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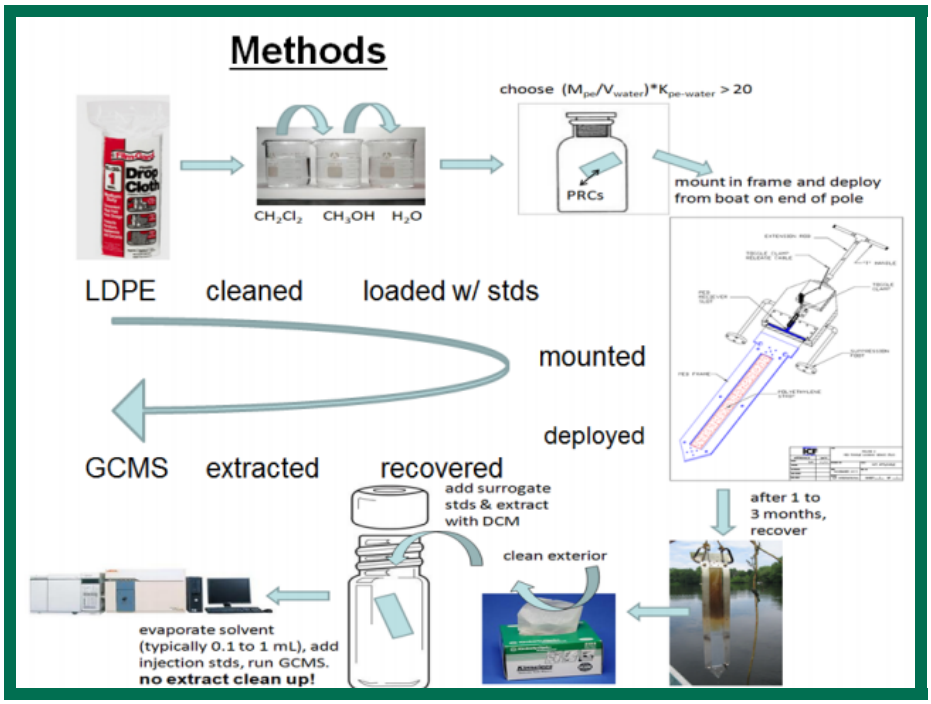

Passive Polyethylene Sampling in Support of In Situ Remediation of Contaminated Sediments

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ENVIRONMENTAL SECURITY
TECHNOLOGY CERTIFICATION PROGRAM

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Our overarching goal was to show PE passive sampling is suited to assessing contaminated sediment sites. Hence, we sought to demonstrate: (a) PE effectively evaluates porewater concentrations of contaminants, (b) PE can delineate the horizontal and vertical extent of contamination, (c) PE is suited for long term monitoring, and (d) the PE passive sampling approach is commercially viable. Laboratory testing showed the PE samplers measured pore waters more accurately than the common commercial practice of using sediment concentrations. PE sampling readily revealed the distribution of sediment contamination by PCBs at the demonstration site. PE samplers showed the site had pg/L levels of individual PCBs in pore waters and bottom waters. Sand cap data indicated no upward PCB fluxes through those caps. Finally, QA/QC, sensitivity, ease of use, and cost metrics all supported the conclusion that PE passive sampling is commercially viable.

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ACRONYMS AND ABBREVIATIONS

$C_{porewater}$	concentration of HOC in pore water (e.g., µgHOC/mLpore water)
$C_{sediment}$	concentration of HOC in dry sediment (e.g., µgHOC/gsediment)
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
EPA	Environmental Protection Agency
EqP	equilibrium partitioning model
ESTCP	Environmental Security Technology Certification Program
f_{oc}	organic carbon weight fraction in sediment (gorganic carbon/gsediment)
GC/MS	gas chromatography/mass spectrometry
HOC	hydrophobic organic compound
IDW	investigation-derived waste
K_d	sediment-water partition coefficient (e.g., mLwater/gsediment)
K_{oc}	organic carbon normalized sorption coefficient (mLwater/gorganic carbon)
K_{ow}	octanol-water partition coefficient (mLwater/mLoctanol)
K_{PEw}	PE-water partition coefficient (e.g., mLwater/gPE)
LDPE	low density polyethylene
LTM	long term monitoring
µL	microliter
MDL	method detection limit
mg/kg	milligram per kilogram
ng/g	nanogram per gram
ng/L	nanogram per liter
NPL	National Priorities List
NSSC	U.S. Army Natick Soldier Systems Center
PAH	polycyclic aromatic hydrocarbon
PCB	polychlorinated biphenyl
PE	polyethylene
PED	polyethylene device
pg/L	picogram per liter
PPE	personal protection equipment
PRC	performance reference compound

