													
1	-2	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	7.3	<4.36	<4.09	2.7	3.9	6.7	3.3	1.5	1.7	2.1	2.5	<2.22	1.0	0.3	0.5	0.7	0.2	<0.12	0.4	0.2	<0.03	<0.05
3	1	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	7.1	<4.36	<4.09	2.6	3.6	3.3	4.4	2.1	1.9	2.1	2.5	<2.22	1.1	0.3	0.6	0.8	0.2	<0.12	0.4	0.1	<0.03	<0.05
5	4	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	6.9	<4.36	<4.09	3.2	4.6	7.3	4.5	2.0	2.1	2.6	2.8	<2.22	1.4	0.4	0.5	1.0	0.2	<0.12	0.4	0.2	0.0	<0.05
7	6	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	6.0	<4.36	<4.09	2.4	4.1	4.0	3.4	1.6	1.8	1.6	1.9	<2.22	1.1	0.4	0.4	0.8	0.2	<0.12	0.3	0.1	<0.03	<0.05
9	9	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	4.8	<4.36	<4.09	2.1	3.3	2.9	2.2	1.3	1.7	1.4	1.2	<2.22	0.7	0.2	0.4	0.5	0.2	<0.12	0.3	0.2	0.0	<0.05
11	11	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	<3.59	<4.36	<4.09	1.5	2.3	3.0	1.2	0.8	1.4	1.0	0.8	<2.22	0.5	0.2	0.4	0.4	0.1	<0.12	<0.16	<0.08	0.0	<0.05
13	14	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	3.8	<4.36	<4.09	1.7	1.8	9.1	1.4	0.9	1.2	<0.73	0.8	<2.22	0.6	0.2	0.3	0.4	0.2	<0.12	0.2	0.1	0.0	<0.05
15	16	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	4.3	<4.36	<4.09	1.7	2.7	3.1	1.2	0.8	1.4	0.9	1.0	<2.22	0.6	<0.18	0.3	0.4	0.2	<0.12	<0.16	0.1	<0.03	<0.05
16	23	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	5.5	<4.36	<4.09	3.1	4.3	14.5	4.8	2.0	1.7	2.1	2.4	<2.22	1.7	0.5	0.5	1.2	0.2	<0.12	0.5	0.1	0.0	<0.05
18	25	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	4.4	<4.36	<4.09	2.2	4.3	3.4	4.3	2.2	2.6	2.5	3.2	<2.22	1.8	0.5	0.8	1.6	0.6	<0.12	0.4	0.1	0.1	0.1
20	28	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	4.2	<4.36	<4.09	2.2	3.4	3.3	3.3	1.5	1.5	1.7	1.6	<2.22	1.1	0.4	0.4	0.8	0.2	<0.12	0.5	0.1	<0.03	<0.05
22	31	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	4.5	<4.36	<4.09	2.4	2.7	3.5	2.6	1.4	1.5	1.1	1.2	<2.22	1.0	0.3	0.4	0.7	0.2	<0.12	0.3	0.2	<0.03	<0.05
24	33	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	5.7	<4.36	<4.09	3.1	4.4	2.6	5.8	2.5	1.3	2.3	2.2	<2.22	1.7	0.6	0.5	1.5	0.2	<0.12	0.6	0.2	0.0	<0.05
26	36	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	5.6	<4.36	<4.09	3.5	5.7	6.0	7.2	3.0	1.4	3.5	3.7	<2.22	2.1	0.8	0.6	2.0	0.2	<0.12	0.7	0.2	0.0	<0.05
28	38	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	10.0	4.4	<4.09	5.8	9.0	6.2	12.2	5.2	2.3	5.2	5.5	<2.22	3.7	1.4	1.0	3.0	0.4	<0.12	1.5	0.3	0.1	<0.05
30	41	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	6.5	<4.36	<4.09	4.2	5.6	4.5	9.5	3.6	1.7	4.4	4.0	<2.22	2.7	1.1	0.6	2.3	0.3	<0.12	1.1	0.2	0.1	<0.05
31	47	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	11.9	4.4	<4.09	7.5	10.5	3.1	13.7	6.4	2.2	5.9	5.8	<2.22	3.5	1.4	0.8	3.1	0.4	<0.12	1.5	0.3	0.0	<0.05
33	50	<19.2	<23.91	19.0	<15.80	<8.58	<5.20	11.3	5.4	<4.09	6.4	9.4	3.3	14.9	6.4	2.2	5.8	6.4	<2.22	3.9	1.8	1.0	3.8	0.3	<0.12	2.0	0.3	0.1	<0.05
35	52	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	7.5	<4.36	<4.09	5.3	8.0	3.6	11.1	4.7	1.9	4.8	5.9	<2.22	2.8	1.2	0.7	2.8	0.3	<0.12	1.1	0.3	0.1	<0.05
37	55	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	7.4	<4.36	<4.09	5.0	7.6	3.7	12.4	6.1	3.4	6.0	5.1	<2.22	3.5	1.4	1.2	3.3	0.6	<0.12	1.3	0.4	0.1	0.1
39	58	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	7.7	<4.36	<4.09	6.6	10.0	4.3	14.3	6.2	1.5	7.7	6.5	<2.22	3.8	1.7	0.9	3.7	0.4	<0.12	1.6	0.3	0.0	<0.05
41	60	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	7.2	<4.36	<4.09	4.7	6.3	2.0	9.2	3.6	1.5	3.8	4.1	<2.22	2.3	0.9	0.6	2.0	0.3	<0.12	1.0	0.3	0.0	<0.05
43	63	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	6.5	<4.36	<4.09	4.7	7.1	4.9	9.5	3.9	1.8	3.9	4.7	<2.22	2.6	0.9	0.6	2.3	0.2	<0.12	1.0	0.2	0.0	<0.05
45	65	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	6.1	<4.36	<4.09	4.3	6.9	3.0	9.3	4.5	1.6	4.6	4.6	<2.22	2.5	1.0	0.8	2.4	0.2	<0.12	0.9	0.2	0.0	<0.05
Sample ID	Depth (cm)	8	5	18	16	32	28	52	44	66	101	110	118	153	132	105	164	138	126	187	183	128+167	174	193	169	170	195	206	209
SediMite - South																													
1	5	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	<3.59	<4.36	<4.09	1.4	1.4	5.0	0.7	<0.71	1.1	<0.73	<0.41	<2.22	0.4	<0.18	0.4	0.3	0.1	<0.12	<0.16	<0.08	<0.03	<0.05
3	8	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	<3.59	<4.36	<4.09	1.8	1.4	5.4	1.0	0.8	0.8	<0.73	0.6	<2.22	0.6	<0.18	0.3	0.4	0.1	<0.12	0.2	0.1	<0.03	<0.05
5	11	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	<3.59	<4.36	<4.09	1.2	1.4	6.3	1.6	0.8	0.9	0.9	1.1	<2.22	0.7	0.3	0.4	0.6	0.2	<0.12	0.4	0.1	<0.03	<0.05
7	13	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	<3.59	<4.36	<4.09	1.1	1.2	4.9	0.7	<0.71	1.1	<0.73	0.5	<2.22	0.5	<0.18	0.3	0.4	0.2	<0.12	0.2	0.1	<0.03	<0.05
9	16	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	<3.59	<4.36	<4.09	<1.10	1.2	6.8	0.9	<0.71	0.9	<0.73	0.6	<2.22	0.6	<0.18	0.3	0.4	0.2	<0.12	<0.16	0.1	<0.03	<0.05
11	18	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	<3.59	<4.36	<4.09	1.1	1.2	4.8	0.9	<0.71	0.9	<0.73	0.5	<2.22	0.6	<0.18	0.3	0.4	0.2	<0.12	<0.16	0.1	<0.03	<0.05
13	21	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	<3.59	<4.36	<4.09	1.3	1.1	8.9	1.0	<0.71	0.9	<0.73	0.7	<2.22	0.7	0.2	0.4	0.5	0.2	<0.12	0.2	0.2	0.0	<0.05
15	23	<19.2	<23.91	15.9	<15.80	<8.58	<5.20	11.4	5.7	<4.09	2.7	2.7	11.9	2.0	1.0	2.3	0.7	1.2	<2.22	0.8	0.2	0.9	0.7	0.2	<0.12	0.3	0.2	<0.03	<0.05
16	30	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	<3.59	<4.36	<4.09	2.1	2.4	6.3	5.7	2.1	1.2	2.5	2.2	<2.22	2.2	0.8	0.5	1.9	0.2	<0.12	0.8	0.2	0.0	<0.05
18	32	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	<3.59	<4.36	<4.09	2.8	2.7	7.8	6.9	2.4	1.2	2.8	2.6	<2.22	2.3	0.9	0.7	1.9	0.3	<0.12	1.2	0.2	0.0	<0.05
20	35	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	<3.59	<4.36	<4.09	2.9	3.4	6.3	5.9	2.1	1.2	2.2	2.7	<2.22	1.9	0.6	0.5	1.7	0.3	<0.12	0.9	0.2	0.0	<0.05
22	38	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	5.0	<4.36	<4.09	4.4	5.9	7.1	8.5	3.0	1.7	3.6	3.3	<2.22	2.4	1.0	0.7	2.2	0.3	<0.12	1.1	0.2	0.0	<0.05
24	40	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	4.7	<4.36	<4.09	5.0	6.9	5.9	12.6	4.6	1.4	5.3	4.2	<2.22	3.7	1.6	0.9	3.2	0.3	<0.12	1.4	0.4	0.1	<0.05
26	43	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	7.1	<4.36	<4.09	7.1	10.3	11.3	17.3	6.7	1.7	7.3	5.6	<2.22	4.7	2.0	1.0	4.3	0.4	<0.12	1.9	0.4	0.1	<0.05
28	45	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	8.2	<4.36	<4.09	9.1	13.3	10.0	20.4	6.8	1.7	10.6	8.1	<2.22	5.4	2.2	1.1	4.9	0.4	<0.12	2.4	0.4	0.0	<0.05
30	48	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	6.3	<4.36	<4.09	8.2	11.2	9.6	21.2	8.8	1.7	8.5	8.3	<2.22	6.2	2.8	1.2	6.3	0.5	<0.12	2.7	0.5	0.1	<0.05
31	54	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	5.4	<4.36	<4.09	7.6	9.2	6.1	18.5	8.4	1.4	7.7	6.9	<2.22	5.4	2.3	0.9	5.4	0.4	<0.12	2.5	0.4	0.1	<0.05
33	57	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	5.1	<4.36	<4.09	8.3	10.4	4.6	23.9	10.4	1.5	9.8	9.1	<2.22	6.4	2.8	1.0	6.7	0.5	<0.12	2.8	0.4	0.1	<0.05

35	59	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	5.8	<4.36	<4.09	6.6	7.2	9.5	15.1	6.5	1.8	6.6	6.8	<2.22	4.5	2.2	0.9	4.2	0.3	<0.12	1.9	0.3	0.0	<0.05
37	62	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	3.8	<4.36	<4.09	3.5	3.8	2.2	6.4	2.8	1.4	3.2	2.3	<2.22	1.9	0.8	0.5	1.8	0.2	<0.12	0.9	0.2	0.0	<0.05
39	65	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	<3.59	<4.36	<4.09	2.5	2.0	2.9	4.2	1.9	1.2	1.7	1.4	<2.22	1.7	0.7	0.5	1.7	0.2	<0.12	0.7	0.2	0.0	<0.05
41	67	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	<3.59	<4.36	<4.09	2.1	1.8	2.2	3.6	1.9	1.1	1.4	1.7	<2.22	1.4	0.6	0.3	1.3	0.2	<0.12	0.5	0.2	0.0	<0.05
43	70	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	<3.59	<4.36	<4.09	3.1	3.1	2.4	7.5	3.7	0.9	2.9	2.8	<2.22	2.4	0.9	0.5	2.3	0.2	<0.12	0.8	0.2	<0.03	<0.05
45	72	<19.2	<23.91	26.9	15.8	12.5	5.2	5.3	<4.36	4.2	7.3	5.3	17.3	8.6	4.1	5.0	3.8	4.7	2.6	4.2	1.3	1.3	3.6	0.8	<0.12	1.0	0.7	0.1	0.1
Sample ID	Depth (cm)	8	5	18	16	32	28	52	44	66	101	110	118	153	132	105	164	138	126	187	183	128+167	174	193	169	170	195	206	209
SediMite + Bioaugmented - North																													
1	1	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	<3.59	<4.36	<4.09	1.4	1.4	1.9	3.1	1.5	1.3	1.7	1.0	<2.22	1.3	0.5	0.6	1.2	0.2	<0.12	0.5	0.2	<0.03	<0.05
3	4	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	<3.59	<4.36	<4.09	1.1	1.5	0.6	2.7	1.3	1.1	1.1	0.8	<2.22	1.2	0.5	0.3	1.1	0.2	<0.12	0.5	0.2	0.0	<0.05
5	7	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	<3.59	<4.36	<4.09	1.6	1.8	1.8	4.4	2.0	1.3	2.7	2.1	<2.22	2.0	0.8	0.5	1.8	0.3	<0.12	0.7	0.2	0.0	<0.05
7	9	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	<3.59	<4.36	<4.09	2.0	2.6	10.7	4.7	2.0	1.7	2.1	1.6	<2.22	2.1	0.7	0.6	1.8	0.3	<0.12	0.7	0.2	0.0	<0.05
9	12	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	<3.59	<4.36	<4.09	1.9	3.3	0.6	4.3	2.0	2.0	2.2	3.4	<2.22	2.0	0.5	0.7	1.5	0.6	<0.12	0.5	0.4	0.1	0.1
11	14	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	<3.59	<4.36	<4.09	1.4	1.9	1.4	3.1	1.3	1.2	1.5	1.1	<2.22	1.3	0.5	0.5	1.0	0.2	<0.12	0.4	0.2	0.0	<0.05
13	17	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	7.6	<4.36	<4.09	7.0	8.9	5.4	23.7	9.1	2.1	10.5	10.0	<2.22	6.8	2.7	1.4	6.1	0.5	<0.12	2.5	0.4	0.1	<0.05
15	19	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	4.5	<4.36	<4.09	4.3	5.5	2.6	15.9	6.5	1.7	6.1	7.7	<2.22	5.3	2.3	1.1	4.8	0.5	<0.12	2.1	0.3	0.1	<0.05
16	26	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	11.6	<4.36	<4.09	9.7	11.7	3.2	32.3	13.9	1.8	14.3	14.0	<2.22	9.0	3.9	1.5	8.8	0.6	<0.12	3.6	0.5	0.1	<0.05
18	28	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	12.7	<4.36	4.2	11.5	14.5	0.9	30.5	13.7	3.2	14.8	13.2	2.9	8.6	3.6	1.8	8.3	1.0	<0.12	3.8	0.6	0.1	0.1
20	31	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	29.4	7.0	4.3	23.1	27.3	4.8	60.4	25.4	2.7	23.7	27.5	<2.22	13.8	6.7	2.4	13.9	1.0	<0.12	6.4	0.7	0.1	<0.05
22	34	<19.2	<23.91	22.5	<15.80	13.2	17.1	47.4	22.8	12.3	30.4	43.8	6.4	57.2	24.7	3.4	24.7	25.1	<2.22	14.1	6.5	2.8	14.0	0.8	<0.12	6.4	0.7	0.1	<0.05
24	36	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	21.5	7.6	4.2	23.6	29.0	5.8	80.2	32.9	2.9	30.0	30.5	<2.22	20.8	9.8	3.7	21.2	1.3	<0.12	9.0	1.1	0.2	<0.05
26	39	<19.2	<23.91	16.3	<15.80	<8.58	8.8	29.9	14.0	6.4	19.4	27.6	4.3	39.2	17.9	4.2	16.2	13.1	<2.22	10.0	4.4	2.6	9.6	0.7	<0.12	4.1	0.6	0.1	<0.05
28	41	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	23.0	6.7	5.1	24.2	29.6	17.7	64.3	26.6	3.2	24.4	17.5	<2.22	16.9	7.5	3.0	15.9	1.1	<0.12	7.8	0.9	0.1	<0.05
30	44	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	8.3	<4.36	<4.09	10.2	11.9	3.3	32.9	13.0	1.9	12.1	12.8	<2.22	9.8	4.2	1.7	9.2	0.6	<0.12	4.0	0.6	0.1	<0.05
31	50	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	20.4	4.5	4.7	23.4	28.0	7.8	64.2	27.9	2.9	29.6	23.7	<2.22	16.0	7.5	2.5	16.6	1.1	<0.12	7.3	0.9	0.1	<0.05
33	53	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	22.2	5.2	5.2	27.5	31.9	5.5	82.0	34.2	2.7	34.9	38.9	<2.22	21.8	10.3	3.1	21.5	1.3	<0.12	10.2	1.1	0.2	<0.05
35	55	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	23.3	5.9	4.9	22.7	28.2	6.4	54.0	22.5	2.3	25.4	19.0	<2.22	13.8	6.5	2.1	13.5	1.0	<0.12	6.5	0.8	0.2	<0.05
37	58	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	31.7	7.2	6.2	31.8	37.8	6.3	86.6	36.1	3.1	37.4	39.9	<2.22	21.9	10.4	3.5	22.1	1.4	<0.12	9.9	1.1	0.2	<0.05
39	61	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	19.4	<4.36	4.3	24.0	28.9	5.7	71.8	29.8	2.5	33.7	29.2	<2.22	18.2	8.3	3.0	18.4	1.2	<0.12	8.6	1.0	0.2	<0.05
41	63	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	24.4	5.9	5.8	27.7	32.8	5.9	80.7	34.2	2.6	36.3	33.5	<2.22	19.6	9.3	3.0	20.7	1.3	<0.12	9.7	1.0	0.1	<0.05
43	66	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	11.0	<4.36	<4.09	13.0	15.7	32.9	35.3	15.3	2.3	15.2	10.5	<2.22	9.9	4.4	1.7	9.2	0.7	<0.12	4.4	0.6	0.1	<0.05
45	68	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	8.2	<4.36	<4.09	6.7	7.2	1.9	15.1	7.0	1.7	5.6	6.1	<2.22	4.5	1.9	1.1	4.0	0.4	<0.12	1.7	0.3	0.1	<0.05
Sample ID	Depth (cm)	8	5	18	16	32	28	52	44	66	101	110	118	153	132	105	164	138	126	187	183	128+167	174	193	169	170	195	206	209
SediMite + Bioaugmented - Center																													
1	4	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	4.9	<4.36	<4.09	1.7	2.4	1.8	2.7	1.1	1.4	1.3	1.6	<2.22	1.0	0.3	0.6	1.0	0.2	<0.12	0.4	0.1	0.0	<0.05
3	7	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	6.4	<4.36	<4.09	1.9	2.7	15.7	2.8	1.3	1.7	1.3	1.2	<2.22	1.3	0.4	0.8	1.1	0.2	<0.12	0.5	0.2	0.1	<0.05
5	10	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	6.0	<4.36	<4.09	1.5	2.1	2.1	2.2	<0.71	1.5	0.9	1.4	<2.22	0.8	0.3	0.6	0.7	0.2	<0.12	0.3	0.1	<0.03	<0.05
7	12	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	6.4	<4.36	<4.09	2.3	2.9	2.5	3.3	1.3	1.7	1.9	1.5	<2.22	1.1	0.3	0.7	1.0	0.2	<0.12	0.5	0.1	<0.03	<0.05
9	15	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	6.0	<4.36	<4.09	2.5	4.1	0.6	2.7	1.5	3.1	1.6	2.2	<2.22	1.3	<0.18	0.9	1.0	0.6	<0.12	0.3	0.4	0.1	0.1
11	17	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	6.8	<4.36	<4.09	2.6	3.7	2.1	4.3	1.4	1.4	1.9	2.3	<2.22	1.3	0.4	0.8	1.1	0.2	<0.12	0.5	0.2	0.0	<0.05
13	20	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	7.5	<4.36	<4.09	2.5	3.9	2.0	4.7	1.7	1.3	1.9	1.8	<2.22	1.3	0.4	0.7	1.1	0.2	<0.12	0.4	0.2	<0.03	<0.05
15	22	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	6.5	<4.36	<4.09	3.0	4.1	1.6	6.9	2.7	1.5	3.0	2.5	<2.22	2.0	0.7	0.8	1.8	0.2	<0.12	0.8	0.2	0.0	<0.05
16	29	36.8	<23.91	53.9	28.7	25.4	34.2	46.3	33.7	7.7	6.5	8.2	6.8	6.0	2.8	3.4	2.4	3.1	<2.22	2.0	0.7	1.8	1.9	0.3	<0.12	0.8	0.4	0.1	<0.05
18	31	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	12.3	<4.36	4.2	5.9	8.9	3.5	10.8	4.8	2.3	5.4	4.0	<2.22	3.2	1.1	1.0	3.1	0.6	<0.12	1.1	0.5	0.1	0.1
20	34	<19.2	<23.91	15.8	<15.80	<8.58	<5.20	28.6	7.9	5.8	26.4	32.1	5.2	58.1	24.9	3.0	26.8	25.8	<2.22	13.6	6.4	2.7	14.6	0.9	<0.12	6.8	0.9	0.1	<0.05
22	37	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	18.1	5.1	<4.09	19.4	22.8	4.7	50.3	19.9	2.3	22.3	25.0	<2.22	13.0	6.1	2.2	13.5	0.8	<0.12	6.4	0.8	0.2	<0.05
24	39	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	19.2	6.2	4.1	19.5	22.8	7.2	53.1	21.5	2.4	24.4	19.8	<2.22	13.5	6.2	2.4	13.8	0.9	<0.12	6.0	0.8	0.1	<0.05
26	42	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	17.8	5.5	<4.09	11.8	13.6	5.5	26.1	10.4	1.8	10.7	10.6	<2.22	6.4	3.2	1.4	6.7	0.6	<0.12	3.0	0.4	0.1	<0.05
28	44	<19.2	<23.91	17.9	<15.80	9.2	15.0	33.0	19.7	6.9	18.5	23.6	6.1	24.2	11.0	1.5	9.6	9.0	<2.22	6.0	2.8	1.4	6.2	0.5	<0.12	2.6	0.4	0.1	<0.05
31	53	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	8.2	<4.36	<4.09	4.1	5.3	1.3	8.8	3.6	1.4	3.9	3.7	<2.22	2.9	1.2	0.9	2.6	0.2	<0.12	1.1	0.2	0.0	<0.05
33	56	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	4.4	<4.36	<4.09	3.0	3.3	0.9	5.0	1.8	1.2	1.9	2.1	<2.22	1.7	0.7	0.7	1.7	0.2	<0.12	0.7	0.2	0.0	<0.05
35	58	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	6.7	<4.36	<4.09	5.5	7.0	1.7	13.5	5.5	1.5	6.1	6.5	<2.22	3.8	1.6	1.0	4.0	0.3	<0.12	1.8	0.3	0.1	<0.05
37	61	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	8.6	<4.36	<4.09	6.5	8.6	3.3	16.0	7.3	1.6	6.9	7.9	<2.22	4.5	2.0	1.1	4.5	0.4	<0.12	2.0	0.3	0.1	<0.05
39	64	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	6.7	<4.36	<4.09	3.8	4.3	2.0	6.7	2.9	1.2	2.6	3.1	<2.22	2.3	0.9	0.7	2.1	0.3	<0.12	1.1	0.2	0.0	<0.05
41	66	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	5.3	<4.36	<4.09	2.3	3.1	1.2	4.9	2.1	1.3	2.2	2.1	<2.22	1.9	0.7	0.6	1.8	0.2	<0.12	0.9	0.2	0.1	<0.05
43	69	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	7.7	<4.36	<4.09	3.6	4.6	2.4	6.2	2.6	1.2	2.5	3.1	<2.22	2.1	0.7	0.6	1.9	0.2	<0.12	0.9	0.2	0.1	<0.05
Sample ID	Depth (cm)	8	5	18	16	32	28	52	44	66	101	110	118	153	132	105	164	138	126	187	183	128+167	174	193	169	170	195	206	209
SediMite + Bioaugmented - South																													
1	8	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	5.2	<4.36	<4.09	2.9	3.4	8.1	4.0	2.0	2.7	1.7	2.2	<2.22	1.6	0.7	1.4	1.6	0.2	<0.12	0.5	0.2	<0.03	<0.05
3	11	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	4.3	<4.36	<4.09	2.2	2.8	1.3	3.5	1.7	1.7	1.9	2.1	<2.22	1.2	0.5	0.7	1.1	0.2	<0.12	0.5	0.1	<0.03	<0.05
5	14	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	4.3	<4.36	<4.09	1.9	3.0	<0.50	3.1	1.4	1.5	1.5	1.9	<2.22	1.2	0.4	0.6	0.9	0.2	<0.12	0.4	0.1	<0.03	<0.05
7	16	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	4.1	<4.36	<4.09	1.9	2.5	1.0	3.0	1.5	1.5	1.5	2.0	<2.22	1.2	0.4	0.7	1.1	0.2	<0.12	0.4	0.2	<0.03	<0.05
9	19	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	4.6	<4.36	<4.09	3.2	4.1	<0.50	5.7	2.4	1.7	2.8	3.0	<2.22	1.9	0.7	0.8	1.7	0.2	<0.12	0.6	0.2	<0.03	<0.05
11	21	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	3.9	<4.36	<4.09	2.1	2.4	2.5	3.4	1.6	1.7	1.6	1.6	<2.22	1.5	0.5	0.6	1.3	0.2	<0.12	0.4	0.1	<0.03	<0.05
13	24	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	<3.59	<4.36	<4.09	2.6	3.1	2.0	5.4	2.2	1.5	2.3	3.1	<2.22	2.1	0.7	0.6	1.8	0.2	<0.12	0.8	0.2	<0.03	<0.05
15	26	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	5.2	<4.36	<4.09	5.1	5.5	2.1	12.3	5.1	1.5	4.9	5.5	<2.22	3.5	1.5	1.0	3.6	0.3	<0.12	1.5	0.2	0.1	<0.05
16	33	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	6.2	<4.36	<4.09	4.9	5.5	1.3	11.4	4.6	1.6	5.2	5.0	<2.22	3.5	1.4	1.0	3.3	0.3	<0.12	1.6	0.2	0.1	<0.05
18	35	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	6.8	<4.36	<4.09	6.4	8.1	5.7	16.9	7.7	3.4	8.2	9.0	<2.22	4.8	1.9	1.5	4.4	0.7	<0.12	2.2	0.5	0.1	0.1
20	38	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	11.0	<4.36	<4.09	12.3	15.3	<0.50	30.4	12.1	2.2	11.7	9.4	<2.22	7.5	3.0	1.8	7.5	0.6	<0.12	3.1	0.4	0.1	<0.05
22	41	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	15.1	<4.36	<4.09	16.0	19.1	<0.50	37.1	13.9	2.4	16.9	16.2	<2.22	9.2	3.8	1.9	9.2	0.6	<0.12	3.8	0.5	0.1	<0.05
24	43	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	13.8	<4.36	<4.09	14.6	17.1	<0.50	34.4	13.3	2.0	12.3	18.3	<2.22	8.4	3.6	1.7	7.6	0.5	<0.12	2.9	0.4	0.1	<0.05
26	46	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	11.7	<4.36	<4.09	11.7	14.6	<0.50	26.3	10.7	2.1	10.6	11.5	<2.22	6.7	2.7	1.6	6.0	0.4	<0.12	2.3	0.3	0.1	<0.05
28	48	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	15.7	5.0	<4.09	18.1	21.3	<0.50	46.9	18.3	2.9	19.1	20.2	<2.22	12.1	5.1	2.5	11.0	0.8	<0.12	4.6	0.6	0.1	<0.05
30	51	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	17.1	4.5	<4.09	19.6	22.5	4.0	54.2	19.9	2.6	22.3	22.7	<2.22	14.2	5.8	2.7	13.0	0.9	<0.12	5.2	0.7	0.1	<0.05
31	57	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	12.9	<4.36	<4.09	14.2	16.1	<0.50	35.0	14.7	2.5	13.8	15.5	<2.22	9.2	3.7	1.8	8.6	0.7	<0.12	3.8	0.4	0.1	<0.05
33	60	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	12.2	<4.36	<4.09	16.5	19.6	3.0	45.1	19.3	2.5	19.8	20.3	<2.22	12.3	5.4	2.0	12.0	0.9	<0.12	5.6	0.7	0.1	<0.05
35	62	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	16.7	4.4	4.5	22.4	26.0	0.7	58.4	23.7	3.4	25.8	27.7	<2.22	15.1	6.7	2.6	15.1	0.9	<0.12	6.6	0.8	0.1	<0.05
37	65	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	6.8	<4.36	<4.09	7.8	8.9	2.1	22.8	9.5	3.6	6.4	10.5	2.4	6.8	2.5	1.5	6.5	1.0	<0.12	2.9	0.6	0.1	0.1
39	68	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	5.5	<4.36	<4.09	7.4	8.4	4.8	22.0	8.4	1.8	8.2	9.0	<2.22	6.5	2.5	1.3	6.1	0.5	<0.12	2.7	0.4	0.1	<0.05
41	70	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	7.7	<4.36	<4.09	8.8	9.1	3.1	21.8	8.5	1.6	10.2	8.7	<2.22	6.0	2.2	1.3	5.9	0.4	<0.12	2.4	0.3	0.1	<0.05
43	73	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	5.7	<4.36	<4.09	8.0	8.1	3.2	20.8	8.8	1.6	8.0	8.2	<2.22	5.5	2.2	1.1	5.4	0.4	<0.12	2.2	0.3	0.0	<0.05
45	75	<19.2	<23.91	<13.27	<15.80	<8.58	<5.20	12.3	<4.36	4.3	19.1	20.9	7.0	47.2	19.2	3.8	19.9	17.2	<2.22	14.1	5.2	3.0	12.2	1.1	<0.12	4.4	0.8	0.1	<0.05