ACRONYMS AND ABBREVIATIONS (continued)

QA/QC	quality assurance/quality control
RPD	relative percent difference
SOP	standard operating procedure

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Meanwhile, at ICF International, Dean Gouveia provided critiques concerning analytical chemistry and regulatory issues and Steve Reichenbacher accomplished the several rounds of field sampling and much of the cost analysis. Finally, James Connolly of the US Army Natick Soldier Systems Center provided logistical support at the demonstration site and critiqued the work from the point of view of the client (i.e., Department of Defense [DoD]).

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EXECUTIVE SUMMARY

OBJECTIVES OF THE DEMONSTRATION

The overarching goal of this work was to show polyethylene (PE) passive sampling is suited to assessing contaminated sediment sites by enabling the measurement of porewater concentrations of hydrophobic organic compounds, like polychlorinated biphenyls (PCB) and polycyclic aromatic hydrocarbons. To this end, the project team sought to demonstrate: a) the PE technology accurately evaluates concentrations of target contaminants in pore water; b) PE data can be used to delineate the horizontal and vertical extents of sediment contamination; c) PE sampling is suited for long term monitoring; and d) the PE passive sampling approach is commercially viable.

TECHNOLOGY DESCRIPTION

The PE passive sampling method involves inserting a strip of low density polyethylene, impregnated with suited performance reference compounds (PRC), into sediments (and/or surface waters) of interest. After suitable deployment times, the PE strips are recovered and analyzed for the concentrations of the contaminants of concern. The concentrations in the PE may require adjustment based on the PRC losses, to values that would reflect equilibration with the surroundings. This equilibrated result can then be normalized by the contaminant's polyethylene-water partition coefficient to yield the compound's porewater (or surface water) concentration.

DEMONSTRATION RESULTS

Laboratory testing showed the PE samplers measured pore waters much more accurately than the common commercial practice of using sediment concentration data. Moreover, the PE data readily revealed the extent of PCB contamination at the demonstration, both laterally and with depth into the sediment bed. Also, the PE samplers were capable of showing that the demonstration site has concentrations of individual PCB congeners at picogram per liter levels in the uppermost pore waters and the site's bottom waters. The PE sampler results indicated that the uppermost porewater concentrations were not equilibrated with the sediment solids in which they occurred, perhaps due to significant downward flow of lake water into the bed at the site. Finally, quality assurance/quality control, sensitivity, ease of use, and cost metrics, all supported the conclusion that the PE passive sampling approach is commercially viable.

IMPLEMENTATION ISSUES

The development of standard operating procedures and an on-line calculator suited to using PRC data should enable interested environmental consultants and contract laboratories to implement PE passive sampling.

The chief remaining obstacle to widespread use of this PE passive sampling site evaluation approach involves enabling regulatory personnel to relate pore water concentration data with currently available regulatory standards.

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1.0 INTRODUCTION

Hydrophobic organic compounds (HOC), like polychlorinated biphenyls (PCB) and polycyclic aromatic hydrocarbons (PAH), contaminate sediments at many sites. Assessment requires expensive field sampling and laboratory analyses. High costs are driven by the need to obtain enough samples to characterize risks and to design remediation efforts that will be sufficient to lower risks to acceptable levels.

While recent research has shown that porewater concentrations allow the most accurate estimates of impacts like bioaccumulation of HOCs, work has also demonstrated the inaccuracy of using sediment concentrations to infer exposures of receptors and corresponding risks. However, measuring porewater concentrations of low-solubility compounds like PCBs and PAHs can be quite difficult. As a result, this project sought to demonstrate an alternative approach, passive sampling, that can accurately evaluate pore waters and thereby assess organism and ecosystem exposures to such contaminants.

1.1 BACKGROUND

Passive samplers accumulate contaminants from the environmental in proportion to the chemical activities in the sampled medium (Huckins et al., 1990; Arthur and Pawliszyn, 1990). In this project, the project team sought to demonstrate that polyethylene (PE) passive samplers, inserted in contaminated sediments, would reveal the presence of contaminants like PCBs in pore water. Moreover, the team proposed that PE passive sampling can be easier, safer, and more cost effective than the collection and analysis of sediments. This allows for better problem delineation and enables effective monitoring of any long term changes after remediation.

1.2 OBJECTIVE OF THE DEMONSTRATION

Hence, the overall objective of this study was to demonstrate that PE passive sampling is a commercially viable technology that is well suited to determining horizontal and vertical distributions of HOCs in sediment pore waters (and overlying waters) for purposes of assessing remediation needs and/or long term monitoring (LTM). The project-specific objectives included:

a) Demonstrating the PE samplers effectively evaluate pore water concentrations of target HOCs comparable to direct pore water assessment methods;

b) Demonstrating that PE passive sampling can define the horizontal and vertical extents of sediment contamination;

c) Demonstrating that PE sampling is suited for LTM programs; and

d) Establishing the commercial viability of PE sampling and analysis, including costs and analytical metrics such as accuracy, precision, and limits of detection.

1.3 REGULATORY DRIVERS

Regulatory goals typically involve limiting human and ecosystem risks associated with exposures to contaminants. For contaminated sediments, these risks are best evaluated using

sediment porewater concentrations. If PE allows site managers to delineate areas of concern, it should become a valid tool for making informed decisions in the risk management process.

2.0 TECHNOLOGY

2.1 TECHNOLOGY DESCRIPTION

The PE passive sampling approach utilizes low density polyethylene (LDPE) to accumulate organic contaminants from sediment beds (or overlying waters) in proportion to the surrounding dissolved concentrations. As discussed in Fernandez et. al. (2009), compounds like PCBs and PAHs diffuse through the surrounding environmental media, partition into the PE, and accumulate until the PE concentrations are equilibrated with the environment. Because, in practice, investigators often cannot leave the sampler exposed in sediments long enough to achieve partitioning equilibration, internal standards called performance reference compounds (PRC) are impregnated in the PE films before they are deployed. And, because the PRCs experience the same mass transfer limitations while diffusing out of the PE as the target compounds that are diffusing into the PE, one can use the measured losses of the PRCs to also know the fractional approaches to equilibrium of the target compounds (Fernandez et. al., 2009; Apell and Gschwend, 2014). Using this result, the concentrations of target compounds accumulated in the PE during the finite deployment time can be adjusted to the levels the samplers would have achieved at equilibrium. Finally, these equilibrium concentrations can be normalized with PE-water partition coefficients, K_{Pew}'s, to find the porewater concentrations of the contaminants of interest.

Detailed information concerning the methods for preparing, deploying, and analyzing PE samplers can be found in on-line guidance documents (Gschwend et. al., 2012a, 2012b, and 2012c). Just before field deployments, the PRC-loaded PE sheets are mounted in rigid, aluminum, sheet metal frames creating a polyethylene device (PED; see Figure 1). Such samplers can be deployed a) in shallow waters by hand; b) at modest depths (<5 m) using a pole with a releasing mechanism; c) in deeper waters by divers (5-20 m); and d) in deeper sites using a frame lowered from a boat. Samplers are marked with buoys or tag lines to facilitate their recoveries.

After the desired deployment period, samplers are recovered, rinsed of any adhering mud, wrapped in clean aluminum foil, and placed in clean storage (e.g., an ice chest without ice in it). Upon return to the lab, the PE surface is cleaned with a water-wetted Kimwipe® and cut into sections (e.g., to obtain replicates or to acquire samples from varying depths into a sediment bed). The PE pieces, usually 10 to 100 milligram masses, are placed in pre-cleaned, amber glass vials, spiked with method recovery standards, and submerged in methylene chloride for at least 12 hours. The PE is re-extracted two more times in methylene chloride and the extracts combined. PE extracts are concentrated to suitable volumes, and appropriate injection standards are added before analysis. Using the PRC recovery data found in each PE section, the sediment-equilibrated target compound concentrations in the PE are calculated. A graphic user interface called the "PRC Correction Calculator" can be used to assist such calculations (Tcaciuc et. al., 2014). Using the corresponding PE-water partition coefficients (also given in the PRC Correction Calculator), each contaminant's porewater concentration is calculated.