Abraham's Creek Geochemistry and Velocity Results

Sample ID	Depth (cm)	fss	Cl- (mg/L)	SO4-- (mg/L)	Fe+2 (mg/L)	S-- (ug/L)	Depth U (cm)	U (cm/d)	U-95% (cm/d)	U+95% (cm/d)
PQL =				**0.3**	**1.5**	**0.09**	**25**			
Control - North										
1	2	0.92	7.2	<1.5	N.A.	N.A.	0	8	3	17
3	5	0.91	7.3	<1.5	63	49	25	6	2	13
5	8	0.90	7.7	<1.5	65	50	49	7	0	36
7	10	0.90	8.1	<1.5	66	50	74	1	0	3
9	13	0.90	8.2	<1.5	69	33				
11	15	0.90	8.4	<1.5	66	33				
13	18	0.91	8.5	<1.5	71	66				
15	20	0.92	8.4	<1.5	71	82				
16	27	0.92	8.2	<1.5	71	81				
18	29	0.90	7.9	<1.5	77	120				
20	32	0.88	7.7	<1.5	71	83				
22	35	0.86	7.2	<1.5	80	57				
24	37	0.85	6.8	<1.5	79	64				
26	40	0.85	6.2	<1.5	80	71				
28	42	0.86	6.2	<1.5	74	64				
30	45	0.88	5.7	<1.5	76	58				
31	51	0.87	5.1	<1.5	74	51				
33	54	0.84	5.1	<1.5	76	109				
35	56	0.82	5.2	<1.5	88	95				
37	59	0.82	5.2	<1.5	81	67				
39	62	0.81	5.3	<1.5	89	67				
41	64	0.82	5.4	<1.5	92	74				
43	67	0.84	5.5	<1.5	91	61				
45	69	0.88	5.6	<1.5	89	48				
Sample ID	Depth (cm)	fss	Cl- (mg/L)	SO4-- (mg/L)	Fe+2 (mg/L)	S-- (ug/L)	Depth U (cm)	U (cm/d)	U-95% (cm/d)	U+95% (cm/d)
Control - Center										
1	1	0.99	5.8	<1.5	N.A.	N.A.	0	83	57	>100
3	4	0.97	6.3	<1.5	43	<25	24	4	2	7
5	7	0.95	6.8	<1.5	67	<25	49	2	1	5
7	9	0.93	7.7	<1.5	64	<25				
9	12	0.93	8.4	<1.5	66	<25				
11	14	0.92	9.2	<1.5	66	<25				
13	17	0.92	10.1	<1.5	64	<25				
15	19	0.93	10.6	<1.5	66	<25				
16	26	0.92	11.7	<1.5	67	<25				
18	28	0.90	12.1	<1.5	63	27				
20	31	0.88	11.8	<1.5	67	56				
22	34	0.87	11.9	<1.5	64	28				
24	36	0.87	12.0	<1.5	64	34				
26	39	0.87	11.7	<1.5	64	<25				
28	41	0.88	11.3	<1.5	69	<25				
30	44	0.90	11.3	<1.5	68	28				
31	50	0.88	11.0	<1.5	68	167				
33	53	0.85	11.1	<1.5	66	<25				
35	55	0.84	11.2	<1.5	80	<25				
37	58	0.82	11.6	<1.5	76	<25				
39	61	0.82	11.6	<1.5	80	<25				
41	63	0.82	12.0	<1.5	81	43				
43	66	0.83	12.5	<1.5	80	<25				
45	68	0.86	12.6	<1.5	86	60				
Sample ID	Depth (cm)	fss	Cl- (mg/L)	SO4-- (mg/L)	Fe+2 (mg/L)	S-- (ug/L)	Depth U (cm)	U (cm/d)	U-95% (cm/d)	U+95% (cm/d)
Control - South										
1	-4	1.00	2.6	<1.5	N.A.	N.A.	-5	43	28	67
3	-1	1.00	2.6	<1.5	2	<25	20	12	3	37
5	2	0.99	5.8	<1.5	2	<25	44	3	1	5
7	4	0.98	6.3	<1.5	53	<25	69	1	0	1
9	7	0.96	6.7	<1.5	30	<25				
11	9	0.95	7.2	<1.5	65	<25				
13	12	0.94	7.5	<1.5	66	26				
15	14	0.95	7.8	<1.5	75	53				
16	21	0.92	8.3	<1.5	64	32				
18	23	0.90	8.3	<1.5	68	27				
20	26	0.88	8.2	<1.5	67	<25				
22	29	0.87	8.0	<1.5	80	28				
24	31	0.87	7.4	<1.5	61	<25				
26	34	0.88	6.9	<1.5	86	<25				
28	36	0.89	6.6	<1.5	73	<25				
30	39	0.90	6.1	<1.5	70	28				
31	45	0.89	5.3	<1.5	72	55				
33	48	0.87	5.0	<1.5	66	56				
35	50	0.84	4.9	<1.5	70	58				
37	53	0.83	4.8	<1.5	86	47				

	39	56	0.82	4.8	<1.5		78	54					
	41	58	0.83	4.7	<1.5		82	55					
	43	61	0.84	4.6	<1.5		72	55					
	45	63	0.87	4.6	<1.5		70	48					
Sample ID	Depth (cm)	fss	Cl- (mg/L)	SO4-- (mg/L)		Fe+2 (mg/L)	S-- (ug/L)		Depth U (cm)	U (cm/d)		U-95% (cm/d)	U+95% (cm/d)
Activated Carbon - North													
	1	1	1.00	4.0	2.2	N.A.	N.A.		0	54		39	73
	3	4	1.00	5.5	<1.5		1	25	25	8		4	14
	5	7	0.99	5.3	<1.5		47	40	49	14		0	85
	7	9	0.98	5.3	<1.5		51	<25	74	1		0	2
	9	12	0.97	5.4	<1.5		54	25					
	11	14	0.96	5.6	<1.5		60	<25					
	13	17	0.95	5.9	<1.5		62	<25					
	15	19	0.94	6.1	<1.5		62	26					
	16	26	0.95	7.2	<1.5		66	53					
	18	28	0.95	7.7	<1.5		65	26					
	20	31	0.95	8.2	<1.5		59	<25					
	22	34	0.94	9.2	<1.5		57	37					
	24	36	0.92	10.2	<1.5		60	32					
	26	39	0.91	12.0	<1.5		59	27					
	28	41	0.92	10.5	<1.5		62	33					
	30	44	0.93	10.3	<1.5		45	33					
	31	50	0.91	15.0	<1.5		59	43					
	33	53	0.87	11.9	<1.5		46	39					
	35	55	0.84	11.2	<1.5		47	<25					
	37	58	0.81	10.4	<1.5		53	30					
	39	61	0.80	9.6	<1.5		60	<25					
	41	63	0.80	9.0	<1.5		56	25					
	43	66	0.82	8.5	<1.5		65	44					
	45	68	0.86	8.1	<1.5		89	61					
Sample ID	Depth (cm)	fss	Cl- (mg/L)	SO4-- (mg/L)		Fe+2 (mg/L)	S-- (ug/L)		Depth U (cm)	U (cm/d)		U-95% (cm/d)	U+95% (cm/d)
Activated Carbon - Center													
	1	-2	1.00	2.9	1.6	N.A.	N.A.		0	72		51	>100
	3	1	1.00	3.5	<1.5		2	<25	24	15		9	23
	5	4	1.00	5.3	<1.5		9	35	49	5		0	27
	7	6	0.99	5.9	<1.5		41	40	73	1		0	2
	9	9	0.99	6.6	<1.5		58	25					
	11	11	0.97	6.9	<1.5		62	25					
	13	14	0.96	7.6	<1.5		58	26					
	15	16	0.95	8.3	<1.5		65	104					
	16	23	0.95	9.4	<1.5		67	52					
	18	25	0.94	9.8	<1.5		63	116					
	20	28	0.93	10.2	<1.5		63	53					
	22	31	0.92	10.5	<1.5		69	75					
	24	33	0.92	11.0	<1.5		71	43					
	26	36	0.91	10.9	<1.5		68	65					
	28	38	0.91	11.0	<1.5		65	49					
	30	41	0.91	11.3	<1.5		63	132					
	31	47	0.90	10.8	<1.5		75	104					
	33	50	0.88	9.9	<1.5		77	67					
	35	52	0.86	9.2	<1.5		64	57					
	37	55	0.84	8.7	<1.5		83	134					
	39	58	0.83	8.0	<1.5		86	84					
	41	60	0.84	7.2	<1.5		88	102					
	43	63	0.85	6.8	<1.5		76	66					
	45	65	0.89	6.3	<1.5		75	106					
Sample ID	Depth (cm)	fss	Cl- (mg/L)	SO4-- (mg/L)		Fe+2 (mg/L)	S-- (ug/L)		Depth U (cm)	U (cm/d)		U-95% (cm/d)	U+95% (cm/d)
Activated Carbon - South													
	1	5	0.97	6.7	<1.5	N.A.	N.A.		-5	18		14	22
	3	8	0.95	7.0	<1.5		65	26	20	6		3	10
	5	11	0.94	7.4	<1.5		65	<25	69	1		0	2
	7	13	0.94	7.8	<1.5		67	<25					
	9	16	0.93	8.0	<1.5		34	<25					
	11	18	0.93	8.3	<1.5		64	<25					
	13	21	0.93	8.5	<1.5		60	<25					
	15	23	0.94	8.7	<1.5		59	<25					
	16	30	0.93	7.8	<1.5		77	<25					
	18	32	0.92	7.5	<1.5		69	157					
	20	35	0.90	7.2	<1.5		62	33					
	22	38	0.89	6.9	<1.5		71	39					
	24	40	0.89	6.6	<1.5		70	<25					
	26	43	0.89	6.1	<1.5		64	39					
	28	45	0.89	5.7	<1.5		71	34					
	30	48	0.90	5.6	<1.5		68	<25					
	31	54	0.87	5.5	<1.5		65	<25					
	33	57	0.83	5.3	<1.5		56	40					

	35	59	0.79	5.4	<1.5		72	<25						
	37	62	0.77	5.6	<1.5		74		38					
	39	65	0.76	5.5	<1.5		69		58					
	41	67	0.78	5.1	<1.5		71		33					
	43	70	0.80	5.2	<1.5		73		135					
	45	72	0.85	5.2	<1.5		71		106					
Sample ID	Depth (cm)	fss	Cl- (mg/L)	SO4-- (mg/L)		Fe+2 (mg/L)	S-- (ug/L)			Depth U (cm)	U (cm/d)		U-95% (cm/d)	U+95% (cm/d)
Activated Carbon + Bioaumented - North														
	1	1	0.99	4.9	<1.5	N.A.	N.A.			0	73		47	>100
	3	4	0.98	4.7	<1.5		35	<25		25	6		3	10
	5	7	0.97	4.7	<1.5		38	<25		49	2		0	7
	7	9	0.96	4.7	<1.5		34	<25		74	0		0	1
	9	12	0.94	4.9	<1.5		36	<25						
	11	14	0.93	4.8	<1.5		40	<25						
	13	17	0.92	5.5	<1.5		35	<25						
	15	19	0.94	5.6	<1.5		35	<25						
	16	26	0.98	5.8	<1.5		38		37					
	18	28	0.98	5.7	<1.5		37	<25						
	20	31	0.95	6.3	<1.5		38	<25						
	22	34	0.90	7.0	<1.5		37	<25						
	24	36	0.88	7.6	<1.5		38	<25						
	26	39	0.86	8.3	<1.5		42	<25						
	28	41	0.86	8.6	<1.5		38	<25						
	30	44	0.86	9.3	<1.5		39	<25						
	31	50	0.87	9.4	<1.5		43		41					
	33	53	0.85	9.0	<1.5		26	<25						
	35	55	0.83	8.5	<1.5		23	<25						
	37	58	0.81	7.9	<1.5		43	<25						
	39	61	0.80	7.2	<1.5		36	<25						
	41	63	0.79	6.7	<1.5		39		38					
	43	66	0.81	6.5	<1.5		47	<25						
	45	68	0.85	6.2	<1.5		44	<25						
Sample ID	Depth (cm)	fss	Cl- (mg/L)	SO4-- (mg/L)		Fe+2 (mg/L)	S-- (ug/L)			Depth U (cm)	U (cm/d)		U-95% (cm/d)	U+95% (cm/d)
Activated Carbon + Bioaumented - Center														
	1	4	0.99	5.4	<1.5	N.A.	N.A.			0	>100		74	>100
	3	7	0.98	5.2	<1.5		46	<25		24	5		2	9
	5	10	0.96	5.3	<1.5		59	<25		49	2		1	3
	7	12	0.95	5.5	<1.5		51	<25		73	1		0	2
	9	15	0.93	6.3	<1.5		53	<25						
	11	17	0.93	5.7	<1.5		53	<25						
	13	20	0.93	5.8	<1.5		59	<25						
	15	22	0.93	6.2	<1.5		57	<25						
	16	29	0.92	6.6	<1.5		56	<25						
	18	31	0.90	7.1	<1.5		67	<25						
	20	34	0.87	7.3	<1.5		49	<25						
	22	37	0.85	7.7	<1.5		58	<25						
	24	39	0.84	8.1	<1.5		61	<25						
	26	42	0.84	8.3	<1.5		55	<25						
	28	44	0.85	8.7	<1.5		61	<25						
	30	47	0.87	9.0	<1.5		52	<25						
	31	53	0.88	8.6	<1.5		60	<25						
	33	56	0.86	8.4	<1.5		56	<25						
	35	58	0.83	8.5	<1.5		58	<25						
	37	61	0.82	8.2	<1.5		66	<25						
	39	64	0.82	8.1	<1.5		63	<25						
	41	66	0.82	8.0	<1.5		69	<25						
	43	69	0.83	8.1	<1.5		68	<25						
	45	71	0.86	8.1	<1.5		59	<25						
Sample ID	Depth (cm)	fss	Cl- (mg/L)	SO4-- (mg/L)		Fe+2 (mg/L)	S-- (ug/L)			Depth U (cm)	U (cm/d)		U-95% (cm/d)	U+95% (cm/d)
Activated Carbon + Bioaumented - South														
	1	8	0.96	6.0	<1.5	N.A.	N.A.			20	3		1	6
	3	11	0.95	6.1	<1.5		54	<25		44	14		2	56
	5	14	0.93	6.3	<1.5		57	<25		69	0		0	1
	7	16	0.91	6.4	<1.5		74	<25						
	9	19	0.87	6.7	<1.5		31		28					
	11	21	0.83	6.9	<1.5		56	<25						
	13	24	0.82	6.8	<1.5		65	<25						
	15	26	0.83	6.7	<1.5		59	<25						
	16	33	0.90	5.7	<1.5		64	<25						
	18	35	0.87	5.7	<1.5		65		33					
	20	38	0.85	5.6	<1.5		69	<25						
	22	41	0.83	5.4	<1.5		77		47					
	24	43	0.81	5.3	<1.5		64	<25						
	26	46	0.80	5.2	<1.5		68	<25						
	28	48	0.81	5.1	<1.5		71	<25						
	30	51	0.84	4.9	<1.5		84	<25						