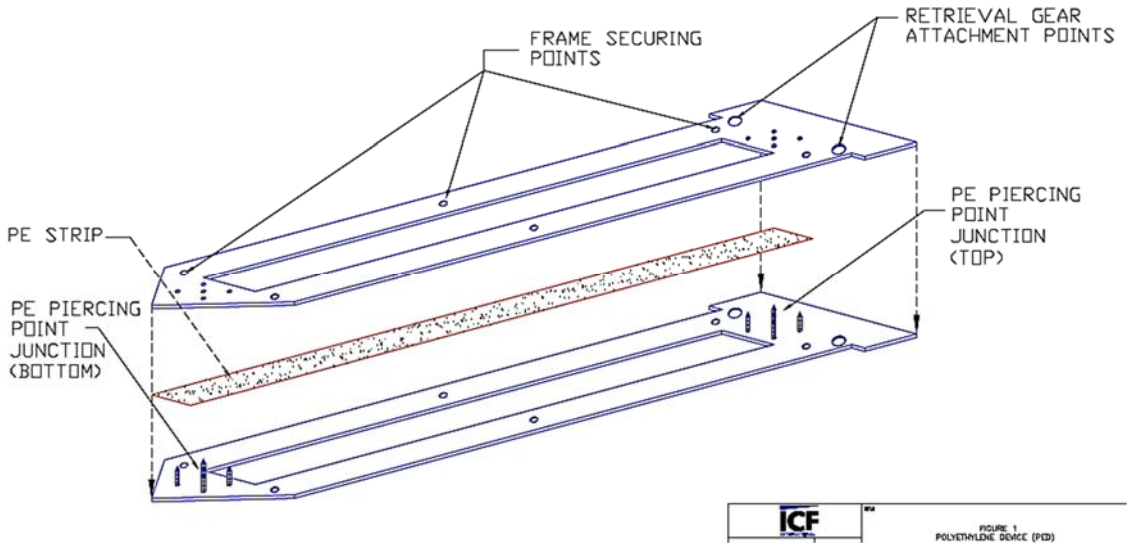

Figure 1. A PE passive sampling device made using aluminum sheet metal cut into two frames (blue) so as to "sandwich" a strip of PRC-loaded PE (red). The resultant PED allows the 5-cm wide by 50-cm long PE strip to be exposed to the sediment and bottom water on both sides (drawing by ICF International).

2.2 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

PE passive sampling offers several advantages. It yields data that reveal:

1. Vertical HOC concentration variations (e.g., indicating burial of contaminated sediment);
2. Sediment porewater-bottom water concentration gradients enabling estimation of fluxes; and
3. Bioavailable contaminant levels needed to evaluate bioaccumulation and biodegradation.

When compared with traditional sediment site characterization techniques, the PE method enables a reduction in manpower, equipment and shipping costs, and investigation-derived waste (IDW) costs. It is also safer than traditional sediment sampling techniques.

Limitations of the PE passive sampler approach may include:

(1) Resultant data are not yet accepted by all regulators because clean up criteria are not yet expressed as porewater concentrations;

(2) Current samplers may require "prolonged" deployments (>2 month) to assess some HOCs;

(3) Sediment beds at some sites (e.g., rocky substrates) may present some difficulties for deploying the PE; and

(4) Reasonable deployment times may be an obstacle to a cost-effective deployment/retrieval program and to avoid sampler losses during deployment due to

vandalism, exposures to strong propeller wash, or as a consequence of extreme weather events.

3.0 PERFORMANCE OBJECTIVES

Table 1. Performance objectives.