31	57	0.84	4.8 <1.5	69 <25	
33	60	0.81	4.9 <1.5	72 <25	
35	62	0.79	5.0 <1.5	67 <25	
37	65	0.78	5.0 <1.5	74	25
39	68	0.78	5.2 <1.5	76 <25	
41	70	0.77	5.3 <1.5	80 <25	
43	73	0.79	5.4 <1.5	77	32
45	75	0.84	5.2 <1.5	80	32

Abraham Creek Exsitu PCB

Pore Water Concentration Ex-Situ, Cpw (pg/L)

			8	5	18	16	32	28	52	44	66	101	110	118	153	132	105	164	138	126	187	183	128+167	174	193	169	170	195	206	209
	PQL =		**20.76**	**25.82**	**14.33**	**17.06**	**9.27**	**7.01**	**3.87**	**5.89**	**1.77**	**1.49**	**2.40**	**1.36**	**0.92**	**3.86**	**0.83**	**0.79**	**0.56**	**2.40**	**0.21**	**0.25**	**0.76**	**0.30**	**0.18**	**0.32**	**0.43**	**0.46**	**0.04**	**0.06**
	Starts (cm)	End (cm)																												
Control North	0	8	26.5	<25.82	<14.33	<17.06	20.1	15.0	26.5	11.4	5.4	34.4	95.5	11.7	172.4	32.7	6.8	96.9	56.9	7.1	35.0	15.8	6.1	37.1	1.1	0.4	14.7	2.1	0.2	<0.06
	23	38	<20.76	<25.82	<14.33	<17.06	17.6	20.5	<3.87	<5.89	<1.77	6.0	9.2	<1.36	16.3	<3.86	1.7	7.8	8.5	5.4	4.0	1.8	1.4	3.6	0.8	0.4	1.8	0.7	0.1	<0.06
	38	53	<20.76	<25.82	<14.33	<17.06	21.9	13.5	<3.87	<5.89	<1.77	3.4	8.0	<1.36	3.3	<3.86	2.2	1.2	1.3	5.2	1.2	0.6	1.3	0.9	0.7	0.4	0.7	0.6	<0.04	<0.06
Control Center	0	14	22.1	<25.82	<14.33	<17.06	19.7	8.9	26.4	12.4	6.1	42.4	92.2	8.1	176.3	31.7	6.6	93.6	64.4	10.3	35.3	15.9	5.6	37.3	2.2	0.4	11.0	2.2	0.2	<0.06
	27	42	<20.76	<25.82	<14.33	<17.06	11.4	7.1	<3.87	<5.89	<1.77	8.6	6.9	<1.36	20.7	4.3	1.8	8.0	8.9	5.2	4.7	2.2	1.4	4.5	0.5	0.4	2.3	0.7	0.1	<0.06
	42	57	<20.76	<25.82	<14.33	<17.06	12.6	14.4	<3.87	<5.89	<1.77	2.3	3.8	<1.36	2.1	<3.86	1.6	1.0	1.2	5.0	0.5	0.5	1.1	0.7	0.5	0.4	0.7	0.6	<0.04	<0.06
Control South	0	12	23.2	<25.82	<14.33	<17.06	25.7	13.2	43.8	13.7	8.6	48.8	122.2	14.3	225.2	37.7	7.1	128.0	69.1	7.8	47.8	21.2	6.3	46.8	1.9	0.5	17.4	2.6	0.3	<0.06
	23	33	<20.76	<25.82	<14.33	<17.06	13.9	9.9	<3.87	<5.89	<1.77	2.2	4.4	<1.36	2.2	<3.86	1.6	1.3	1.7	5.3	0.5	0.4	1.1	0.6	0.6	0.4	0.7	0.6	<0.04	<0.06
	33	43	<20.76	<25.82	<14.33	<17.06	18.9	15.3	<3.87	<5.89	<1.77	1.8	8.4	<1.36	<0.92	<3.86	2.0	<0.79	<0.56	5.6	<0.21	0.3	1.0	<0.30	0.6	0.4	0.6	0.6	<0.04	<0.06
SediMite North	0	14	<20.76	<25.82	<14.33	<17.06	15.7	11.5	22.1	8.3	5.7	40.3	84.1	<1.36	145.3	24.9	5.2	74.8	45.3	8.5	30.9	13.2	4.7	29.2	1.6	0.4	11.1	1.9	0.2	<0.06
	32	43	<20.76	<25.82	<14.33	<17.06	14.9	13.4	5.6	<5.89	<1.77	10.3	15.3	<1.36	26.0	5.5	1.9	10.7	16.2	5.4	6.3	3.2	1.6	6.1	0.8	0.4	2.8	0.9	0.1	<0.06
	43	55	<20.76	<25.82	<14.33	<17.06	19.8	9.3	<3.87	<5.89	<1.77	3.2	3.9	<1.36	<0.92	<3.86	1.8	<0.79	0.8	5.5	<0.21	1.3	1.0	0.4	0.5	0.4	0.6	0.6	<0.04	<0.06
SediMite Center	0	12	<20.76	<25.82	<14.33	<17.06	9.9	7.8	8.1	<5.89	2.4	21.6	36.2	<1.36	84.2	18.4	4.1	37.3	21.9	6.9	21.2	9.3	3.0	20.9	0.2	0.4	6.6	1.4	0.1	<0.06
	24	33	21.3	<25.82	<14.33	<17.06	28.4	12.6	<3.87	<5.89	<1.77	5.2	4.8	<1.36	4.2	<3.86	2.0	<0.79	2.9	5.8	1.3	0.8	1.3	1.4	0.5	0.4	0.8	0.7	0.0	<0.06
	33	42	<20.76	<25.82	<14.33	<17.06	20.6	9.6	<3.87	<5.89	<1.77	2.4	3.1	<1.36	1.6	<3.86	2.0	1.2	1.7	5.7	0.8	0.5	1.3	0.7	0.6	0.4	0.7	0.6	<0.04	<0.06
SediMite South	0	13	<20.76	<25.82	<14.33	<17.06	32.0	12.6	29.2	12.9	8.2	38.2	110.3	10.9	223.0	40.4	7.1	139.6	75.0	8.6	47.7	21.3	6.9	49.6	2.7	0.4	17.5	2.7	0.3	<0.06
	26	36	<20.76	<25.82	<14.33	<17.06	21.1	15.4	<3.87	<5.89	<1.77	2.6	5.6	<1.36	6.2	<3.86	2.1	3.0	3.6	5.7	1.8	0.8	1.2	1.6	0.7	0.4	0.9	0.6	<0.04	<0.06
	36	46	<20.76	<25.82	<14.33	<17.06	9.6	9.2	<3.87	<5.89	<1.77	1.7	3.4	<1.36	1.1	<3.86	1.8	1.5	<0.56	5.6	0.4	0.4	0.9	0.5	0.7	0.4	0.6	0.6	<0.04	<0.06
SediMite + Bio North	10	19	25.6	<25.82	<14.33	<17.06	21.5	17.9	111.4	32.3	19.0	163.6	247.1	30.1	457.9	87.8	13.6	258.0	158.2	9.5	90.3	41.5	11.4	98.3	5.1	0.4	29.5	3.5	0.5	<0.06
	19	45	20.9	<25.82	<14.33	<17.06	22.6	9.0	83.2	13.1	13.1	130.1	135.6	7.1	268.6	48.6	6.7	53.9	152.1	7.7	56.7	25.6	6.6	56.5	3.7	0.4	18.4	2.6	0.3	<0.06
	45	71	28.9	<25.82	<14.33	<17.06	20.7	15.3	3.9	6.0	<1.77	3.7	6.6	<1.36	2.3	<3.86	2.2	<0.79	2.7	5.6	1.1	0.5	1.3	0.7	0.5	0.4	0.7	0.6	<0.04	<0.06
SediMite + Bio Center	0	16	<20.76	<25.82	<14.33	<17.06	13.4	9.5	33.3	10.1	8.6	69.7	110.3	15.2	317.6	51.7	8.1	212.9	146.6	8.4	60.9	27.4	7.2	63.1	2.6	0.4	12.4	2.8	0.3	<0.06
	30	47	<20.76	<25.82	<14.33	<17.06	29.1	10.5	16.2	6.9	3.7	50.9	51.1	<1.36	107.3	17.1	4.3	23.5	60.7	6.5	21.9	6.9	3.4	19.6	1.8	0.4	7.9	1.4	0.2	<0.06
	47	65	22.6	<25.82	<14.33	<17.06	18.5	8.3	<3.87	<5.89	<1.77	4.6	5.2	<1.36	6.5	<3.86	1.6	1.8	4.8	5.3	1.9	0.8	1.0	1.5	0.6	0.4	0.9	0.6	0.0	<0.06
SediMite + Bio South	0	15	<20.76	<25.82	<14.33	<17.06	17.6	26.2	6.4	<5.89	3.4	18.3	35.4	<1.36	143.3	28.0	5.3	77.1	48.3	9.3	48.6	19.0	4.9	48.6	2.2	0.4	13.5	2.8	0.4	<0.06
	31	46	<20.76	<25.82	<14.33	<17.06	19.5	10.1	226.7	17.4	18.0	185.8	187.9	10.7	322.0	55.9	7.2	91.1	140.7	9.6	59.0	22.7	8.0	52.8	3.5	0.4	21.3	3.0	0.3	<0.06
	46	61	<20.76	<25.82	<14.33	<17.06	11.6	8.7	<3.87	<5.89	<1.77	2.3	3.9	<1.36	2.9	<3.86	2.3	1.7	1.8	5.4	1.1	0.5	1.2	0.7	0.5	0.4	0.7	0.6	<0.04	<0.06

Abraham's Creek PCBs T-Bar

Cw of PCBs (pg/L) (use of average fss)

Sample ID	Depth (cm)	8	5	18	16	32	28	52	44	66	101	110	118	153	132	105	164	138	126	187	183	128+167	174	193	169	170	195	206	209
PQL =		**23.07**	**28.69**	**15.92**	**18.96**	**10.29**	**6.23**	**4.30**	**5.24**	**4.91**	**1.33**	**1.07**	**0.60**	**0.41**	**0.86**	**0.74**	**0.88**	**0.50**	**2.66**	**0.24**	**0.22**	**0.34**	**0.27**	**0.16**	**0.14**	**0.19**	**0.10**	**0.04**	**0.07**
Control - North																													
	2.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	12.56	7.75	<4.91	2.89	4.00	14.56	1.18	<0.86	2.03	<0.88	0.63	<2.66	0.39	<0.22	0.90	0.31	0.18	<0.14	<0.19	0.13	<0.44	<0.07
	7.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	15.74	8.68	<4.91	2.31	4.44	1.68	1.42	0.86	1.62	<0.88	0.80	<2.66	0.46	<0.22	0.69	<0.27	0.18	<0.14	<0.19	<0.10	<0.44	<0.07
	12.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	29.06	14.13	<4.91	3.01	7.99	2.52	8.01	3.10	2.11	3.35	5.64	<2.66	2.11	0.65	0.79	1.72	0.27	<0.14	0.89	0.18	<0.44	<0.07
	17.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	25.34	13.62	<4.91	2.95	9.73	2.92	10.23	3.68	2.07	5.09	4.25	<2.66	2.55	0.89	1.03	2.26	0.34	<0.14	0.91	0.21	0.05	<0.07
	22.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	25.21	12.30	<4.91	2.94	8.94	2.33	11.86	4.51	2.07	5.83	5.35	<2.66	3.01	1.12	1.09	2.70	0.33	<0.14	1.36	0.22	<0.44	<0.07
	27.5	<23.07	<28.69	<15.92	<18.96	<10.29	6.34	36.26	19.16	<4.91	3.32	11.57	3.43	14.90	5.64	2.33	6.92	8.64	<2.66	3.77	1.41	1.21	3.24	0.41	<0.14	1.41	0.27	0.04	<0.07
	32.5	<23.07	<28.69	31.15	<18.96	10.57	13.06	70.32	39.08	9.15	5.82	25.84	7.42	25.84	10.95	4.08	14.96	16.54	<2.66	6.10	2.74	2.00	6.07	0.56	<0.14	2.62	0.47	0.06	<0.07
	37.5	<23.07	<28.69	17.02	<18.96	<10.29	<6.23	43.21	20.99	5.84	4.21	18.40	5.67	24.90	9.56	2.96	12.83	17.27	<2.66	5.90	2.74	2.08	5.84	0.48	<0.14	2.74	0.38	0.07	<0.07
	42.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	30.33	15.84	<4.91	3.42	13.18	4.66	18.40	7.12	2.40	9.19	12.12	<2.66	4.65	1.99	1.60	4.53	0.38	<0.14	2.10	0.28	0.07	<0.07
	47.5	<23.07	<28.69	16.79	<18.96	<10.29	<6.23	27.68	14.09	<4.91	5.04	19.17	35.59	25.91	9.73	3.54	12.38	13.88	<2.66	6.75	2.54	2.07	6.08	0.48	<0.14	2.77	0.44	0.08	<0.07
Sample ID	Depth (cm)	8	5	18	16	32	28	52	44	66	101	110	118	153	132	105	164	138	126	187	183	128+167	174	193	169	170	195	206	209
Control - Center																													
	2.5	<23.07	<28.69	16.19	<18.96	<10.29	7.32	13.08	6.50	<4.91	2.56	3.73	2.44	2.55	1.21	1.55	1.20	1.01	<2.66	0.76	0.25	0.51	0.48	0.19	<0.14	0.19	0.13	<0.44	<0.07
	7.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	13.20	5.74	<4.91	4.71	5.27	3.52	4.67	1.97	2.29	1.82	2.47	<2.66	0.63	0.42	0.75	0.87	0.23	<0.14	0.50	0.15	0.05	<0.07
	12.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	12.68	6.55	<4.91	4.35	5.39	2.24	6.98	2.38	1.51	1.95	3.31	<2.66	0.34	0.69	0.62	1.61	0.26	<0.14	0.80	0.22	<0.44	<0.07
	17.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	12.80	6.68	<4.91	5.04	5.83	2.79	7.04	2.76	1.58	4.04	3.79	<2.66	1.28	0.75	0.52	1.86	0.30	<0.14	0.82	0.22	<0.44	<0.07
	22.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	11.23	<5.24	<4.91	5.45	6.52	3.27	10.72	4.16	1.56	5.66	5.93	<2.66	0.51	1.10	0.82	2.89	0.41	<0.14	1.80	0.26	0.05	<0.07
	27.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	10.65	<5.24	<4.91	7.96	10.30	4.58	19.78	6.74	1.68	8.74	11.02	<2.66	2.52	2.09	1.07	4.98	0.45	<0.14	2.37	0.37	0.09	<0.07
	32.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	18.52	7.63	<4.91	12.94	17.41	5.61	31.21	12.19	2.44	14.05	17.83	<2.66	4.08	3.48	1.62	7.85	0.60	<0.14	3.79	0.46	0.06	<0.07
	37.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	18.53	7.02	<4.91	18.82	23.29	6.56	46.89	19.22	2.39	25.02	18.46	<2.66	5.69	5.03	1.96	11.78	0.84	<0.14	5.44	0.63	0.10	<0.07
	42.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	17.87	5.94	<4.91	17.79	25.63	6.10	47.99	19.95	2.39	23.43	21.51	<2.66	5.85	5.35	2.08	11.92	0.86	<0.14	5.51	0.59	0.12	<0.07
	47.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	21.33	8.63	<4.91	15.83	21.06	6.12	35.29	14.00	2.24	17.70	16.71	<2.66	4.13	3.82	1.75	8.37	0.69	<0.14	4.27	0.50	0.11	<0.07
	52.5	<23.07	<28.69	35.17	<18.96	15.56	16.24	34.57	15.07	7.37	31.04	40.48	7.80	70.91	31.52	3.56	28.44	33.78	<2.66	7.68	7.94	2.54	17.01	0.96	<0.14	8.25	0.84	0.11	<0.07
	57.5	<23.07	<28.69	19.51	<18.96	<10.29	7.25	22.66	7.82	5.36	24.47	31.11	21.39	53.47	24.71	3.82	23.50	23.44	<2.66	6.14	5.91	2.33	13.22	0.85	<0.14	6.26	0.73	0.07	<0.07
Sample ID	Depth (cm)	8	5	18	16	32	28	52	44	66	101	110	118	153	132	105	164	138	126	187	183	128+167	174	193	169	170	195	206	209
Control - South																													
	2.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	12.26	6.67	<4.91	4.15	4.30	10.92	3.20	1.15	1.75	1.46	1.20	<2.66	0.97	0.28	0.84	0.74	0.21	<0.14	0.37	0.16	<0.44	<0.07
	7.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	13.68	6.80	<4.91	3.76	4.20	1.43	2.48	1.27	1.52	1.30	1.22	<2.66	0.69	<0.22	0.41	0.59	0.20	<0.14	0.29	0.12	<0.44	<0.07
	12.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	14.91	7.92	<4.91	3.58	4.21	1.49	3.04	1.29	1.53	1.43	1.14	<2.66	0.85	0.26	0.56	0.75	0.23	<0.14	0.34	0.14	<0.44	<0.07
	17.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	17.49	8.48	<4.91	4.96	5.48	1.27	5.53	1.87	1.67	2.50	2.19	<2.66	1.53	0.54	0.69	1.25	0.26	<0.14	0.64	0.18	0.05	<0.07
	22.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	11.52	5.91	<4.91	4.27	4.62	1.10	6.75	2.31	1.51	3.17	2.72	<2.66	1.78	0.61	0.72	1.59	0.27	<0.14	0.68	0.19	0.04	<0.07
	27.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	12.56	6.54	<4.91	5.61	6.84	1.31	9.40	3.14	1.75	4.67	3.86	<2.66	2.64	0.90	0.83	2.45	0.28	<0.14	1.29	0.26	0.07	<0.07
	32.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	10.06	<5.24	<4.91	4.09	5.60	0.87	8.79	2.95	1.49	4.84	3.79	<2.66	2.65	1.01	0.87	2.44	0.29	<0.14	1.13	0.25	0.05	<0.07
	37.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	12.90	6.85	<4.91	5.71	7.20	1.57	10.65	3.82	1.16	4.69	4.04	<2.66	3.17	1.25	0.81	2.93	0.35	<0.14	1.34	0.23	0.06	<0.07
	42.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	11.19	6.44	<4.91	5.17	6.27	1.12	9.72	3.72	1.60	4.19	4.08	<2.66	2.73	1.02	0.94	2.51	0.37	<0.14	1.37	0.22	0.06	<0.07
	47.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	13.67	5.75	<4.91	8.94	12.07	2.49	19.71	7.49	1.83	9.59	9.49	<2.66	4.78	2.09	1.12	4.66	0.49	<0.14	2.28	0.32	0.06	<0.07
	52.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	10.69	<5.24	<4.91	11.31	14.37	19.80	25.16	9.61	2.17	8.68	12.77	<2.66	6.40	2.84	1.43	6.34	0.51	<0.14	2.77	0.42	0.09	<0.07
Sample ID	Depth (cm)	8	5	18	16	32	28	52	44	66	101	110	118	153	132	105	164	138	126	187	183	128+167	174	193	169	170	195	206	209
SediMite - North																													
	2.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	8.71	<5.24	<4.91	1.94	2.77	18.72	3.57	1.12	1.94	1.72	1.47	<2.66	1.17	0.32	0.47	0.92	0.30	<0.14	0.32	0.21	0.04	<0.07
	7.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	14.76	5.81	<4.91	2.32	2.93	<0.60	5.55	2.23	1.34	3.02	2.14	<2.66	2.02	0.70	0.43	1.67	0.28	<0.14	0.89	0.22	0.05	<0.07
	12.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	8.04	<5.24	<4.91	2.02	2.27	0.73	3.89	1.76	1.30	1.77	2.11	<2.66	1.43	0.54	0.39	1.10	0.21	<0.14	0.53	0.18	0.04	<0.07
	17.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	11.68	<5.24	<4.91	4.45	5.62	1.49	11.89	4.43	1.59	6.53	4.99	<2.66	3.11	1.30	0.74	2.91	0.38	<0.14	1.36	0.25	0.06	<0.07
	22.5	<23.07	<28.69	<15.92	21.90	11.32	<6.23	10.99	<5.24	5.20	5.42	7.34	1.44	7.69	3.22	4.99	2.30	3.87	2.98	3.39	0.74	1.18	2.47	0.97	<0.14	1.14	0.67	0.17	0.13
	27.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	21.30	7.79	<4.91	5.81	7.10	1.94	14.93	5.73	2.03	6.96	6.99	<2.66	4.43	1.58	0.89	3.72	0.38	<0.14	1.78	0.31	0.06	<0.07
	32.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	16.52	6.58	<4.91	5.52	7.78	1.40	17.72	5.30	1.82	7.63	5.32	<2.66	4.99	1.88	1.00	4.14	0.47	<0.14	2.25	0.39	0.09	<0.07
	37.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	15.97	6.45	<4.91	4.17	5.98	1.72	11.64	3.82	1.57	5.63	4.98	<2.66	3.31	1.28	0.77	3.11	0.37	<0.14	1.59	0.30	0.07	<0.07
	42.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	14.55	6.05	<4.91	5.23	7.17	1.16	13.25	5.59	1.64	6.45	4.00	<2.66	3.76	1.62	0.75	3.38	0.32	<0.14	1.55	0.33	0.06	<0.07
	47.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	26.76	8.89	6.80	24.58	33.69	6.08	71.77	28.47	3.23	34.06	19.01	<2.66	17.20	7.69	2.62	17.02	1.11	<0.14	7.63	0.85	0.11	<0.07
	52.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	10.64	<5.24	<4.91	9.65	13.73	2.47	30.26	12.17	1.84	13.08	11.63	<2.66	7.85	3.67	1.33	7.74	0.67	<0.14	3.14	0.53	0.10	<0.07
Sample ID	Depth (cm)	8	5	18	16	32	28	52	44	66	101	110	118	153	132	105	164	138	126	187	183	128+167	174	193	169	170	195	206	209
SediMite - Center																													
	2.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	16.74	8.38	<4.91	3.01	3.06	2.45	2.63	1.59	1.57	1.26	1.31	<2.66	1.11	0.46	0.46	0.77	0.24	<0.14	0.48	0.21	0.05	<0.07
	7.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	4.52	<5.24	<4.91	2.02	1.92	1.07	1.36	<0.86	1.30	<0.88	0.88	<2.66	0.68	<0.22	<0.34	0.55	0.20	<0.14	<0.19	0.15	0.05	<0.07
	12.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	7.24	<5.24	<4.91	3.44	3.33	1.84	3.52	1.90	1.64	1.35	1.66	<2.66	1.46	0.49	0.51	1.18	0.25	<0.14	0.54	0.22	<0.44	<0.07
	17.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	6.24	<5.24	<4.91	2.92	2.92	2.07	3.46	1.31	1.21	1.47	1.35	<2.66	1.44	0.43	0.46	1.10	0.22	<0.14	0.47	0.17	0.05	<0.07
	22.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	9.08	<5.24	<4.91	3.47	4.22	1.84	6.46	2.59	1.40	2.79	2.97	<2.66	2.04	0.72	0.51	1.68	0.28	<0.14	1.01	0.26	0.05	<0.07
	27.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	9.54	<5.24	<4.91	4.48	6.67	2.06	11.95	3.94	1.22	4.37	5.24	<2.66	3.47	1.42	0.67	2.91	0.30	<0.14	1.36	0.37	0.05	<0.07
	32.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	6.91	<5.24	<4.91	5.26	6.98	4.37	7.82	3.09	1.78	2.71	3.79	<2.66	2.54	0.99	0.61	2.30	0.31	<0.14	0.99	0.22	0.06	<0.07
	37.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	7.01	<5.24	<4.91	3.47	4.89	1.92	7.26	2.30	1.33	3.41	2.41	<2.66	2.09	0.76	0.50	1.87	0.28	<0.14	0.83	0.28	0.04	<0.07
	42.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	11.67	6.28	<4.91	7.32	8.54	2.30	14.31	4.96	1.71	5.78	7.10	<2.66	3.95	1.57	0.69	3.45	0.37	<0.14	1.78	0.30	0.06	<0.07
	47.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	10.94	<5.24	<4.91	10.77	14.53	3.24	29.83	11.35	1.95	11.78	12.87	<2.66	8.24	3.62	1.28	7.24	0.69	<0.14	3.34	0.55	0.09	<0.07
	52.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	8.41	<5.24	<4.91	7.96	11.46	2.63	23.99	9.13	2.08	10.40	10.40	<2.66	7.22	3.12	1.08	6.49	0.56	<0.14	3.04	0.50	0.07	<0.07
Sample ID	Depth (cm)	8	5	18	16	32	28	52	44	66	101	110	118	153	132	105	164	138	126	187	183	128+167	174	193	169	170	195	206	209
SediMite - South																													
	2.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	9.59	<5.24	<4.91	2.65	2.41	1.54	3.21	1.35	1.10	1.27	1.59	<2.66	1.25	0.46	0.38	1.07	0.20	<0.14	0.41	0.17	0.04	<0.07
	7.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	10.33	<5.24	<4.91	3.80	3.82	2.04	6.83	2.53	1.66	3.03	3.09	<2.66	2.60	0.90	0.56	2.10	0.25	<0.14	0.98	0.23	0.04	<0.07
	12.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	12.00	<5.24	<4.91	3.87	4.33	2.11	7.42	3.16	1.38	2.74	2.95	<2.66	2.36	0.99	0.60	2.02	0.28	<0.14	1.00	0.25	<0.44	<0.07
	17.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	14.67	6.66	<4.91	8.51	9.35	3.38	21.18	8.37	1.41	9.53	9.71	<2.66	6.37	2.77	0.91	5.72	0.51	<0.14	2.26	0.41	0.06	<0.07
	22.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	16.79	6.82	<4.91	12.10	13.87	3.91	25.82	10.67	1.84	10.01	10.40	<2.66	7.38	3.16	1.17	6.84	0.53	<0.14	2.78	0.41	0.09	<0.07
	27.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	13.85	5.93	<4.91	13.49	16.57	5.25	31.76	13.57	2.07	13.13	16.87	<2.66	7.86	3.57	1.35	7.97	0.59	<0.14	3.54	0.45	0.08	<0.07
	32.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	19.67	7.46	<4.91	24.30	30.73	6.09	67.15	26.34	2.58	31.74	28.69	<2.66	16.40	7.54	2.59	18.05	1.17	<0.14	7.56	0.72	0.13	<0.07
	37.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	16.89	6.57	<4.91	18.98	25.78	5.44	49.70	21.22	2.34	21.82	20.45	<2.66	11.65	5.40	2.24	12.34	0.87	<0.14	6.18	0.71	0.10	<0.07
	42.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	18.40	7.88	<4.91	13.97	18.52	5.08	29.38	12.22	2.37	14.84	13.63	<2.66	7.51	3.56	1.69	7.92	0.70	<0.14	3.62	0.47	0.09	<0.07
	47.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	8.46	<5.24	<4.91	6.07	7.19	2.57	12.28	5.04	1.36	4.23	4.41	<2.66	3.94	1.52	0.82	3.61	0.30	<0.14	1.45	0.30	0.05	<0.07
	52.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	8.99	<5.24	<4.91	6.09	6.64	3.54	11.82	5.08	1.46	4.69	6.10	<2.66	3.41	1.30	0.75	3.18	0.29	<0.14	1.24	0.26	0.06	<0.07
Sample ID	Depth (cm)	8	5	18	16	32	28	52	44	66	101	110	118	153	132	105	164	138	126	187	183	128+167	174	193	169	170	195	206	209
SediMite + Bioaugmented - North																													
	2.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	17.88	8.43	<4.91	3.41	4.37	10.87	5.68	2.43	1.86	2.34	2.65	<2.66	1.88	0.76	0.83	1.57	0.25	<0.14	0.50	0.21	0.06	<0.07
	7.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	9.80	<5.24	<4.91	3.12	4.44	1.56	6.50	2.62	1.55	2.92	2.66	<2.66	2.07	0.78	1.04	1.90	0.27	<0.14	0.71	0.18	<0.44	<0.07
	12.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	11.28	<5.24	<4.91	4.21	5.33	1.76	7.36	3.11	1.87	2.82	3.31	<2.66	2.21	0.88	1.25	2.14	0.30	<0.14	0.81	0.21	0.08	<0.07
	17.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	9.58	<5.24	<4.91	3.37	5.06	1.67	8.58	3.18	1.66	3.63	3.03	<2.66	2.72	0.98	0.85	2.53	0.31	<0.14	1.12	0.22	0.05	<0.07
	22.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	5.37	<5.24	<4.91	3.07	4.55	<0.60	6.86	3.15	3.38	3.29	3.44	<2.66	3.33	0.90	1.29	2.70	0.84	<0.14	1.24	0.51	0.09	0.09
	27.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	<4.30	<5.24	<4.91	<1.33	1.53	<0.60	3.64	1.46	0.88	5.23	4.51	<2.66	1.79	0.67	0.76	1.62	0.36	<0.14	0.70	0.20	0.04	<0.07
	32.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	<4.30	<5.24	<4.91	<1.33	<1.07	<0.60	0.41	<0.86	1.20	<0.88	1.16	<2.66	0.39	<0.22	0.46	0.34	0.26	<0.14	<0.19	0.20	0.04	<0.07
	37.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	<4.30	<5.24	<4.91	3.24	3.73	<0.60	13.70	5.61	1.01	<0.88	<0.50	<2.66	4.40	1.99	1.02	4.68	0.17	<0.14	1.90	0.13	<0.44	<0.07
	42.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	6.89	<5.24	4.96	10.45	12.25	0.79	38.45	17.41	4.52	19.38	23.44	3.62	13.28	5.79	2.04	12.30	1.48	<0.14	5.26	1.19	0.21	0.10
Sample ID	Depth (cm)	8	5	18	16	32	28	52	44	66	101	110	118	153	132	105	164	138	126	187	183	128+167	174	193	169	170	195	206	209
SediMite + Bioaugmented - Center																													
	2.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	17.29	6.95	<4.91	8.99	10.80	2.30	17.75	7.65	1.60	6.92	9.83	<2.66	4.87	2.16	0.94	4.58	0.38	<0.14	1.46	0.29	0.05	<0.07
	7.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	18.25	8.27	<4.91	3.62	4.64	1.09	3.84	2.00	1.30	1.40	2.35	<2.66	1.53	0.47	0.53	1.28	0.23	<0.14	0.44	0.14	0.04	<0.07
	12.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	22.43	10.03	<4.91	4.77	5.47	1.90	4.13	1.96	1.78	1.17	2.07	<2.66	1.51	0.61	0.68	1.37	0.26	<0.14	0.51	0.23	0.04	<0.07
	17.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	22.24	9.90	<4.91	3.99	4.88	2.10	2.94	1.56	1.71	1.65	1.83	<2.66	1.28	0.37	0.52	1.01	0.20	<0.14	0.37	0.19	0.05	<0.07
	22.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	27.62	12.88	<4.91	5.56	5.11	2.09	3.71	1.87	1.92	1.48	1.53	<2.66	1.49	0.45	0.71	1.25	0.25	<0.14	0.34	0.17	0.04	<0.07
	27.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	28.18	13.47	<4.91	5.82	5.84	1.83	4.54	2.05	1.96	1.40	2.08	<2.66	1.65	0.56	0.67	1.35	0.28	<0.14	0.64	0.18	<0.44	<0.07
	32.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	24.79	11.23	<4.91	5.41	5.11	1.66	4.04	1.97	1.43	1.80	1.59	<2.66	1.50	0.53	0.58	1.23	0.25	<0.14	0.50	0.12	<0.44	<0.07
	37.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	18.84	9.29	<4.91	4.39	4.73	1.50	2.38	0.95	1.51	0.95	0.98	<2.66	0.64	<0.22	0.52	0.52	0.21	<0.14	0.25	0.12	<0.44	<0.07
	42.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	17.48	8.70	<4.91	4.44	5.35	1.45	2.79	1.41	1.64	1.26	1.19	<2.66	0.81	0.24	0.63	0.56	0.21	<0.14	0.22	0.15	<0.44	<0.07
	47.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	13.72	7.65	<4.91	3.09	3.48	2.30	1.27	<0.86	1.48	<0.88	0.63	<2.66	0.42	<0.22	0.54	0.37	0.18	<0.14	<0.19	0.13	<0.44	<0.07
Sample ID	Depth (cm)	8	5	18	16	32	28	52	44	66	101	110	118	153	132	105	164	138	126	187	183	128+167	174	193	169	170	195	206	209
SediMite + Bioaugmented - South																													
	2.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	23.18	5.74	<4.91	16.52	19.71	10.04	33.91	15.34	2.97	12.49	14.66	<2.66	8.96	3.79	1.77	8.27	0.59	<0.14	3.44	0.43	0.10	<0.07
	7.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	9.55	<5.24	<4.91	4.90	6.62	1.99	7.58	3.44	1.57	3.25	3.76	<2.66	2.19	0.78	0.97	1.94	0.28	<0.14	0.61	0.18	0.04	<0.07
	12.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	8.26	<5.24	<4.91	3.29	3.41	1.39	3.35	1.53	1.52	<0.88	1.75	<2.66	1.19	0.47	0.58	1.14	0.20	<0.14	0.47	0.15	0.06	<0.07
	17.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	13.97	5.95	<4.91	4.25	3.77	1.06	3.76	1.75	1.52	1.67	2.18	<2.66	1.66	0.60	0.52	1.46	0.24	<0.14	0.72	0.22	0.04	<0.07
	22.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	13.93	6.22	<4.91	4.10	3.98	<0.60	4.59	1.94	1.72	1.64	2.42	<2.66	1.78	0.56	0.60	1.51	0.27	<0.14	0.76	0.22	0.06	<0.07
	27.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	14.11	<5.24	<4.91	6.41	7.04	2.37	17.63	6.37	1.53	6.47	8.45	<2.66	5.78	2.49	1.17	5.32	0.46	<0.14	2.62	0.40	0.09	<0.07
	32.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	11.11	<5.24	<4.91	4.86	6.12	1.56	11.41	4.20	1.52	5.10	4.97	<2.66	3.82	1.47	0.91	3.54	0.38	<0.14	1.47	0.29	0.05	<0.07
	37.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	14.33	6.41	<4.91	5.33	6.93	1.14	11.18	4.34	1.83	5.20	4.78	<2.66	3.77	1.36	1.20	3.01	0.44	<0.14	1.01	0.27	0.05	<0.07
	42.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	16.90	8.22	<4.91	5.70	7.83	2.22	11.26	4.37	1.94	3.67	4.80	<2.66	3.25	1.07	0.89	2.59	0.40	<0.14	1.12	0.22	0.06	<0.07
	47.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	8.10	<5.24	<4.91	3.50	3.85	1.28	3.71	1.57	1.69	1.46	2.12	<2.66	1.55	0.58	0.73	1.23	0.22	<0.14	0.70	0.21	0.06	<0.07
	52.5	<23.07	<28.69	<15.92	<18.96	<10.29	<6.23	20.63	10.18	<4.91	3.98	4.53	1.52	4.72	2.18	1.30	2.12	3.11	<2.66	1.96	0.59	0.59	1.58	0.24	<0.14	0.61	0.19	0.04	<0.07

APPENDIX F3. QUANTICO EMBAYMENT

Embayment DDX sHRPP

		Cpw (ng/L)					
Sample ID	Depth (cm)	op-DDE	pp-DDE	op-DDD	pp-DDD	op-DDT	pp-DDT
PQL =		**0.11**	**0.08**	**0.16**	**0.22**	**0.05**	**0.21**
L1: 9 ft - South							
1	-1	<0.11	1.53	1.00	2.21	0.09	<0.21
3	2	<0.11	0.68	0.94	2.19	0.11	<0.21
5	5	<0.11	0.57	0.86	1.79	0.09	<0.21
7	7	<0.11	0.89	1.26	2.57	0.09	<0.21
9	10	<0.11	0.77	1.07	1.98	0.08	<0.21
11	12	<0.11	0.60	0.85	1.68	0.10	0.22
13	15	<0.11	0.63	1.03	2.00	0.09	<0.21
15	17	<0.11	0.65	1.03	2.00	0.09	<0.21
16	24	<0.11	0.52	0.81	1.87	0.08	<0.21
18	26	<0.11	0.57	1.08	2.60	0.08	<0.21
20	29	<0.11	0.41	0.80	2.24	0.10	<0.21
22	32	<0.11	0.28	0.68	2.00	0.07	<0.21
24	34	<0.11	0.22	0.51	1.58	0.09	<0.21
26	37	<0.11	0.40	0.75	2.21	0.06	<0.21
28	39	<0.11	0.32	0.67	1.96	0.08	<0.21
30	42	<0.11	0.58	0.90	2.43	0.09	<0.21
31	48	<0.11	0.53	0.70	2.26	0.06	<0.21
33	51	<0.11	0.43	0.80	3.83	0.07	<0.21
35	53	<0.11	0.45	0.73	6.82	0.06	<0.21
37	56	<0.11	0.40	0.74	3.54	<0.05	<0.21
39	59	<0.11	0.45	0.78	2.28	0.05	<0.21
41	61	<0.11	0.75	0.93	2.61	<0.05	<0.21
43	64	<0.11	0.31	0.61	7.46	0.09	<0.21
45	66	<0.11	0.88	1.12	9.84	0.07	<0.21
Sample ID	Depth (cm)	op-DDE	pp-DDE	op-DDD	pp-DDD	op-DDT	pp-DDT
L1: 9 ft - Center							
1	1	<0.11	0.56	1.18	2.76	0.16	0.28
3	4	<0.11	0.35	0.82	2.25	0.11	0.24
5	7	<0.11	0.35	0.86	2.18	0.11	0.35
7	9	<0.11	0.37	0.84	1.94	0.14	0.37
9	12	<0.11	0.31	0.85	1.98	0.16	0.33
11	14	<0.11	0.34	0.75	1.72	0.11	0.31
13	17	<0.11	0.32	0.83	1.86	0.10	<0.21
15	19	<0.11	0.43	0.78	1.89	0.12	0.23
16	26	<0.11	0.38	0.86	2.06	0.08	<0.21
18	28	<0.11	0.35	0.84	1.94	0.13	<0.21
20	31	<0.11	0.25	0.79	1.96	0.11	<0.21
22	34	<0.11	0.27	0.86	2.28	0.13	<0.21
24	36	<0.11	0.24	0.80	2.25	0.15	<0.21
26	39	<0.11	0.33	0.91	2.43	0.10	<0.21
28	41	<0.11	0.32	0.82	2.16	0.07	<0.21
30	44	<0.11	0.36	0.93	2.40	0.09	<0.21

31	50	<0.11	0.21	0.53	1.26	0.13	<0.21
33	53	<0.11	0.36	0.76	2.19	0.09	<0.21
35	55	<0.11	0.28	0.74	2.06	0.07	<0.21
37	58	<0.11	0.38	0.79	2.26	0.10	<0.21
39	61	<0.11	0.29	0.78	2.13	0.12	<0.21
41	63	<0.11	0.28	0.72	2.00	0.11	<0.21
43	66	<0.11	0.36	0.87	2.35	0.10	<0.21
45	68	<0.11	0.55	1.33	3.77	0.16	<0.21