Performance Objective	Data Requirements	Success Criteria	Results
1. Demonstrate PE passive sampling accurately provides measures of porewater concentrations.	Porewater concentrations measured via porewater extractions and via PE passive samplers	• Average relative percent difference (RPD) of -50% / +100% or less (i.e., ≤ factor of 2)	• *Ex situ* PE sampling of sediments from many sites for individual PCB congeners yielded results that were 79±47% (N=60) of results obtained by porewater extractions
2. Demonstrate PE passive sampling is effective for site mapping.	PCB porewater concentrations deduced using PE samplers in a spatially-distributed array of samples suited to mapping site	• Lower uncertainty value in areal delineation • Cost for PE sampler approach less or comparable to traditional sampling and analysis	• PE porewater results were more accurate than sediment-based data, allowing better delineation of PCB chemical activities in sediments • Cost for PE use virtually the same as current practice of collecting and analyzing sediments
3. Demonstrate PE Passive sampling is suited to LTM after site remediation	PE passive sampler data from same sediment sites through time	• PE porewater data from same locations shows temporal trend of increasing, unchanging, or decreasing porewater PCBs	• PE data collected annually and as a function of depth into sediment bed showed little or no change in porewater concentrations • Note: project ended only few years after dredging at site
4. Demonstrate PE passive sampling as commercially viable based on (QA/QC) metrics, ease of use, and costs	• Replicate PE sampling data from representative sediment samples • PE data from samples analyzed by both MIT and contract lab (Pace Analytical) • Experience of environmental consulting firm using PE passive samplers at Department of Defense site • Costs of time and materials needed for PE passive sampling and traditional sampling of PCBs at same site	• Accuracy, precision, MDLs using PE are comparable to or better than those found using accepted porewater analyses procedures • Gain environmental consultant and contract lab acceptance • Cost for use of PE samplers less than or comparable to traditional sampling and analysis	• For congeners with >30% approach to equilibrium during sampler deployment, data precisions were better than ±50%. MDLs were near 1 pg/L for individual PCB congeners. • Comparisons to direct porewater extractions shows PE data yield accurate results within error. • Environmental regulators (EPA Regions 2 and 9) and companies besides ICF International (CH2M-Hill, Louis Berger, HDR) have used PE sampling and/or PE data to characterize contaminated sites • Contract lab charges for congener-specific PCB analysis of PE samples are the same as for sediment samples. Costs of field sampling and analysis comparable to traditional approaches relying on sediment sampling

EPA = U.S. Environmental Protection Agency
MDL = method detection limit
pg/L = picogram per liter
QA = quality assurance
QC = quality control

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4.0 SITE DESCRIPTION

4.1 SITE LOCATION

Pegan Cove, located in the South Pond of Lake Cochituate, Natick, Massachusetts, was the site for the PE passive sampling technology demonstration (Figure 2). This site was added to the National Priorities List (NPL) under Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) in May 1994 to evaluate and implement responses to past releases of hazardous substances, particularly PCBs. In particular, one confirmed PCB-containing transformer release occurred here in the mid-1980s, and is believed to be largely responsible for the elevated PCB concentrations in sediment.