Sample ID	Depth (cm)	op-DDE	pp-DDE	op-DDD	pp-DDD	op-DDT	pp-DDT
L1: 9 ft - North							
1	2	<0.11	0.11	0.85	2.59	0.14	1.00
3	5	<0.11	0.13	0.85	2.33	0.17	0.92
5	8	<0.11	0.11	0.73	2.18	0.15	0.39
7	10	<0.11	0.16	0.75	2.30	0.15	0.42
9	13	<0.11	0.22	0.94	2.66	0.18	0.71
11	15	<0.11	0.19	0.97	2.60	0.12	0.63
13	18	<0.11	0.21	0.92	2.79	0.26	0.55
15	20	<0.11	0.12	0.64	1.70	0.15	0.57
16	27	<0.11	0.19	0.70	2.27	0.13	0.27
18	29	<0.11	0.17	0.93	2.47	0.10	0.67
20	32	<0.11	0.15	0.71	1.93	0.10	0.40
22	35	<0.11	0.22	0.80	2.08	0.12	0.51
24	37	<0.11	0.14	0.55	1.51	0.06	0.37
26	40	<0.11	0.19	0.72	1.85	0.09	0.31
28	42	<0.11	0.18	0.75	2.09	0.12	0.41
30	45	<0.11	0.20	0.90	2.46	0.10	0.43
31	51	<0.11	0.25	0.80	1.97	0.14	0.58
33	54	<0.11	0.27	0.90	2.68	0.15	0.68
35	56	<0.11	0.20	0.70	2.09	0.10	0.26
37	59	<0.11	0.24	0.86	2.59	0.14	0.52
39	62	<0.11	0.25	0.95	2.89	0.16	0.71
41	64	<0.11	0.21	0.95	2.50	0.09	0.68
43	67	<0.11	0.23	0.84	2.05	0.09	1.05
45	69	<0.11	0.27	1.48	5.31	0.13	0.61

Sample ID	Depth (cm)	op-DDE	pp-DDE	op-DDD	pp-DDD	op-DDT	pp-DDT
L2: 50 ft - South							
1	-3	<0.11	0.13	1.51	3.57	0.10	<0.21
3	-2	<0.11	0.11	2.02	4.69	0.15	0.21
5	1	<0.11	0.11	1.30	3.26	0.11	<0.21
7	3	<0.11	0.10	0.98	2.55	0.11	<0.21
9	6	<0.11	0.13	0.54	1.93	0.10	<0.21
11	8	<0.11	0.08	0.24	0.76	<0.05	<0.21
13	11	<0.11	<0.08	0.17	0.65	0.10	<0.21
15	13	<0.11	<0.08	<0.16	0.59	0.08	<0.21
16	20	<0.11	<0.08	<0.16	0.26	0.08	<0.21
18	22	<0.11	<0.08	<0.16	0.42	0.06	<0.21
20	25	<0.11	<0.08	<0.16	0.52	0.08	<0.21

	22	28	<0.11	<0.08	<0.16	0.60	0.06	<0.21
	24	30	<0.11	<0.08	<0.16	0.62	0.08	<0.21
	26	33	<0.11	<0.08	<0.16	0.56	<0.05	<0.21
	28	35	<0.11	<0.08	<0.16	0.55	0.06	<0.21
	30	38	<0.11	<0.08	<0.16	0.58	0.06	<0.21
	31	44	<0.11	<0.08	<0.16	0.56	0.09	<0.21
	33	47	<0.11	<0.08	<0.16	0.55	0.24	<0.21
	35	49	<0.11	<0.08	<0.16	0.40	<0.05	<0.21
	37	52	<0.11	<0.08	<0.16	0.49	0.07	<0.21
	39	55	<0.11	<0.08	<0.16	0.52	0.06	<0.21
	41	57	<0.11	<0.08	<0.16	0.51	0.05	<0.21
	43	60	<0.11	<0.08	<0.16	0.56	0.05	<0.21
	45	62	<0.11	<0.08	<0.16	0.62	<0.05	<0.21

Sample ID	Depth (cm)	op-DDE	pp-DDE	op-DDD	pp-DDD	op-DDT	pp-DDT
L2: 50 ft - Center							
1	-4	<0.11	0.22	4.68	7.83	0.14	<0.21
3	-1	<0.11	0.22	5.18	8.68	0.13	<0.21
5	2	<0.11	0.21	4.12	7.17	0.12	<0.21
7	4	<0.11	0.16	3.09	5.80	0.08	<0.21
9	7	<0.11	0.13	2.52	4.81	0.05	<0.21
11	9	<0.11	0.14	1.33	2.64	0.09	<0.21
13	12	<0.11	0.15	0.65	1.30	0.10	<0.21
15	14	<0.11	0.13	0.72	1.44	0.08	<0.21
16	21	<0.11	0.30	1.70	3.38	0.05	<0.21
18	23	<0.11	0.23	1.15	2.54	0.07	<0.21
20	26	<0.11	0.22	0.49	1.06	0.06	<0.21
22	29	<0.11	0.28	0.48	1.01	0.09	<0.21
24	31	<0.11	0.23	0.44	0.92	0.06	<0.21
26	34	<0.11	0.43	0.43	0.94	0.05	<0.21
28	36	<0.11	0.67	0.43	0.96	0.07	<0.21
30	39	<0.11	0.52	0.38	0.86	0.11	<0.21
31	45	<0.11	0.48	0.37	0.99	0.05	<0.21
33	48	<0.11	0.26	0.44	0.86	0.08	<0.21
35	50	<0.11	0.31	0.33	0.87	0.11	<0.21
37	53	<0.11	0.23	0.41	1.16	0.14	<0.21
39	56	<0.11	0.28	0.38	0.95	0.07	<0.21
41	58	<0.11	0.27	0.41	1.07	0.11	<0.21
43	61	<0.11	0.46	0.55	1.30	0.07	<0.21
45	63	<0.11	0.40	0.54	1.45	0.09	<0.21

Sample ID	Depth (cm)	op-DDE	pp-DDE	op-DDD	pp-DDD	op-DDT	pp-DDT
L2: 50 ft - North							
1	-8	<0.11	0.16	2.01	4.64	0.23	1.40
2	-6	<0.11	0.17	2.44	6.15	0.31	1.87
5	-2	<0.11	0.13	2.36	5.14	0.21	1.90
7	0	<0.11	0.13	2.03	4.82	0.22	2.75
9	3	<0.11	0.12	1.04	2.68	0.30	1.50
11	5	<0.11	0.12	0.47	1.11	0.23	1.20

13	8	<0.11	0.11	0.32	1.03	0.25	0.82	
15	10	<0.11	<0.08	0.28	0.76	0.19	1.11	
16	17	<0.11	<0.08	0.19	0.62	0.16	0.76	
18	19	<0.11	<0.08	0.17	0.90	0.15	0.52	
20	22	<0.11	<0.08	0.19	1.42	0.21	0.90	
22	25	<0.11	<0.08	0.16	1.13	0.13	0.59	
24	27	<0.11	<0.08	<0.16	0.80	0.12	0.84	
26	30	<0.11	<0.08	0.19	0.66	0.11	0.44	
28	32	<0.11	<0.08	0.16	0.76	0.15	0.55	
30	35	<0.11	<0.08	0.23	0.60	0.08	0.79	
33	44	<0.11	<0.08	0.28	0.64	0.15	0.85	
35	46	<0.11	<0.08	0.43	1.61	0.11	0.50	
37	49	<0.11	<0.08	<0.16	0.65	0.15	0.55	
39	52	<0.11	<0.08	0.41	1.78	0.15	0.73	
41	54	<0.11	<0.08	0.23	1.02	0.14	0.75	
43	57	<0.11	<0.08	0.62	2.43	0.12	0.80	
45	59	<0.11	<0.08	0.56	1.91	0.08	0.54	

Sample ID	Depth (cm)	op-DDE	pp-DDE	op-DDD	pp-DDD	op-DDT	pp-DDT
L3: 100 ft - South							
1	-2	<0.11	0.21	0.59	1.80	0.09	<0.21
3	1	<0.11	0.13	0.26	1.26	0.07	<0.21
5	4	<0.11	0.09	<0.16	0.48	0.08	<0.21
7	6	<0.11	<0.08	<0.16	0.35	0.08	<0.21
9	9	<0.11	<0.08	<0.16	0.38	0.07	<0.21
11	11	<0.11	<0.08	<0.16	0.33	0.08	<0.21
13	14	<0.11	<0.08	<0.16	0.39	0.06	<0.21
15	16	<0.11	<0.08	<0.16	0.43	0.07	<0.21
16	23	<0.11	<0.08	<0.16	0.49	0.05	<0.21
18	25	<0.11	<0.08	<0.16	0.43	<0.05	<0.21
20	28	<0.11	<0.08	<0.16	0.53	0.11	<0.21
22	31	<0.11	0.08	<0.16	0.56	0.05	<0.21
24	33	<0.11	<0.08	<0.16	0.61	0.06	<0.21
26	36	<0.11	<0.08	<0.16	0.62	0.06	<0.21
28	38	<0.11	<0.08	<0.16	1.88	0.07	<0.21
30	41	<0.11	<0.08	<0.16	2.65	0.09	<0.21
31	47	<0.11	0.15	0.16	0.85	0.06	<0.21
33	50	<0.11	0.10	<0.16	1.15	0.05	<0.21
35	52	<0.11	0.11	<0.16	0.84	0.06	<0.21
37	55	<0.11	0.11	<0.16	0.71	0.05	<0.21
39	58	<0.11	0.15	<0.16	0.57	0.09	0.22
41	60	<0.11	0.17	<0.16	0.69	0.10	0.27
43	63	<0.11	0.14	<0.16	0.64	0.08	0.31
45	65	<0.11	0.19	<0.16	1.18	0.11	0.29

Sample ID	Depth (cm)	op-DDE	pp-DDE	op-DDD	pp-DDD	op-DDT	pp-DDT
L3: 100 ft - Center							
1	-2	<0.11	0.28	0.86	1.73	0.08	0.23
3	-1	<0.11	0.29	1.01	1.99	0.05	<0.21

5	2	<0.11	0.30	1.24	2.92	0.16	0.23
7	4	<0.11	0.25	0.91	2.47	0.21	0.50
9	7	<0.11	0.26	0.57	1.35	0.20	0.33
11	9	<0.11	0.20	0.36	0.85	0.23	0.30
13	12	<0.11	0.21	0.40	1.02	0.20	<0.21
15	14	<0.11	0.18	0.35	0.72	0.14	0.23
16	21	<0.11	0.27	0.56	1.22	0.13	0.33
18	23	<0.11	0.22	0.30	0.92	0.10	0.22
20	26	<0.11	0.18	0.30	0.79	0.11	<0.21
22	29	<0.11	0.16	0.30	0.73	0.12	<0.21
24	31	<0.11	0.18	0.30	0.85	0.13	<0.21
26	34	<0.11	0.20	0.32	1.10	0.08	0.22
28	36	<0.11	0.33	0.49	1.17	0.13	0.23
30	39	<0.11	0.39	0.54	1.51	0.12	0.28
31	45	<0.11	0.36	0.56	1.25	0.11	<0.21
33	48	<0.11	0.32	0.47	1.21	0.10	<0.21
35	50	<0.11	0.28	0.48	1.17	0.08	<0.21
37	53	<0.11	0.24	0.45	1.08	0.13	<0.21
39	56	<0.11	0.33	0.53	1.26	0.11	<0.21
41	58	<0.11	0.30	0.53	1.18	0.15	<0.21
43	61	<0.11	0.20	0.37	1.01	0.12	<0.21
45	63	<0.11	0.12	0.27	0.88	0.16	<0.21

Sample ID	Depth (cm)	op-DDE	pp-DDE	op-DDD	pp-DDD	op-DDT	pp-DDT
L3: 100 ft - North							
1	-1	<0.11	0.34	1.06	2.10	0.29	1.73
3	0	<0.11	0.38	4.21	10.84	0.24	1.55
5	3	<0.11	0.24	0.80	2.02	1.14	4.44
7	5	<0.11	0.20	0.51	0.96	0.60	2.52
9	8	<0.11	0.22	0.27	0.66	0.87	2.13
11	10	<0.11	0.22	0.22	0.39	0.64	2.46
13	13	<0.11	0.21	0.32	0.78	0.44	1.92
15	15	<0.11	0.25	0.32	1.16	0.52	1.53
16	22	<0.11	0.18	0.24	0.68	0.32	1.35
18	24	<0.11	0.19	0.20	0.42	0.36	1.05
20	27	<0.11	0.19	0.21	0.40	0.22	1.29
22	30	<0.11	0.20	<0.16	0.40	0.20	1.75
24	32	<0.11	0.15	<0.16	0.36	0.25	1.20
26	35	<0.11	0.13	0.25	0.57	0.28	1.54
28	37	<0.11	0.33	0.17	0.53	0.36	1.32
30	40	<0.11	0.27	<0.16	0.31	0.12	0.99
31	46	<0.11	0.34	0.21	0.73	0.21	1.03
33	49	<0.11	0.71	0.47	1.36	0.32	1.42
35	51	<0.11	0.73	0.49	0.89	0.26	1.26
37	54	<0.11	0.55	0.30	0.85	0.26	0.99
39	57	<0.11	0.70	0.50	0.96	0.19	1.25
41	59	<0.11	0.94	0.35	1.05	0.26	1.19
43	62	<0.11	1.83	0.40	1.23	0.20	0.67

45	64	<0.11	1.00	0.22	0.93	0.16	0.88
Sample ID	Depth (cm)	op-DDE	pp-DDE	op-DDD	pp-DDD	op-DDT	pp-DDT
L4: 140 ft - South							
1	3	<0.11	0.13	0.27	0.99	0.08	0.57
3	4	<0.11	<0.08	<0.16	0.81	0.19	0.57
5	7	<0.11	0.08	<0.16	0.38	0.15	0.26
7	9	<0.11	0.14	<0.16	0.48	0.06	0.25
9	12	<0.11	0.20	<0.16	0.49	0.09	0.25
11	14	<0.11	0.17	<0.16	0.46	0.10	0.27
13	17	<0.11	0.46	0.23	0.41	0.19	0.45
15	19	<0.11	0.41	0.22	0.59	0.12	0.48
16	26	<0.11	0.45	0.24	0.64	0.13	0.52
18	28	<0.11	0.42	0.22	0.61	0.13	0.54
20	31	<0.11	0.28	0.18	0.39	0.11	0.42
22	34	<0.11	0.37	<0.16	0.48	0.13	0.57
24	36	<0.11	0.40	0.22	0.35	0.17	0.48
26	39	<0.11	0.33	<0.16	0.45	0.15	0.50
28	41	<0.11	0.38	0.26	0.54	0.14	0.56
30	44	<0.11	0.27	0.22	0.65	0.17	0.48
31	50	<0.11	0.32	0.20	0.78	0.10	0.35
33	53	<0.11	0.32	0.23	0.99	0.16	0.64
35	55	<0.11	0.32	0.22	0.80	0.14	0.41
37	58	<0.11	0.38	0.23	0.50	0.18	0.63
39	61	<0.11	0.38	0.34	0.87	0.16	0.53
41	63	<0.11	0.41	0.51	1.43	0.18	0.60
43	66	<0.11	0.40	0.38	1.09	0.20	0.56
45	68	<0.11	0.34	0.42	1.64	0.15	0.69
Sample ID	Depth (cm)	op-DDE	pp-DDE	op-DDD	pp-DDD	op-DDT	pp-DDT
L4: 140 ft - Center							
1	-4	<0.11	0.14	0.66	1.62	0.14	<0.21
3	-3	<0.11	0.11	0.48	1.22	0.12	<0.21
5	0	<0.11	0.13	0.36	1.05	0.09	<0.21
7	2	<0.11	0.09	0.27	0.79	0.11	<0.21
9	5	<0.11	0.10	0.16	0.48	0.06	<0.21
11	7	<0.11	0.11	0.16	0.40	0.06	<0.21
13	10	<0.11	0.11	<0.16	0.40	0.09	<0.21
15	12	<0.11	0.18	0.17	0.43	0.06	<0.21
16	19	<0.11	0.23	0.20	0.50	0.05	<0.21
18	21	<0.11	0.25	<0.16	0.51	0.06	<0.21
20	24	<0.11	0.24	0.17	0.57	0.06	<0.21
22	27	<0.11	0.29	0.21	0.71	0.06	<0.21
24	29	<0.11	0.29	0.20	0.61	<0.05	<0.21
26	32	<0.11	0.23	<0.16	0.59	0.06	<0.21
28	34	<0.11	0.24	0.17	0.85	0.06	<0.21
30	37	<0.11	0.37	0.23	0.86	0.06	<0.21
31	43	<0.11	0.36	0.22	0.66	0.07	<0.21
33	46	<0.11	0.33	0.24	0.69	0.09	<0.21

35	48	<0.11	0.27	0.21	0.63	0.06	<0.21
37	51	<0.11	0.35	0.21	0.61	0.06	<0.21
39	54	<0.11	0.24	0.20	0.74	0.06	<0.21
41	56	<0.11	0.26	0.19	0.73	0.08	<0.21
43	59	<0.11	0.31	0.23	0.75	0.06	<0.21
45	61	<0.11	0.23	0.19	0.85	0.07	<0.21

Sample ID	Depth (cm)	op-DDE	pp-DDE	op-DDD	pp-DDD	op-DDT	pp-DDT
L4: 140 ft - North							
1	0	<0.11	0.11	0.54	1.23	0.23	0.97
3	3	<0.11	<0.08	0.34	0.49	0.19	0.79
5	6	<0.11	<0.08	0.16	0.51	0.22	0.76
7	8	<0.11	<0.08	<0.16	0.54	0.12	0.74
9	11	<0.11	<0.08	0.18	0.53	0.12	1.18
11	13	<0.11	<0.08	<0.16	0.78	0.11	0.77
13	16	<0.11	<0.08	0.18	0.57	0.13	0.54
15	18	<0.11	<0.08	0.28	0.72	0.17	0.61
16	25	<0.11	<0.08	0.27	0.67	0.17	0.88
18	27	<0.11	<0.08	0.25	0.77	0.12	0.60
20	30	<0.11	<0.08	0.17	0.45	0.13	0.64
22	33	<0.11	<0.08	0.19	0.43	0.12	0.78
24	35	<0.11	<0.08	0.19	0.72	0.10	0.47
26	38	<0.11	<0.08	<0.16	0.53	0.08	0.57
28	40	<0.11	0.09	<0.16	0.92	0.17	1.40
30	43	<0.11	0.10	<0.16	0.63	0.17	1.04
31	49	<0.11	<0.08	0.20	0.53	0.11	0.55
33	52	<0.11	0.09	0.19	0.45	0.11	0.80
35	54	<0.11	<0.08	0.20	0.70	0.14	0.46
37	57	<0.11	<0.08	0.21	1.27	0.13	0.57
39	60	<0.11	0.10	0.18	1.68	0.10	0.85
41	62	<0.11	<0.08	0.24	1.68	0.14	0.94
43	65	<0.11	<0.08	0.30	1.44	0.10	0.56
45	67	<0.11	<0.08	0.25	4.31	0.12	0.78

Quantico Embayment Anions and Velocity

Sample ID	Depth (cm)	fss	Cl (mg/L)	SO4-- (mg/	Fe2+ (mg/L)	S2- (ug/L)	DOC (mg C/L)		Depth U (cm)	U (cm/d)	U-95% (cm/d)	U+95% (cm/d)	
PQL =			**0.3**	**1.5**	**0.1**	**17**	**2**						
L1: 9 ft - South													
1	-1	0.98	75	59.9	2.5	<17				-4	>100	>100	>100
3	2	0.99	117	52.3	6.2	145				21	90	61	>100
5	5	0.99	144	41.9	3.8	356				45	19	14	27
7	7	0.99	149	43.4	3.3	531				69	0	0	1
9	10	0.99	140	46.4	2.9	683	10						
11	12	0.99	138	48.3	2.0	745							
13	15	0.99	146	48.2	1.4	1009							
15	17	0.99	141	49.4	1.6	934							
16	24	0.99	192	39.7	2.0	579							
18	26	0.99	253	50.7	3.9	323							
20	29	0.99	306	61.9	4.7	307							
22	32	0.99	381	70.3	5.2	239	4						
24	34	0.99	411	75.0	8.2	236							
26	37	0.99	415	75.7	7.6	239							
28	39	1.00	408	66.8	6.8	340							
30	42	0.99	375	41.0	11.1	314							
31	48	0.92	148	5.1	43.8	83							
33	51	0.89	100	4.9	51.6	41							
35	53	0.86	91	4.6	55.1	39	5						
37	56	0.90	51	4.6	50.1	92							
39	59	0.92	44	4.2	56.0	47							
41	61	0.89	75	4.5	50.5	49							
43	64	0.95	36	4.1	46.6	42							
45	66	0.97	20	4.1	41.6	31							
Sample ID	Depth (cm)	fss	Cl (mg/L)	SO4-- (mg/	Fe2+ (mg/L)	S2- (ug/L)	DOC (mg C/L)		Depth U (cm)	U (cm/d)	U-95% (cm/d)	U+95% (cm/d)	
L1: 9 ft - Center													
1	1	1.00	54	48.7	0.9	<17				-2	>100	>100	>100
3	4	1.00	83	42.4	5.6	80				23	>100	>100	>100
5	7	1.00	103	38.3	7.2	120				47	17	10	28
7	9	1.00	133	29.9	7.6	240	11			71	14	5	31
9	12	0.99	189	19.4	7.4	429							
11	14	0.99	217	15.2	7.1	494							
13	17	0.99	242	12.2	6.1	544							
15	19	0.99	244	16.1	5.6	517							
16	26	1.00	243	33.3	4.9	293							
18	28	0.99	288	38.0	6.0	279							
20	31	0.99	313	37.2	8.6	222							
22	34	0.99	337	39.8	9.7	202	4						
24	36	0.99	359	38.6	10.2	199							
26	39	1.00	367	37.3	13.3	150							
28	41	0.99	386	38.8	16.6	155							
30	44	0.99	396	40.6	16.2	172							
31	50	0.99	370	25.2	19.5	155							
33	53	0.99	296	11.1	29.8	121							
35	55	0.99	118	4.8	32.3	101	6						
37	58	0.98	139	4.7	36.6	51							
39	61	0.98	110	4.6	41.7	58							
41	63	0.98	89	4.4	42.7	24							
43	66	0.98	88	4.1	41.4	20							
45	68	0.98	88	4.5	36.1	47							
Sample ID	Depth (cm)	fss	Cl (mg/L)	SO4-- (mg/	Fe2+ (mg/L)	S2- (ug/L)	DOC (mg C/L)		Depth U (cm)	U (cm/d)	U-95% (cm/d)	U+95% (cm/d)	
L1: 9 ft - North													
1	2	1.00	64	53.4	12.1	97				-1	>100	>100	>100
3	5	1.00	68	50.7	10.1	120				24	2	1	4
5	8	1.00	64	47.8	11.1	160				48	2	0	5
7	10	1.00	87	41.5	10.8	220	19			72	>100	>100	>100
9	13	1.00	100	37.9	9.3	317							
11	15	1.00	116	33.5	9.5	340							
13	18	0.99	162	22.1	11.1	394							
15	20	0.99	245	10.5	12.8	407							
16	27	0.99	324	4.7	13.2	250							
18	29	0.99	325	4.9	18.5	192							
20	32	0.99	316	4.8	22.8	98							
22	35	0.99	293	5.2	24.0	47	20						
24	37	0.99	250	4.8	23.8	54							
26	40	0.99	235	4.7	42.1	41							
28	42	0.99	246	4.4	40.0	47							
30	45	0.98	278	4.8	39.6	61							
31	51	0.98	93	4.5	36.1	<17							
33	54	0.99	87	4.4	32.7	<17							
35	56	0.98	86	4.7	31.1	<17	20						
37	59	0.97	87	4.6	35.7	<17							
39	62	0.96	88	4.6	40.9	<17							
41	64	0.97	86	5.3	43.1	<17							
43	67	0.98	88	4.3	36.2	<17							
45	69	0.99	87	4.8	32.9	<17							
Sample ID	Depth (cm)	fss	Cl (mg/L)	SO4-- (mg/	Fe2+ (mg/L)	S2- (ug/L)	DOC (mg C/L)		Depth U (cm)	U (cm/d)	U-95% (cm/d)	U+95% (cm/d)	
L2: 50 ft - South													

1	-5	0.99	68	43.3	0.3	<17					-8	>100	>100	>100	
3	-2	1.00	69	41.1	0.3	<17					17	5	2	10	
5	1	1.00	62	47.5	0.3	<17					41	1	1	2	
7	3	1.00	40	64.7	0.2	<17					65	1	1	1	
9	6	1.00	32	73.1	1.4	<17		13							
11	8	1.00	35	74.8	1.6	<17									
13	11	1.00	35	74.6	2.7	<17									
15	13	1.00	37	70.2	5.1	<17									
16	20	1.00	44	49.3	13.6	<17									
18	22	1.00	46	39.9	17.6	<17									
20	25	0.99	51	28.9	21.9	<17									
22	28	0.99	54	21.3	24.3	<17		15							
24	30	0.99	54	16.0	31.6	<17									
26	33	0.99	54	11.7	32.2	<17									
28	35	0.98	55	8.9	36.9	<17									
30	38	0.99	57	7.7	30.9	<17									
31	44	0.98	62	4.4	35.7	<17									
33	47	0.97	66	4.7	42.0	<17									
35	49	0.96	71	4.3	44.1	<17		21							
37	52	0.94	81	4.4	45.9	<17									
39	55	0.91	90	5.2	47.2	<17									
41	57	0.86	102	4.9	50.2	<17									
43	60	0.84	111	3.9	51.3	<17									
45	62	0.87	118	3.4	51.5	<17									

Sample ID	Depth (cm)	fss	Cl (mg/L)	SO4-- (mg/	Fe2+ (mg/L)	S2- (ug/L)	DOC (mg C/L)		Depth U (cm)	U (cm/d)	U-95% (cm/d)	U+95% (cm/d)	
L2: 50 ft - Center													
1	-4	1.00	70	49.1	0.3	<17				-7	>100	>100	>100	
3	-1	1.00	66	48.1	0.2	<17				18	10	3	26	
5	2	1.00	53	59.1	0.2	<17				42	2	0	7	
7	4	0.99	33	67.8	0.5	<17				66	>100	>100	>100	
9	7	1.00	33	76.1	1.2	<17		13						
11	9	1.00	38	72.9	5.2	<17								
13	12	1.00	36	67.5	5.2	<17								
15	14	1.00	37	61.7	7.8	<17								
16	21	0.98	45	43.8	18.2	<17								
18	23	0.98	45	36.3	19.2		17							
20	26	0.97	49	29.3	22.6	<17								
22	29	0.96	51	23.2	25.0	<17		18						
24	31	0.94	54	20.2	20.8	<17								
26	34	0.94	58	16.3	25.7	<17								
28	36	0.94	57	12.0	43.5	<17								
30	39	0.96	64	13.3	39.9	<17								
31	45	0.91	67	7.6	47.0		18							
33	48	0.90	69	6.2	54.3		19							
35	50	0.84	77	7.0	54.3	<17		18						
37	53	0.79	91	6.9	61.3	<17								
39	56	0.76	101	7.5	64.3	<17								
41	58	0.77	113	8.1	62.4	<17								
43	61	0.84	114	6.7	58.2	<17								
45	63	0.90	117	6.9	51.8	<17								

Sample ID	Depth (cm)	fss	Cl (mg/L)	SO4-- (mg/	Fe2+ (mg/L)	S2- (ug/L)	DOC (mg C/L)		Depth U (cm)	U (cm/d)	U-95% (cm/d)	U+95% (cm/d)	
L2: 50 ft - North													
1	-8	1.00	55	50.1	0.2	<17				-11	>100	>100	>100	
3	-5	1.00	59	48.7	0.3	<17				14	19	9	39	
5	-2	1.00	61	51.2	0.1	<17				38	1	0	2	
7	0	1.00	63	49.8	0.2	<17		10		62	0	0	0	
9	3	1.00	38	69.9	0.3	<17								
11	5	1.00	35	71.5	0.8	<17								
13	8	1.00	36	70.7	2.0	<17								
15	10	1.00	38	69.5	6.5	<17								
16	17	0.99	43	45.8	20.5	<17								
18	19	0.99	45	30.0	22.4	<17								
20	22	0.97	49	18.5	32.8	<17								
22	25	0.93	54	7.7	36.7	<17		16						
24	27	0.92	61	3.9	38.7	<17								
26	30	0.93	61	6.7	38.9	<17								
28	32	0.95	64	7.1	40.7	<17								
30	35	0.96	67	7.9	42.8	<17								
31	41	0.81	94	6.9	48.3	<17								
33	44	0.74	109	7.6	54.8	<17								
35	46	0.73	119	8.2	58.3	<17		16						
37	49	0.76	124	7.6	61.7	<17								
39	52	0.79	129	7.5	51.1	<17								
41	54	0.83	132	7.0	52.2	<17								
43	57	0.86	136	6.4	50.1	<17								
45	59	0.90	138	6.3	83.8		19							

Sample ID	Depth (cm)	fss	Cl (mg/L)	SO4-- (mg/	Fe2+ (mg/L)	S2- (ug/L)	DOC (mg C/L)		Depth U (cm)	U (cm/d)	U-95% (cm/d)	U+95% (cm/d)	
L3: 100 ft - South													
1	-2	1.00	96	40.1	0.3	<17				-5	>100	>100	>100	
3	1	1.00	82	43.3	4.3		60			20	11	1	51	
5	4	1.00	94	39.1	6.4		100			44	75	21	>100	
7	6	0.99	119	34.4	6.5		127	17		68	2	0	4	

9	9	0.99	140	31.2	7.0	111							
11	11	0.99	168	27.5	8.8	111							
13	14	0.99	198	22.6	11.1	117							
15	16	0.99	226	17.4	12.9	104							
16	23	0.99	251	14.1	17.5	105							
18	25	0.98	275	10.7	18.6	122							
20	28	0.99	280	8.4	18.5	125							
22	31	0.98	299	7.7	18.2	129	17						
24	33	0.98	298	6.2	17.8	130							
26	36	0.97	289	4.5	29.2	83							
28	38	0.96	252	4.4	39.5	38							
30	41	0.95	222	4.6	43.8	28							
31	47	0.91	200	4.9	50.2	26							
33	50	0.88	194	5.0	45.9	23							
35	52	0.88	198	4.9	45.0	27	32						
37	55	0.88	215	5.0	46.7	<17							
39	58	0.88	243	5.1	50.4	23							
41	60	0.89	274	4.6	58.8	<17							
43	63	0.90	330	4.9	67.0	19							
45	65	0.91	376	4.9	70.4	<17							

Sample ID	Depth (cm)	fss	Cl (mg/L)	SO4-- (mg/	Fe2+ (mg/L)	S2- (ug/L)	DOC (mg C/L)	Depth U (cm)	U (cm/d)	U-95% (cm/d)	U+95% (cm/d)
L3: 100 ft - Center											
1	-4	1.00	106	38.9	0.8	<17		-7	>100	>100	>100
3	-1	0.99	104	39.3	0.5	<17		18	11	7	17
5	2	0.99	101	36.9	0.6	<17		42	11	5	21
7	4	1.00	139	35.5	4.8	<17	6	66	3	2	4
9	7	1.00	183	24.6	9.6	<17					
11	9	0.99	198	21.8	11.9	<17					
13	12	0.99	203	21.1	12.2	<17					
15	14	0.99	244	20.3	12.8	<17					
16	21	0.99	272	21.5	15.6	<17					
18	23	0.97	315	22.8	17.2	<17					
20	26	0.98	338	23.0	19.8	<17					
22	29	0.97	360	23.9	21.3	<17	5				
24	31	0.99	393	23.7	19.4	<17					
26	34	0.97	413	27.2	30.8	<17					
28	36	0.98	394	24.5	26.9	<17					
30	39	0.98	238	20.4	30.8	<17					
31	45	0.90	221	7.3	35.1	<17					
33	48	0.88	212	7.6	47.5	<17					
35	50	0.89	210	7.0	40.7	<17	8				
37	53	0.86	217	7.0	36.5	<17					
39	56	0.87	225	7.2	38.7	<17					
41	58	0.89	236	6.5	39.2	<17					
43	61	0.90	244	6.0	35.3	<17					
45	63	0.92	255	5.5	31.4	<17					

Sample ID	Depth (cm)	fss	Cl (mg/L)	SO4-- (mg/	Fe2+ (mg/L)	S2- (ug/L)	DOC (mg C/L)	Depth U (cm)	U (cm/d)	U-95% (cm/d)	U+95% (cm/d)
L3: 100 ft - North											
1	-3	1.00	125	42.6	0.6	<17		-6	>100	>100	>100
3	0	1.00	105	43.8	2.3	<17		19	10	8	13
5	3	1.00	137	42.3	6.9	<17		43	5	3	7
7	5	1.00	189	34.4	14.8	<17	12	67	1	0	2
9	8	0.99	229	31.9	16.2	<17					
11	10	0.99	242	30.3	20.6	<17					
13	13	0.99	261	29.4	21.4	<17					
15	15	0.99	261	26.3	27.4	<17					
16	22	0.99	288	15.0	21.4	<17					
18	24	0.99	291	14.6	22.2	<17					
20	27	0.99	306	13.0	21.2	<17					
22	30	0.99	315	13.0	19.4	<17	15				
24	32	0.99	312	16.4	20.7	<17					
26	35	0.99	315	15.5	23.5	<17					
28	37	0.99	302	11.9	23.8	<17					
30	40	0.96	289	7.1	32.2	<17					
31	46	0.85	236	5.2	41.8	<17					
33	49	0.84	225	4.9	44.1	<17					
35	51	0.92	172	3.0	37.6	<17	24				
37	54	0.91	132	3.2	36.8	<17					
39	57	0.93	122	2.9	36.2	<17					
41	59	0.94	122	2.9	37.0	<17					
43	62	0.95	122	2.9	33.0	<17					
45	64	0.97	86	3.0	35.2	<17					

Sample ID	Depth (cm)	fss	Cl (mg/L)	SO4-- (mg/	Fe2+ (mg/L)	S2- (ug/L)	DOC (mg C/L)	Depth U (cm)	U (cm/d)	U-95% (cm/d)	U+95% (cm/d)
L4: 140 ft - South											
1	1	0.99	110	71.5	19.5	<17		-2	>100	>100	>100
3	4	0.99	165	66.2	17.0	27		23	2	0	4
5	7	0.99	258	52.0	20.5	<17		47	0	0	1
7	9	0.98	363	42.1	21.5	<17	9	71	1	0	2
9	12	0.96	403	36.9	25.9	28					
11	14	0.95	414	25.8	26.3	25					
13	17	0.93	537	18.5	26.8	36					
15	19	0.95	355	5.1	26.4	35					

16	26	0.77	196	5.1	32.4	177							
18	28	0.75	170	5.6	62.0	80							
20	31	0.76	163	5.6	46.7	<17							
22	34	0.76	192	6.0	56.1	17	9						
24	36	0.78	198	4.9	57.3	<17							
26	39	0.79	205	5.1	50.3	<17							
28	41	0.80	227	5.2	44.9	<17							
30	44	0.83	270	5.0	46.5	<17							
31	50	0.80	336	5.4	53.0	112							
33	53	0.79	316	5.6	54.3	50							
35	55	0.78	286	5.7	46.4	26	9						
37	58	0.79	256	5.3	34.8	118							
39	61	0.80	280	5.2	39.1	179							
41	63	0.80	272	5.5	37.6	187							
43	66	0.82	250	5.4	40.1	186							
45	68	0.86	238	4.9	23.2	440							

Sample ID	Depth (cm)	fss	Cl (mg/L)	SO4-- (mg/	Fe2+ (mg/L)	S2- (ug/L)	DOC (mg C/L)		Depth U (cm)	U (cm/d)	U-95% (cm/d)	U+95% (cm/d)	
L4: 140 ft - Center													
1	-6	1.00	96	29.3	<0.1	<17			-9	>100	>100	>100	
3	-3	1.00	85	42.1	<0.1	<17			16	4	2	7	
5	0	1.00	103	70.6	1.7	<17			40	1	0	2	
7	2	1.00	116	74.5	5.0	<17	8		64	1	0	3	
9	5	1.00	120	63.4	6.8	<17							
11	7	0.99	166	57.1	9.0	<17							
13	10	0.98	246	53.2	16.1	<17							
15	12	0.98	321	55.1	19.5	<17							
16	19	0.87	470	41.9	26.3	<17							
18	21	0.83	390	25.8	29.1	<17							
20	24	0.81	303	14.8	28.9	<17							
22	27	0.78	244	12.2	32.2	<17	6						
24	29	0.78	217	11.6	30.0	<17							
26	32	0.78	219	10.5	25.6	<17							
28	34	0.80	236	13.7	26.5	<17							
30	37	0.84	251	17.8	28.1	<17							
31	43	0.77	242	26.3	26.8	<17							
33	46	0.76	263	21.0	23.6	<17							
35	48	0.73	307	16.0	28.5	<17	7						
37	51	0.72	372	14.6	34.9	19							
39	54	0.73	441	17.5	31.3	18							
41	56	0.77	473	21.1	32.5	35							
43	59	0.84	428	17.7	29.8	28							
45	61	0.87	411	10.1	28.9	62							

Sample ID	Depth (cm)	fss	Cl (mg/L)	SO4-- (mg/	Fe2+ (mg/L)	S2- (ug/L)	DOC (mg C/L)		Depth U (cm)	U (cm/d)	U-95% (cm/d)	U+95% (cm/d)	
L4: 140 ft - North													
1	0	1.00	81	64.5	11.5	33			-3	>100	>100	>100	
3	3	0.99	120	68.3	13.0	30			22	3	0	9	
5	6	0.99	200	64.4	14.4	34			46	1	0	2	
7	8	0.98	298	54.5	18.0	54	8		70	0	0	2	
9	11	0.97	385	47.5	23.9	45							
11	13	0.96	423	38.5	23.6	55							
13	16	0.95	411	33.3	25.6	70							
15	18	0.94	398	20.9	26.5	261							
16	25	0.81	206	6.6	28.4	140							
18	27	0.79	204	6.3	28.4	93							
20	30	0.78	221	7.2	37.9	90							
22	33	0.78	230	7.6	33.5	52	6						
24	35	0.78	225	6.8	39.3	81							
26	38	0.82	210	6.4	32.7	73							
28	40	0.82	228	6.6	32.0	90							
30	43	0.86	309	5.8	35.8	97							
31	49	0.82	419	8.0	39.5	676							
33	52	0.79	434	11.1	42.6	860							
35	54	0.78	480	7.8	55.7	1304	8						
37	57	0.78	491	6.3	60.6	1448							
39	60	0.78	430	8.2	57.3	1079							
41	62	0.72	379	10.2	61.4	901							
43	65	0.77	449	7.6	96.8	637							
45	67	0.81	262	5.1	92.5	415							

Embayment Sediment DDX

				Reported Concentration in sample (ug/kg)					
		Start (cm)	End (cm)	op-DDE	pp-DDE	op-DDD	pp-DDD	op-DDT	pp-DDT
				PQL is different for each sample					
	L1: 9 ft - South								
6T	Top	2	17	4.1	137.7	17.6	70.7	< 0.92	< 0.92
6M	Mid	17	35	< 1.11	61.6	9.9	69.9	< 1.11	5.3
6B	Bottom	35	50	7.0	65.4	68.1	664.1	< 1.52	33.9
	L1: 9 ft - Center								
4T	Top	2	13	1.2	41.4	17.4	51.4	< 0.80	5.6
4M	Mid	13	34	< 0.51	3.1	1.7	5.0	< 0.51	< 0.51
4B	Bottom	34	39	3.5	56.0	69.2	434.7	< 1.38	11.5
	L1: 9 ft - North								
7T	Top	2	16	< 0.99	26.8	7.9	29.6	< 0.99	< 0.99
7M	Mid	16	28	< 0.50	< 0.50	< 0.50	1.2	10.7	< 0.50
7B	Bottom	28	43	2.6	43.3	40.6	3879.0	5.2	39.1
	L2: 50 ft - South								
1T	Top	2	16	< 0.40	3.6	2.9	10.3	< 0.40	2.5
1M	Mid	16	32	< 0.65	2.3	2.1	9.0	< 0.65	< 0.65
1B	Bottom	32	51	8.9	90.7	73.8	321.2	< 2.67	25.3
	L2: 50 ft - Center								
10 T	Top	7	26	< 0.55	1.2	0.6	2.6	< 0.55	< 0.55
10 M	Mid	26	41	2.1	38.6	46.0	214.5	1.8	13.3
10 B	Bottom	41	54	< 1.26	2.8	4.8	17.4	< 1.26	< 1.26
	L2: 50 ft - North								
5T	Top	6	21	< 0.91	12.5	9.6	44.1	< 0.91	< 0.91
5M	Mid	21	37	8.1	91.3	163.5	574.2	5.2	14.6
5B	Bottom	37	48	< 0.52	2.7	4.8	29.7	0.9	< 0.52
	L3: 100 ft - South								
9T	Top	2	28	< 0.55	7.2	4.3	18.4	< 0.55	3.6
9M	Mid	28	38	4.2	89.4	110.2	563.5	1.6	19.7
9B	Bottom	38	51	2.7	32.7	32.2	130.2	< 0.73	21.5
	L3: 100 ft - Center								
2T	Top	2	28	< 0.52	1.3	0.6	2.3	< 0.52	0.8
2M	Mid	28	44	2.1	49.4	41.3	1095.3	< 1.59	20.5
2B	Bottom	44	53	6.2	110.1	192.7	332.8	< 1.56	5.7
	L3: 100 ft - North								
3T	Top	2	16	< 0.63	6.7	3.1	9.8	< 0.63	< 0.63
3M	Mid	16	30	< 0.31	0.6	0.4	1.3	< 0.31	< 0.31
3B	Bottom	30	49	7.1	111.7	115.1	516.6	17.1	< 1.33
	L4: 140 ft - South								
8T	Top	2	18	0.8	11.9	11.6	41.8	10.4	9.6
8M	Mid	18	39	2.6	46.6	45.9	192.6	< 1.26	15.4
8B	Bottom	39	59	< 1.06	14.9	18.7	69.6	< 1.06	24.6
	L4: 140 ft - Center								
12 T	Top	2	17	1.4	22.6	19.7	396.9	< 0.75	17.9
12 M	Mid	17	39	3.2	49.5	39.6	154.0	< 1.31	17.6
12 B	Bottom	39	53	1.7	21.4	18.3	79.3	< 0.75	21.5
	L4: 140 ft - North								
11 T	Top	2	16	0.6	9.2	8.7	36.7	< 0.52	9.0
11 M	Mid	16	26	7.5	148.2	84.3	1463.2	< 0.93	17.9
11 B	Bottom	26	36	2.1	41.6	40.6	174.8	< 1.29	24.0
11 BB	Bottom Bottom	36	46	< 0.73	2.1	1.5	5.8	< 0.73	< 0.73