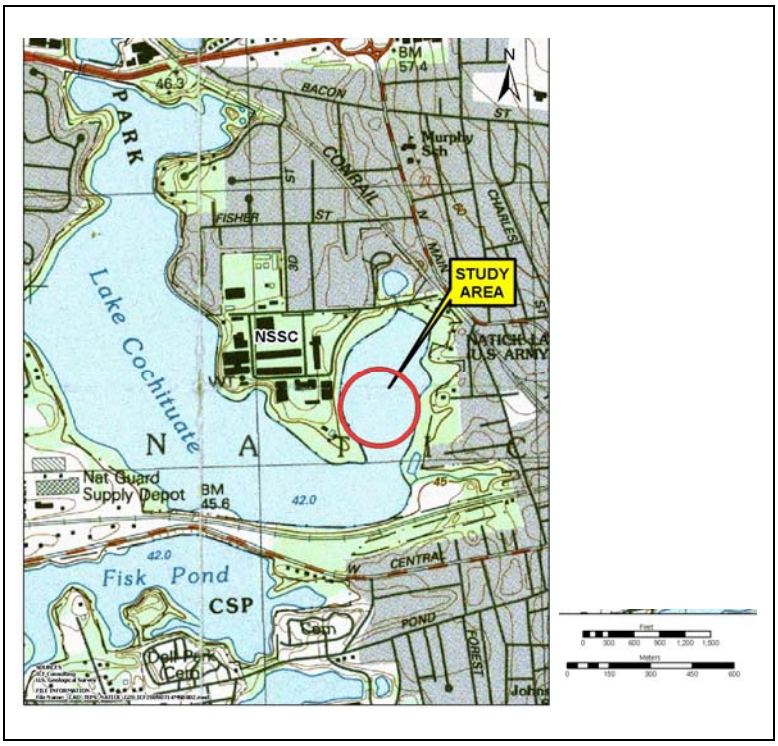


Figure 2. Map showing location of the study area, Pegan Cove, within Lake Cochituate and adjacent to the U.S. Army Natick Soldier Systems Center (NSSC).

4.2 SITE GEOLOGY/HYDROGEOLOGY

The sediment in Pegan Cove is generally silty clay, overlying peaty debris. Nearshore sediment tends to consist of a larger percentage of sand. Surface sediment samples collected within Pegan Cove in 2007 had fractions of organic carbon (f_{oc}) ranging from 1 to 38% (ICF, 2009). The water content in Pegan Cove sediments is also high, and porosities are typically above 90%.

During this project, water supply wells (Natick Springvale wellfield) were found to be pumping year round about 1200 m NW from Pegan Cove. The calculated zone of influence suggests that lake water is constantly being drawn into the sediments of the Cove. Temperature profiles into

the sediment bed support this as they indicate downward porewater flows of centimeters per day. This situation may cause sorptive disequilibrium of PCBs in the porewater and the sediment.

4.3 CONTAMINANT DISTRIBUTION

Since the mid-1990s, hundreds of sediment samples have been collected from Pegan Cove in Lake Cochituate in association with environmental investigations (Figure 3). Total PCB concentrations within the Pegan Cove area ranged from 0.15 to 4.1 milligram per kilogram (mg/kg) (average of 1.7 mg/kg). The 2007 data indicated that elevated total PCB concentrations extend across much of the Pegan Cove area, and are greatest along the western shoreline, particularly at, and to the south of, the main outfall.

Figure 4
Total PCB Sediment Concentrations
Pegan Cove, Lake Cochituate

Figure 3. Distribution of PCB sampling stations and measured ∑PCB concentrations (mg/kg) in the sediments of Pegan Cove (measured in 2007).

5.0 TEST DESIGN

5.1 CONCEPTUAL EXPERIMENTAL DESIGN

In the initial phase of the project, sediment samples were collected from the lake for laboratory or ex situ testing (Table 2). Subsequently, several PE deployments were done within the in situ sediments of Pegan Cove. At each stage, data was used to ascertain the effectiveness of the PE approach, especially as it can be contrasted to the "traditional" means of site assessment. This was done considering both performance and cost metrics.

Table 2. Field sampling performed in this project.

Sample Round	Goal(s)	Sampling or Deployment Date	Retrieval Date	Number of Days Deployed	Sample Numbers	Comments Samplers Lost
Round 1	Recover sediment for lab testing PE passive samplers	Not applicable	Nov 2009	Not applicable	0 – 10	Sediments retrieved
Round 2	Begin PCB site mapping, LTM	Dec 3, 2010	Apr 7, 2011	125 days	11 – 20	Sediments retrieved
Round 3	Continue PCB site mapping, examine field replication	May 27, 2011	June 28, 2011	32 days	21-40	Sediments retrieved
Round 4	Continue PCB site mapping	Oct 17, 2011	Nov 16, 2011	31 days	41-60	44, 49, 55
Round 5	Conduct LTM	Nov 17, 2011	May 3, 2012	168 days	61-70	61, 63-68, 70
Round 6	Test lake water infiltration, LTM, cap testing	Oct 17, 2012	Dec 5, 2012	47 days	71-79	73, 77 (site 50 repeat)