Embayment Exsitu DDX and TOC

				Ex-Situ Pore Water Concentration (ng/L)						%TOC (mg C/mg)
Core Sample ID	Start (cm)	End (cm)	Depth (cm)	op-DDE	pp-DDE	op-DDD	pp-DDD	op-DDT	pp-DDT	
PQL =				**0.04**	**0.03**	**0.06**	**0.09**	**0.02**	**0.09**	
L1: 9 ft - South										
Top	2	17	9	<0.04	0.54	0.75	2.41	<0.02	<0.09	0.37
Mid	17	35	26	0.07	0.56	2.87	26.80	0.03	1.50	0.26
Bottom	35	50	42	0.15	0.66	2.35	18.84	<0.02	<0.09	3.49
L1: 9 ft - Center										
Top	2	13	7	0.10	0.76	1.06	2.38	<0.02	<0.09	3.54
Mid	13	34	23	0.08	0.18	0.74	3.76	<0.02	<0.09	0.05
Bottom	34	39	36	0.08	0.50	3.87	25.26	<0.02	0.26	1.41
L1: 9 ft - North										
Top	2	16	9	0.05	0.62	0.95	2.57	<0.02	<0.09	0.38
Mid	16	28	22	<0.04	0.18	0.22	1.43	<0.02	0.16	0.03
Bottom	28	43	36	0.04	0.30	1.23	12.10	<0.02	<0.09	2.69
L2: 50 ft - South										
Top	2	16	9	<0.04	0.12	0.19	1.09	<0.02	<0.09	0.24
Mid	16	32	24	<0.04	0.19	0.55	2.33	<0.02	0.12	0.16
Bottom	32	51	41	0.29	1.17	2.61	16.38	<0.02	<0.09	2.86
L2: 50 ft - Center										
Top	7	26	16	0.05	0.28	0.81	3.19	<0.02	<0.09	0.15
Mid	26	41	33	0.08	0.70	4.19	26.42	<0.02	<0.09	0.68
Bottom	41	54	47	<0.04	0.07	0.20	0.86	<0.02	<0.09	1.12
L2: 50 ft - North										
Top	6	21	14	<0.04	0.44	1.45	8.38	<0.02	<0.09	2.19
Mid	21	37	29	0.08	0.56	4.55	52.43	<0.02	0.17	1.95
Bottom	37	48	42	<0.04	0.05	<0.06	0.73	<0.02	<0.09	1.59
L3: 100 ft - South										
Top	2	28	15	<0.04	0.16	0.25	1.81	<0.02	<0.09	0.38
Mid	28	38	33	0.06	0.70	2.37	18.34	<0.02	<0.09	2.31
Bottom	38	51	44	0.10	0.52	2.14	14.48	<0.02	0.56	0.61
L3: 100 ft - Center										
Top	2	28	15	<0.04	0.30	0.25	1.35	<0.02	0.11	0.22
Mid	28	44	36	0.11	1.14	3.09	22.85	<0.02	0.14	1.31
Bottom	44	53	48	0.13	1.00	3.71	14.11	<0.02	<0.09	1.67
L3: 100 ft - North										
Top	2	16	9	<0.04	0.41	0.66	2.98	<0.02	0.10	0.54
Mid	16	30	23	<0.04	0.08	<0.06	0.32	<0.02	<0.09	0.21
Bottom	30	49	39	0.07	0.54	4.44	28.92	<0.02	<0.09	3.35
L4: 140 ft - South										
Top	2	18	10	<0.04	0.18	0.55	2.63	<0.02	<0.09	0.27
Mid	18	39	28	0.07	0.69	2.97	15.55	<0.02	<0.09	0.59
Bottom	39	59	49	0.04	0.35	3.02	11.30	<0.02	<0.09	0.27
L4: 140 ft - Center										
Top	2	17	10	0.05	0.40	0.74	4.56	<0.02	0.17	0.71
Mid	17	39	28	0.10	0.75	2.76	14.28	<0.02	<0.09	1.29
Bottom	39	53	46	0.07	0.26	0.83	3.17	<0.02	0.76	0.61
L4: 140 ft - North										
Top	2	16	9	<0.04	0.21	0.51	6.91	<0.02	0.12	0.63
Mid	16	26	21	0.06	0.77	1.41	6.37	<0.02	<0.09	2.37
Bottom	26	36	31	0.09	1.02	6.32	31.72	<0.02	<0.09	0.36
Bottom Bottom	36	46	41	0.05	0.15	0.52	2.00	<0.02	<0.09	0.34

APPENDIX F4. GRAND CALUMET

Grand Cal PAH sHRPP C (ng/L)

Sample ID	Depth (cm)	PAH	Fluorene	Phenanthrene	Anthracene	Fluoranthene	Pyrene	Chrysene	B(a)A	B(b)F	B(k)F	B(a)Pyr	B(ghi)Perylene+Indeno(1,2,3,-cd)Pyr
PQL =			**53**	**4.6**	**5.0**	**2.0**	**2.0**	**1.0**	**0.8**	**0.2**	**0.27**	**0.25**	**0.12**
WT-01													
1	-20		72	<4.6	<5	6	26	3	1	1.2	0.30	0.7	0.22
2	-19		66	<4.6	<5	6	23	2	1	1.0	<0.27	0.6	0.19
3	-18	<53		<4.6	<5	9	27	3	2	1.3	0.45	0.8	0.22
4	-16		95	<4.6	<5	8	24	3	2	1.0	0.28	0.7	0.23
5	-15		58	<4.6	<5	5	18	2	1	0.8	<0.27	0.5	0.14
6	-14		73	<4.6	<5	5	22	3	1	1.1	0.38	0.7	0.18
7	-13		88	<4.6	<5	8	27	3	2	1.1	<0.27	0.7	0.20
8	-11		95	<4.6	<5	7	28	3	2	1.3	0.44	0.8	0.25
10	-9		97	<4.6	<5	8	29	3	2	0.9	0.32	0.7	0.17
12	-6		56	<4.6	<5	7	24	3	2	1.0	0.30	0.7	0.19
14	-4		534	<4.6	<5	4	26	2	1	1.1	0.35	0.6	0.20
16	-1		81	<4.6	<5	7	38	3	2	1.1	0.37	0.8	0.17
17	3		71	7	<5	11	26	4	3	0.9	<0.27	0.6	<0.12
19	6		68	8	<5	10	31	5	3	1.1	0.49	0.9	0.18
21	8		157	7	<5	10	25	4	2	1.1	0.49	0.8	0.16
23	11		103	6	<5	9	28	4	3	1.1	0.48	0.9	0.16
25	13		84	8	<5	10	29	5	3	1.2	0.55	0.9	0.16
27	16		73	6	<5	11	28	5	3	1.3	0.56	1.0	0.17
29	18		59	8	<5	10	28	5	3	1.4	0.64	1.1	0.20
31	21	<53		6	<5	7	17	3	2	0.9	0.36	0.6	0.12
32	25		84	8	<5	10	27	4	3	1.2	0.54	0.9	0.17
33	26		81	9	<5	13	33	6	4	1.6	0.74	1.3	0.21
35	29		63	8	<5	12	30	6	4	1.7	0.66	1.1	0.21
37	31		80	9	<5	15	35	6	4	1.8	0.79	1.2	0.21
39	34		84	7	<5	12	35	6	4	1.8	0.79	1.2	0.25
41	36	<53		5	<5	7	17	3	2	0.9	0.40	0.6	<0.12
43	39		81	7	<5	13	28	5	3	1.6	0.69	1.2	0.23
45	41		103	8	<5	11	31	7	4	1.8	0.77	1.3	0.23
47	44		93	9	<5	12	30	6	3	2.0	0.82	1.2	0.21
48	45		87	10	<5	13	32	6	3	2.0	0.85	1.3	0.24

Sample ID	Depth (cm)	PAH	Fluorene	Phenanthrene	Anthracene	Fluoranthene	Pyrene	Chrysene	B(a)A	B(b)F	B(k)F	B(a)Pyr	B(ghi)Perylene+Indeno(1,2,3,-cd)Pyr
WT-02													
1	-2		64	7	<5	16	46	7	5	1.3	0.68	1.0	0.20
2	-1		111	10	<5	13	37	5	4	1.0	<0.27	0.7	0.18
3	0	<53		10	<5	14	39	6	5	1.1	<0.27	0.8	0.20
4	2	<53		9	<5	12	35	4	3	0.9	<0.27	0.6	0.18
5	3		95	14	5.3	15	43	6	4	1.1	0.55	1.0	0.19
6	4		59	26	10.3	19	47	7	5	1.3	0.65	1.1	0.21
7	5		74	15	<5	16	46	6	4	1.0	<0.27	0.8	0.19
8	7		59	14	5.0	14	45	5	4	0.9	<0.27	0.7	0.14
10	9		96	14	7.2	15	46	6	5	0.9	0.49	0.9	0.17
12	12		89	26	12.1	19	58	6	6	1.1	<0.27	0.8	0.19
14	14		83	20	16.4	22	70	8	6	1.0	<0.27	0.9	0.17
16	17		71	27	20.4	24	77	8	8	0.8	0.48	1.0	0.16
17	21		71	24	24.3	27	90	10	9	1.2	0.69	1.2	0.13
19	24		89	27	25.1	29	93	9	7	1.2	<0.27	1.0	0.14
21	26		74	22	23.2	27	88	8	7	1.0	<0.27	0.9	<0.07
23	29		76	29	26.0	29	96	9	8	1.1	<0.27	1.0	<0.07
25	31		88	30	25.7	24	83	9	9	0.8	<0.27	0.9	<0.07
27	34		63	23	22.2	23	77	7	7	0.6	<0.27	0.7	<0.07
29	36		96	20	19.1	19	67	7	7	0.6	<0.27	0.6	<0.07
31	39		241	28	23.2	21	77	7	7	0.6	<0.27	0.7	<0.07
32	43		71	22	16.4	14	57	4	3	0.4	<0.27	0.5	<0.07
33	44		86	24	22.5	20	72	6	5	0.5	<0.27	0.6	<0.07
35	47		95	21	16.4	16	64	6	6	0.4	<0.27	0.6	<0.07
37	49	<53		16	11.3	11	41	4	4	0.3	<0.27	0.3	<0.07
39	52		74	29	16.4	12	52	5	4	0.3	<0.27	0.5	<0.07
41	54		98	38	20.0	15	67	5	4	0.6	<0.27	0.7	<0.07
45	59		150	40	20.3	14	65	6	5	0.3	<0.27	0.5	<0.07
47	62		100	42	14.8	9	46	4	4	<0.2	<0.04	0.3	<0.07
48	63		121	37	12.7	8	43	3	3	<0.2	<0.04	0.3	<0.07

Sample ID	Depth PAH (cm)	Fluorene	Phenanthrene	Anthracene	Fluoranthene	Pyrene	Chrysene	B(a)A	B(b)F	B(k)F	B(a)Pyr	B(ghi)Perylene+Indeno(1,2,3,-cd)Pyr
WT-03												
1	4	109	18	6.1	14	43	7	6	1.5	<0.27	1.1	0.21
2	5	61	36	14.4	14	41	5	4	1.0	<0.27	0.8	0.15
3	6	125	18	6.1	16	47	7	6	1.1	<0.27	0.8	0.19
4	8	79	21	6.1	14	45	5	4	1.1	<0.27	0.8	0.16
5	9	113	17	5.8	15	42	5	4	0.9	<0.27	0.7	0.16
6	10	96	15	5.8	14	42	5	4	0.9	<0.27	0.8	0.14
7	11	111	26	8.2	20	54	5	5	1.2	<0.27	0.8	0.18
8	13	122	32	9.4	28	77	5	4	1.0	<0.27	0.8	0.21
10	15	180	13	6.2	16	45	6	5	1.1	<0.27	0.8	0.18
12	18	100	13	6.3	16	45	6	5	1.0	<0.27	0.8	0.19
14	20	68	13	6.0	14	41	5	4	0.9	<0.27	0.7	0.14
16	23	103	13	6.0	16	42	5	4	1.0	<0.27	0.8	<0.07
17	27	74	13	6.6	15	42	6	5	1.2	<0.27	1.0	0.20
19	30	61	16	5.1	11	33	4	4	0.8	<0.27	0.6	0.12
21	32	118	67	23.9	21	82	11	9	1.4	<0.27	1.3	0.22
23	35	87	63	25.3	24	81	9	8	1.4	<0.27	1.1	0.18
25	37	70	39	17.6	17	52	6	5	1.0	<0.27	0.8	0.18
27	40	109	65	33.8	28	95	11	10	1.5	<0.27	1.3	0.24
29	42	82	51	23.1	25	82	10	9	1.8	<0.27	1.2	0.24
31	45	112	61	26.3	23	82	10	8	1.4	<0.27	1.1	0.21
32	49	79	35	15.8	16	57	7	6	1.2	<0.27	1.0	0.20
33	50	139	73	27.0	22	84	9	8	1.3	0.37	1.5	0.21
35	53	85	52	22.9	18	65	7	6	0.9	<0.27	0.8	<0.12
37	55	73	59	21.7	19	75	8	7	1.1	<0.27	1.0	0.15
39	58	105	83	29.9	27	109	12	10	1.5	0.45	1.8	0.22
41	60	126	75	23.5	21	88	10	9	1.9	<0.27	1.5	0.26
43	63	115	86	27.9	25	93	10	8	1.5	<0.27	1.2	0.20
45	65	64	43	13.7	14	54	7	6	1.2	<0.27	1.1	0.21
47	68	90	34	12.2	12	49	5	4	0.8	<0.27	0.8	0.15
48	69	70	33	10.1	14	53	7	5	1.2	<0.27	0.9	<0.12

Sample ID	Depth PAH (cm)	Fluorene	Phenanthrene	Anthracene	Fluoranthene	Pyrene	Chrysene	B(a)A	B(b)F	B(k)F	B(a)Pyr	B(ghi)Perylene+Indeno(1,2,3,-cd)Pyr
WT-04												
1	3	116	238	19.3	23	116	8	6	1.5	0.79	1.0	0.18
2	4	126	108	10.5	10	49	4	3	0.9	<0.27	0.6	0.14
4	7	83	35	<5	9	33	4	3	0.9	<0.27	0.5	0.14
5	8	79	74	7.2	8	35	3	2	0.7	<0.27	0.5	<0.12
6	9	89	91	9.0	8	35	3	2	0.7	<0.27	0.5	0.14
7	10	101	56	20.0	12	45	3	3	0.8	<0.27	0.6	0.15
8	12	98	54	7.7	8	34	3	2	0.7	<0.27	0.5	0.12
10	14	86	40	5.7	9	35	4	3	1.0	0.45	0.8	0.17
12	17	59	22	<5	6	23	2	2	0.6	<0.27	0.4	<0.12
14	19	105	39	5.6	7	27	3	2	0.6	<0.27	0.5	<0.12
16	22	92	32	<5	8	31	4	3	0.7	<0.27	0.6	0.14
17	26	90	41	5.7	5	20	2	2	0.5	<0.27	0.4	<0.12
19	29	89	39	5.7	6	23	3	2	0.5	<0.27	0.5	<0.12
21	31	56	25	<5	4	16	2	1	0.3	<0.27	0.3	<0.12
23	34	97	23	5.1	5	22	2	2	0.5	<0.27	0.5	<0.12
25	36	104	33	<5	5	21	2	1	0.4	<0.27	0.4	<0.12
27	39	92	64	7.4	7	34	3	2	0.4	<0.27	0.4	<0.12
29	41	105	33	5.1	7	27	2	2	0.4	<0.27	0.5	<0.12
31	44	124	23	<5	5	19	2	2	0.4	<0.27	0.4	<0.12
32	48	108	28	5.0	9	31	3	3	0.5	<0.27	0.5	<0.12
33	49	66	22	<5	4	16	2	1	0.4	<0.27	0.4	<0.12
35	52	111	25	<5	7	26	4	2	0.6	<0.27	0.6	0.12
37	54	130	46	6.8	7	39	5	4	0.8	<0.27	0.8	0.14
39	57	104	114	10.7	12	57	7	5	1.0	<0.27	1.0	0.21
41	59	126	85	8.1	8	41	4	3	0.7	<0.27	0.7	0.15
43	62	121	66	8.9	8	38	4	3	1.0	<0.27	0.8	0.18
45	64	108	109	9.3	11	49	5	4	1.2	<0.27	0.9	0.23
47	67	130	94	9.6	12	51	5	3	1.2	0.34	0.9	0.21
48	68	103	123	9.2	13	48	6	4	1.3	<0.27	1.0	0.22

Sample ID	Depth PAH (cm)	Fluorene	Phenanthrene	Anthracene	Fluoranthene	Pyrene	Chrysene	B(a)A	B(b)F	B(k)F	B(a)Pyr	B(ghi)Perylene+Indeno
PQL =		**53**	**4.6**	**5.0**	**2.0**	**2.0**	**1.0**	**0.8**	**0.2**	**0.27**	**0.25**	**0.12**
ET-02												
1	2	<53	28	<5	34	86	14	9	2.8	1.51	2.3	0.28
2	3	112	39	5.3	73	153	24	16	4.0	0.85	2.8	0.51

3	4	104	54	8.3	56	143	23	17	3.7	0.81	2.7	0.43
4	6	76	49	6.6	51	131	20	14	3.0	0.64	2.1	0.36
5	7	325	48	6.7	51	133	19	12	2.8	0.56	2.0	0.33
6	8	117	50	7.1	73	140	22	16	3.3	0.97	2.5	0.62
7	9	124	52	8.0	50	121	20	14	3.5	1.95	2.9	0.38
8	11	70	35	5.8	31	90	12	9	2.1	1.17	1.8	0.24
10	13	121	40	6.4	35	84	14	10	2.4	1.32	2.0	0.27
12	16	101	42	6.4	41	113	17	12	2.9	1.58	2.5	0.34
14	18	111	48	7.9	46	114	20	14	3.4	1.81	2.9	0.39
17	25	177	53	6.3	47	114	20	14	3.1	1.76	2.8	0.36
19	28	89	44	7.1	53	126	23	15	4.5	2.48	3.8	0.55
21	30	122	40	6.0	52	130	23	15	4.5	2.52	3.8	0.50
23	33	64	31	5.0	39	93	18	12	3.2	1.77	2.7	0.37
25	35	73	33	<5	39	98	17	11	3.3	1.81	2.8	0.42
27	38	83	44	6.2	53	132	23	15	4.4	2.35	3.6	0.48
31	43	104	42	6.5	63	148	30	21	4.8	2.67	4.0	0.51
32	47	98	33	5.6	73	153	26	17	3.8	1.17	2.8	0.45
33	48	82	33	<5	39	106	19	13	2.4	0.55	1.8	0.30
35	51	77	35	<5	60	118	21	13	3.1	0.93	2.2	0.41
37	53	91	45	6.6	62	154	27	16	3.9	1.17	2.9	0.59
39	56	108	44	7.8	78	152	27	17	4.1	0.90	2.9	0.55
41	58	158	47	7.7	56	146	26	18	4.4	2.46	3.7	1.14
43	61	88	49	8.8	57	149	25	16	4.4	2.43	3.8	0.85
45	63	80	43	6.6	56	140	24	16	3.7	1.45	2.8	0.57
47	66	70	55	7.1	53	137	26	18	4.6	2.48	3.7	0.51
48	67	164	76	9.7	56	146	26	18	4.4	2.46	3.6	0.53

Sample ID	Depth	PAH (cm)	Fluorene	Phenanthrene	Anthracene	Fluoranthene	Pyrene	Chrysene	B(a)A	B(b)F	B(k)F	B(a)Pyr	B(ghi)Perylene	Inde
ET-03														
1	2		73	68	9.6	79	217	42	30	6.5	1.25	4.3		0.62
2	3		73	68	9.3	69	198	38	27	6.1	1.25	4.3		0.66
3	4		89	68	10.8	54	176	33	24	5.2	1.05	3.7		0.59
4	6		95	64	10.7	55	155	28	20	4.4	0.92	3.2		0.52
5	7		92	83	10.7	57	163	28	20	3.9	1.41	3.7		0.50
6	8		108	62	9.6	54	144	21	14	3.6	0.79	2.7		0.48
7	9		80	66	10.2	62	176	24	16	3.6	0.89	3.1		0.54
8	11		64	68	10.2	59	168	24	17	4.3	0.92	3.3		0.59
10	13		74	77	11.9	72	186	27	18	4.7	1.02	3.5		0.71
13	17	<53		75	12.7	62	172	25	18	4.5	0.93	3.6		0.72
16	21		85	70	10.5	71	179	29	19	4.6	0.95	3.6		0.72
17	25		108	70	11.1	61	179	23	17	4.3	0.88	3.4		0.68
19	28		92	70	10.5	66	182	29	20	5.6	1.09	4.3		0.97
21	30		89	66	9.9	101	173	29	21	4.3	0.89	3.2		0.67
23	33		66	56	8.7	53	145	21	14	3.3	0.77	2.9		0.53
25	35		69	64	12.4	61	171	24	17	4.4	0.95	3.4		0.64
27	38		67	75	11.2	65	179	26	19	4.6	0.94	3.8		0.61
29	40		95	68	12.0	64	174	25	17	5.5	1.57	2.1		0.76
31	43		98	53	9.0	62	173	28	20	4.3	0.83	3.4		0.64
32	47		61	53	8.1	46	136	23	16	3.4	0.64	2.4		0.94
33	48		59	64	9.3	56	154	30	21	5.4	1.09	4.2		0.83
35	51		72	58	8.4	56	146	28	18	5.6	2.87	5.0		0.64
37	53		83	49	7.5	54	144	26	17	4.0	0.85	3.1		0.59
39	56		59	41	6.7	47	150	27	19	3.9	0.83	2.8		0.64
41	58		67	45	6.0	43	125	19	12	3.5	0.99	2.9		0.84
43	61		73	45	7.2	43	127	21	14	3.5	0.66	2.7		0.55
45	63		89	42	6.3	35	108	20	14	3.1	1.05	3.3		0.73
47	66		104	26	<5	21	58	11	8	1.8	0.38	1.8		0.32
48	67		89	14	5.3	9	34	7	4	1.1	<0.27	1.1		0.22