5.2 BASELINE CHARACTERIZATION

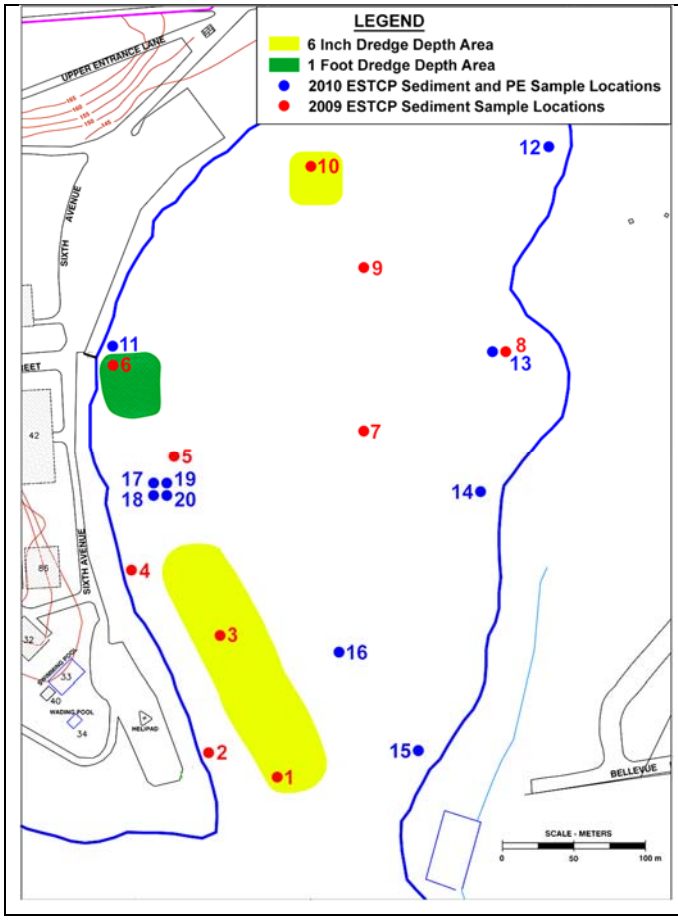
Baseline site characterization had previously been performed as part of ICF International's long term involvement at the demonstration site (ICF International, 2009). As a result, the following information was readily available: 1) lake bathymetry, 2) lake sediment characterization, and 3) PCB distributions in the lake sediment bed as of 2009.

5.3 LABORATORY STUDY RESULTS

The initial efforts of the project team involved demonstrating that the PE sampling technology yields porewater concentration data that are consistent with "traditional" measures of such porewater concentrations. Sediments were collected from 20 stations (Figure 4), distributed around the demonstration site, during the first two sampling rounds. The sediments were returned to the laboratory where they were thoroughly homogenized (Follett, 2011). The lake sediments were very porous (~90%) and they exhibited high organic carbon content (average 14% organic carbon by weight).

Batches of the sediments were centrifuged to isolate porewater, and alum was used to remove colloids (Hawthorne et al., 2005). Recovery standards were added, then the porewater was

extracted with dichloromethane. After the combined solvent volume was reduced, 1 microliter (μL) aliquots were analyzed by gas chromatography/mass spectrometry (GC/MS). Porewater concentrations of individual PCB congeners were calculated correcting for standard recoveries.



site	porosity	f_{oc}	total PCBs in sediment ppm
1	0.88	0.14	2.7
2	0.55	0.0060	2.7
3	0.92	0.16	1.7
4	0.65	0.013	0.1
5	0.92	0.19	1.2
6	0.78	0.046	1.1
7	0.92	0.21	1.5
8	0.90	0.14	3.1
9	0.93	0.29	1.4
10	0.92	0.15	1.9
11	0.96	0.093	1.2
12	0.94	0.15	1.1
13	0.95	0.14	1.9
14	0.96	0.10	0.9
15	0.95	0.14	2.1
16	0.94	0.15	2.9
17	0.94	0.15	2.0
18	0.94	0.17	2.5
19	0.93	0.19	2.3
20	0.94	0.17	2.6

Figure 4. (left) Map of 20 stations distributed in Pegan Cove, Lake Cochituate (right). Sediment porosities (volume fractions), organic carbon contents (weight fractions), and ∑PCBs (mg/kg dw) are shown for each station; stations 2 and 4 were located at near-shore sandy locations and had distinctly lower porosities and organic carbon contents (f_{oc}). Note stations 17, 18, 19, and 20 were located on the corners of square that was 10 m on a side.