Sample ID	Depth	PAH (cm)	Fluorene	Phenanthrene	Anthracene	Fluoranthene	Pyrene	Chrysene	B(a)A	B(b)F	B(k)F	B(a)Pyr	B(ghi)Perylene	Inde
ET_04														
1	2		100	104	17.5	70	215	36	27	5.1	1.82	4.7		0.56
2	3		100	95	16.2	77	202	33	24	5.2	3.00	4.5		0.62
3	4		110	101	17.8	77	222	37	27	5.0	1.81	4.7		0.62
4	6		71	60	10.0	41	122	19	14	2.7	0.98	2.6		0.33
5	7		75	92	16.3	65	204	33	24	4.1	1.48	4.3		0.56
6	8		91	89	16.1	63	192	33	24	4.2	1.17	3.2		0.48
7	9		172	95	14.9	60	179	28	20	3.6	1.33	3.8		0.56
8	11		121	84	15.5	68	194	30	22	4.0	1.44	4.2		0.61
10	13		120	113	18.4	67	204	25	18	4.1	1.39	4.3		0.62
12	16		109	95	14.9	63	189	31	23	4.2	1.50	4.5		0.65
14	18		76	78	15.5	58	169	28	20	3.8	1.34	4.0		0.57
17	25		106	45	8.8	33	85	16	12	2.4	0.84	2.5		0.44
19	28		60	37	5.6	25	62	10	8	1.6	0.55	1.7		0.31
21	30		69	34	6.6	23	60	10	8	1.5	0.52	1.5		0.27
23	33		97	36	6.8	22	66	12	9	1.8	0.62	1.4		0.33

25	35	93	29	5.0	18	54	11	7	1.8	0.97	1.8	0.35
27	38	116	24	<5	16	42	7	5	1.4	0.36	1.2	0.40
29	40	78	23	<5	15	41	9	5	1.2	0.40	1.3	0.29
31	43	76	59	8.8	25	82	15	11	2.7	0.88	2.8	0.53
32	47	82	32	5.8	16	54	16	8	2.1	0.73	2.5	0.57
35	51	70	25	<5	18	49	11	8	1.9	0.31	1.5	0.34
37	53	68	27	<5	23	62	13	9	2.8	1.41	2.6	0.47
39	56	69	28	5.6	26	64	15	11	2.9	1.63	2.9	0.48
41	58	<53	26	<5	20	56	13	10	1.8	0.32	1.9	0.44
43	61	<53	23	7.7	23	62	13	10	2.7	1.59	3.0	0.58
45	63	<53	23	5.6	20	69	11	8	1.7	0.29	1.5	0.44
47	66	103	63	13.9	43	110	25	20	2.9	0.43	2.5	0.38
48	67	76	15	5.9	18	55	5	5	0.9	<0.27	1.0	0.17

Grand Cal Anions and Velocity

Sample ID	Depth (cm)		fss	Cl (mg/L)	SO4-- (mg/L)	Depth U (cm)	U (cm/d)	U-95% (cm/d)	U+95% (cm/d)
PQL =				**0.3**	**1.5**				
ET-02									
	S.W.		1.00	54	57.4	0	>100	64	>100
1		2	0.97	65	2.9	23	7	1	21
3		4	0.96	69	<1.5	46	90	11	>100
5		7	0.95	74	<1.5	69	7	2	17
7		9	0.94	73	1.9				
9		12	0.93	79	1.6				
11		14	0.92	81	1.5				
13		17	0.91	86	2.2				
15		19	0.90	87	2.0				
16		21	0.89	88	2.6				
17		25	0.85	90	2.2				
19		28	0.82	90	2.4				
21		30	0.80	92	2.7				
23		33	0.76	93	2.4				
25		35	0.74	94	2.6				
27		38	0.73	95	2.2				
29		40	0.75	97	2.1				
31		43	0.79	99	1.5				
32		47	0.81	99	<1.5				
33		48	0.80	100	<1.5				
35		51	0.78	101	<1.5				
37		53	0.78	106	<1.5				
39		56	0.79	108	<1.5				
41		58	0.81	109	<1.5				
43		61	0.83	111	<1.5				
45		63	0.85	116	<1.5				
47		66	0.87	128	<1.5				
48		67	0.88	135	<1.5				

Sample ID	Depth (cm)		fss	Cl (mg/L)	SO4-- (mg/L)	Depth U (cm)	U (cm/d)	U-95% (cm/d)	U+95% (cm/d)
ET-03									
	S.W.			54	57.4	0	>100	29	>100
1		2	0.98	62	1.9	23	10	3	27
3		4	0.97	72	1.5	46	2	0	5
5		7	0.94	76	<1.5	69	5	1	13
7		9	0.93	85	<1.5				
9		12	0.91	89	1.8				
11		14	0.89	95	1.6				
13		17	0.88	99	1.8				
15		19	0.88	100	1.7				
16		21	0.88	100	1.9				
17		25	0.83	97	1.8				
19		28	0.79	94	1.8				
21		30	0.76	92	2.0				
23		33	0.72	90	2.5				
25		35	0.70	89	2.2				
27		38	0.71	91	2.3				
29		40	0.72	91	2.6				
31		43	0.73	95	2.1				
32		47	0.75	93	2.5				
33		48	0.73	96	2.2				
35		51	0.71	97	2.1				
37		53	0.72	97	2.1				
39		56	0.75	97	2.1				
41		58	0.80	97	2.1				
43		61	0.84	101	2.1				

45	63	0.86	102	2.3	
47	66	0.88	107	2.2	
48	67	0.90	109	2.0	

Sample ID	Depth (cm)	fss	Cl (mg/L)	SO4-- (mg/L)	Depth U (cm)	U (cm/d)	U-95% (cm/d)	U+95% (cm/d)
ET-04								
	S.W.		54	57.4	0	>100	>100	>100
1	2	0.94	69	<1.5	23	5	0	19
3	4	0.92	66	<1.5	46	4	1	8
5	7	0.89	69	<1.5	69	6	4	8
7	9	0.87	71	<1.5				
9	12	0.84	72	<1.5				
11	14	0.80	76	<1.5				
13	17	0.78	76	<1.5				
15	19	0.77	75	<1.5				
16	21	0.77	72	<1.5				
17	25	0.72	67	<1.5				
19	28	0.71	63	1.6				
21	30	0.72	57	2.1				
23	33	0.74	54	1.9				
25	35	0.76	49	2.6				
27	38	0.79	45	2.7				
29	40	0.82	41	2.6				
31	43	0.85	38	2.4				
32	47	0.87	37	2.6				
33	48	0.88	33	1.8				
35	51	0.87	33	2.1				
37	53	0.85	31	1.9				
39	56	0.86	28	2.1				
41	58	0.87	27	2.3				
43	61	0.87	26	1.9				
45	63	0.88	26	2.5				
47	66	0.90	24	3.2				
48	67	0.91	24	5.2				

Sample ID	Depth (cm)	fss	Cl (mg/L)	SO4-- (mg/L)	Depth U (cm)	U (cm/d)	U-95% (cm/d)	U+95% (cm/d)
WT-01								
					-22	>100	>100	>100
1	-20	1.00	79	64.8	1	3	1	8
3	-18	1.00	79	64.2	24	12	1	53
5	-15	1.00	78	64.2	47	3	2	6
7	-13	1.00	78	64.9				
9	-10	1.00	76	63.8				
11	-8	1.00	78	64.3				
13	-5	1.00	78	63.5				
15	-3	1.00	77	63.5				
16	-1	1.00	77	64.0				
17	3	1.00	69	70.3				
19	6	0.99	68	57.3				
21	8	0.94	73	25.0				
23	11	0.85	81	4.0				
25	13	0.74	87	3.7				
27	16	0.63	103	3.9				
29	18	0.62	112	4.3				
31	21	0.67	110	3.4				
32	25	0.71	109	3.4				
33	26	0.74	111	2.6				
35	29	0.70	118	3.5				
37	31	0.65	126	4.2				
39	34	0.62	132	3.6				
41	36	0.63	134	3.4				

	43	39	0.67	135	3.6				
	45	41	0.74	128	3.1				
	47	44	0.83	122	3.0				
	48	45	0.87	118	2.6				
Sample ID	Depth (cm)	fss		Cl (mg/L)	SO4-- (mg/L)	Depth U (cm)	U (cm/d)	U-95% (cm/d)	U+95% (cm/d)
WT-02									
	S.W.			75	64.7	-4	89	17	>100
	1	-2	1.00	80	65.4	19	6	0	22
	3	0	0.99	75	55.5	42	4	1	10
	5	3	0.91	80	16.9	65	9	3	23
	7	5	0.79	86	4.5				
	9	8	0.71	94	5.9				
	11	10	0.69	100	4.7				
	13	13	0.68	107	4.7				
	15	15	0.71	106	4.2				
	16	17	0.73	110	4.4				
	17	21	0.71	114	3.7				
	19	24	0.69	115	3.2				
	21	26	0.68	118	3.4				
	23	29	0.67	126	3.5				
	25	31	0.69	123	3.0				
	27	34	0.75	113	2.8				
	29	36	0.77	108	2.5				
	31	39	0.80	108	2.4				
	32	43	0.83	106	2.5				
	33	44	0.85	107	2.0				
	35	47	0.84	109	2.6				
	37	49	0.85	108	2.1				
	39	52	0.86	106	2.4				
	41	54	0.86	106	2.1				
	43	57	0.86	106	2.3				
	45	59	0.87	105	2.6				
	47	62	0.89	105	2.9				
	48	63	0.91	105	3.0				
Sample ID	Depth (cm)	fss		Cl (mg/L)	SO4-- (mg/L)	Depth U (cm)	U (cm/d)	U-95% (cm/d)	U+95% (cm/d)
WT-03									
	S.W.			75	64.7	2			
	1	4	0.99	80	3.7	25	4	1	10
	3	6	0.97	80	1.9	48	3	1	8
	5	9	0.94	81	2.1	71	7	3	15
	7	11	0.87	86	2.2				
	9	14	0.83	88	2.3				
	11	16	0.82	97	2.1				
	13	19	0.80	101	3.2				
	15	21	0.80	108	2.6				
	16	23	0.80	109	2.6				
	17	27	0.78	110	3.6				
	19	30	0.75	108	4.6				
	21	32	0.72	107	5.9				
	23	35	0.67	111	2.6				
	25	37	0.66	111	5.5				
	27	40	0.68	109	3.6				
	29	42	0.71	108	2.0				
	31	45	0.77	103	1.9				
	32	49	0.80	102	1.9				
	33	50	0.83	102	1.8				
	35	53	0.81	98	2.2				
	37	55	0.81	96	1.7				
	39	58	0.81	94	1.7				

41	60	0.80	94	<1.5	
43	63	0.81	94	2.0	
45	65	0.83	92	2.8	
47	68	0.86	88	2.4	
48	69	0.87	88	2.6	

Sample ID	Depth (cm)	fss	Cl (mg/L)	SO4-- (mg/L)	Depth U (cm)	U (cm/d)	U-95% (cm/d)	U+95% (cm/d)
WT-04								
	S.W.		75	64.7	1	22	11	41
1	3	0.96	82	5.0	24	4	1	10
3	5	0.88	89	13.9	47	38	11	>100
5	8	0.82	88	8.0	70	11	4	24
7	10	0.74	94	4.0				
9	13	0.70	102	3.5				
11	15	0.70	105	3.5				
13	18	0.71	111	3.8				
15	20	0.72	110	3.8				
16	22	0.73	107	5.4				
17	26	0.74	126	4.8				
19	29	0.74	121	3.6				
21	31	0.77	121	3.9				
23	34	0.81	125	3.9				
25	36	0.83	124	3.8				
27	39	0.87	122	3.4				
29	41	0.87	124	3.3				
31	44	0.88	125	3.7				
32	48	0.88	123	4.1				
33	49	0.87	121	3.5				
35	52	0.86	114	4.3				
37	54	0.84	113	4.0				
39	57	0.83	115	4.0				
41	59	0.84	117	4.7				
43	62	0.84	114	4.6				
45	64	0.85	115	3.8				
47	67	0.87	115	4.0				
48	68	0.87	113	3.9				

Grand Cal PAH Tbar

Sample ID	Depth (cm)	Fluorene	Phenanthrene	Anthracene	Fluoranthene	Pyrene	Chrysene	Benz[a]anthracene	Benzo[b]fluoranthene	Benzo[k]fluoranthene	Benzo[a]pyrene	Benzo[ghi]perylene+Indeno[1,2,3-cd]pyrene
PQL =		**177**	**20**	**21**	**9**	**10**	**4.0**	**4.3**	**1.4**	**1.59**	**1.5**	**0.64**
WT-01	4	<177	39	<21	15	31	<4	<4.3	2.0	<1.6	<1.5	<0.64
	14	<177	<20	<21	11	23	<4	<4.3	2.2	<1.6	<1.5	<0.64
	24	<177	<20	<21	15	36	<4	<4.3	4.0	<1.6	1.6	<0.64
	46	<177	<20	<21	<9	20	<4	<4.3	2.2	<1.6	<1.5	<0.64
	54	1037	230	93	44	154	6.9	7.2	5.7	<1.6	2.8	<0.64
	66	870	189	94	32	126	4.9	4.9	2.2	<1.6	<1.5	<0.64
	76	724	276	88	44	190	6.9	9.0	4.8	<1.6	3.1	<0.64
	86	755	135	48	27	90	6.0	5.1	3.7	<1.6	1.7	<0.64

Sample ID	Depth (cm)	Fluorene	Phenanthrene	Anthracene	Fluoranthene	Pyrene	Chrysene	Benz[a]anthracene	Benzo[b]fluoranthene	Benzo[k]fluoranthene	Benzo[a]pyrene	Benzo[ghi]perylene+Indeno[1,2,3-cd]pyrene
WT-02	4	<177	<20	<21	10	20	<4	<4.3	1.6	<1.6	<1.5	<0.64
	14	234	<20	<21	17	32	<4	<4.3	4.9	<1.6	1.7	0.69
	24	<177	<20	<21	15	37	4.6	<4.3	5.2	<1.6	2.4	0.67
	36	<177	36	<21	22	57	7.4	4.4	5.8	<1.6	2.3	0.69
	44	<177	<20	<21	11	26	<4	<4.3	3.2	<1.6	<1.5	<0.64
	54	839	195	66	34	126	4.9	5.1	<1.4	<1.6	<1.5	<0.64
	66	818	415	101	42	235	7.7	8.7	3.5	<1.6	2.2	<0.64
	74	995	438	94	45	262	8.3	11.5	3.7	<1.6	2.8	<0.64
	86	1245	415	112	44	217	5.4	6.3	2.0	<1.6	<1.5	<0.64

Sample ID	Depth (cm)	Fluorene	Phenanthrene	Anthracene	Fluoranthene	Pyrene	Chrysene	Benz[a]anthracene	Benzo[b]fluoranthene	Benzo[k]fluoranthene	Benzo[a]pyrene	Benzo[ghi]perylene+Indeno[1,2,3-cd]pyrene
WT-03	4	<177	<20	<21	14	32	5.7	4.4	2.9	<1.6	<1.5	<0.64
	14	<177	<20	<21	<9	18	<4	<4.3	<1.4	<1.6	<1.5	<0.64
	24	203	34	39	17	47	<4	4.4	2.2	<1.6	1.5	<0.64
	34	<177	25	<21	<9	13	<4	<4.3	<1.4	<1.6	<1.5	<0.64
	54	<177	45	37	16	54	<4	<4.3	<1.4	<1.6	<1.5	<0.64
	64	672	299	65	24	117	4.6	5.7	<1.4	<1.6	<1.5	<0.64
	74	328	161	39	17	62	<4	<4.3	<1.4	<1.6	<1.5	<0.64
	86	432	145	28	13	55	<4	<4.3	<1.4	<1.6	<1.5	<0.64

Sample ID	Depth (cm)	Fluorene	Phenanthrene	Anthracene	Fluoranthene	Pyrene	Chrysene	Benz[a]anthracene	Benzo[b]fluoranthene	Benzo[k]fluoranthene	Benzo[a]pyrene	Benzo[ghi]perylene+Indeno[1,2,3-cd]pyrene
WT-04	6	<177	<20	<21	17	38	4.9	<4.3	5.1	<1.6	2.3	<0.64
	14	<177	<20	<21	<9	11	<4	<4.3	<1.4	<1.6	<1.5	<0.64
	24	<177	<20	<21	<9	16	<4	<4.3	<1.4	<1.6	<1.5	<0.64
	34	<177	<20	<21	<9	14	<4	<4.3	<1.4	<1.6	<1.5	<0.64
	44	2704	7730	668	301	1596	39.4	47.3	20.3	2.89	9.2	<0.64
	54	1871	4914	481	<9	1088	25.8	31.0	12.1	1.82	8.7	0.88
	64	1975	4153	388	114	616	14.5	14.8	5.8	<1.6	4.9	<0.64
	74	1454	2307	247	79	426	11.4	12.8	5.1	<1.6	3.1	<0.64
	86	1349	2122	212	82	353	14.8	13.4	5.5	<1.6	3.2	<0.64

Sample ID	Depth (cm)	Fluorene	Phenanthrene	Anthracene	Fluoranthene	Pyrene	Chrysene	Benz[a]anthrac	Benzo[b]fluo	Benzo[k]fluora	Benzo[a]pyrene	Benzo[ghi]perylene	Inden
PQL =		**177**	**20**	**21**	**9**	**10**	**4.0**	**4.3**	**1.4**	**1.59**	**1.5**	**0.64**	
ET-02	4	<177	103	<21	44	108	15.6	10.1	7.0	1.64	4.4	0.65	
	14	234	94	<21	39	108	15.6	9.8	7.5	<1.6	3.8	0.77	
	24	<177	85	<21	35	86	12.2	8.4	7.9	<1.6	4.4	1.33	
	34	<177	62	<21	42	108	18.2	11.8	9.2	1.73	4.5	0.86	
	44	297	87	<21	50	126	19.6	13.4	9.9	<1.6	5.2	1.00	
	54	3017	8930	388	161	1124	33.8	32.4	10.8	2.63	8.7	1.35	
	66	9374	52011	2655	1539	10994	591.3	538.4	183.1	35.89	155.5	17.10	
	74	<177	5376	224	117	616	30.9	21.6	9.5	<1.6	6.9	0.86	
	86	776	1361	177	168	906	42.2	43.2	13.7	2.98	12.2	1.12	
ET-03	6	318	<20	<21	<9	46	<4	<4.3	7.6	<1.6	2.1	<0.64	
	14	<177	25	<21	52	135	26.1	14.8	12.4	3.20	6.3	0.88	
	24	276	39	<21	64	163	36.6	22.9	20.3	5.57	9.2	1.27	
	34	<177	22	<21	16	45	5.4	<4.3	2.8	<1.6	1.6	<0.64	
	44	<177	<20	<21	14	45	8.0	5.5	4.6	<1.6	2.1	<0.64	
	54	<177	32	<21	15	58	7.1	5.2	3.1	<1.6	2.1	<0.64	
	64	<177	48	22	15	75	4.6	<4.3	1.6	<1.6	<1.5	<0.64	
	74	516	195	62	52	299	15.6	13.4	4.3	<1.6	3.9	<0.64	
	86	672	461	131	109	580	36.6	28.3	7.8	<1.6	5.8	<0.64	
ET-04	6	<177	<20	<21	30	117	11.4	7.8	12.1	1.64	5.5	<0.64	
	14	<177	<20	30	97	299	47.9	32.4	18.8	2.76	9.8	1.08	
	34	234	117	25	79	244	36.6	24.3	21.8	5.12	12.7	1.25	
	44	<177	117	<21	72	217	30.9	21.6	17.2	2.22	8.7	1.18	
	54	<177	71	<21	66	199	28.1	18.9	14.8	1.96	8.1	1.06	
	86	<177	<20	<21	39	126	14.8	12.9	8.7	<1.6	4.9	<0.64	