In parallel, aliquots of the sediment samples were placed in glass jars for ex situ PE passive sampling to ensure the PE sampled the same porewater as that which was isolated by centrifugation. PE pieces were inserted into the quiescent mud to allow uptake of the target PCBs from the samples. For two of the sites (1 and 8), replicate sampling was done (N = 11 or 13) to allow determination of the passive sampling method's reproducibility. After a month, passive sampling was terminated. Two PE strips from each treatment were sent to Pace Analytical for analyses. At MIT, the PE was extracted and analyzed by GC/MS. The observed build-ups of target PCBs were corrected for not reaching equilibrium using the measured losses of the PRCs (Fernandez et al., 2009b). Finally, porewater concentrations were deduced by dividing the PE concentrations by each congener's PE-water partition coefficient, K_{PEw}.

Also, sediment concentrations of PCBs were determined by solvent extractions and analysis by GC/MS. Subsequently, the Equilibrium Partitioning (EqP) approach (DiToro et al., 1991) was applied to estimate porewater concentrations: ($C_{porewater} = C_{sediment}/K_d$). Sorption coefficients were estimated using the sediment's organic carbon content, f_{oc}, and the HOC's organic carbon-normalized sorption coefficient, K_{oc} (Hansen et al., 1999). Together, the resultant data allowed us to demonstrate how well PE- or sediment-based measures compare with direct measures of porewater concentration for individual PCB congeners.

5.4 FIELD TESTING

Sampling rounds 2 through 6 involved deployments of PE samplers in the field (referred to as in situ measures). Initial efforts were intended to gain data for contamination mapping (rounds 2, 3, and 4). PE samplers in round 2 were also sectioned in 5 cm lengths and analyzed to evaluate vertical profiles of dissolved PCBs into the sediment bed. Superimposed on this effort was the deployment of samplers to annually obtain LTM results (rounds 2, 5, and 6). Finally, field sampling was also performed for the special purposes of assessing the integrity of the sand caps and gaining data indicative of the impact of groundwater pumping.

Table 3. Total number of types of samples collected.

Objective	Location	Matrix	Number of Samples	Analyte Measured at MIT	Duplicate Analyses at Contract Lab
1. Demonstrate PE passive sampling accurately provides measures of porewater concentrations	Sediment surface grabs, distributed locations with range of PCB concentrations from Pegan Cove, Lake Cochituate	PE (lab incubated) Pore water Sediment grabs	25 25 25	25x PCBs 25 x PCBs, 25 x PCBs, 7x f_{oc}, f_{BC}	16 x PCBs 2 x PCBs 2 x PCBs
2. Demonstrate PE passive sampling is effective for site mapping	Distributed locations exhibiting range of PCBs concentrations from Pegan Cove, Lake Cochituate	PE (field incubated) Pore water Sediment cores	60 strips 12 20	264 x PCBs 17 x PCBs 12 x PCBs (7 x 3 depths)	8 x PCBs
3. Demonstrate PE passive sampling is suited to LTM after site remediation	Allow transect from hot spot to relatively clean location from Cove out to larger lake	PE (field incubated)	Annually (i.e., in each of 3 years) at multiple locations and reflecting multiple depths at each location	74 x PCBs	
4. Demonstrate PE passive sampling commercially viable based on QA/QC metrics, ease of use, and costs	Distributed locations exhibiting range of PCBs concentrations from Pegan Cove, Lake Cochituate	PE	Two sediment grab samples, each spiked at three levels: 1) incubated with PE; 2) extracted for porewater; and 3) sediment sampled	80 x PCBs (10 PE replicates of native and three PCB spike levels) 8 PCBs	16 (2 x 4 PCB spike levels in sediments from two stations)

5.5 SAMPLING METHODS

The procedures for preparing, deploying, and analyzing the PE and translating those results into corresponding HOC water concentration data are all described in a set of three Standard Operating Procedures (SOP) posted on-line at the ESTCP web site (Gschwend et al., 2012a, 2012b, and 2012c.) The PE sheet is purchased from a hardware store. It is cleaned using organic solvents, and then loaded with PRCs. To deploy the PE, it is mounted in an aluminum sheet metal frame and inserted into the sediment. After suitable deployment time, the sampler is retrieved, the PE is extracted, and analyzed by GC/MS. The measured concentration data are extrapolated to equilibrium values using the PRCs' data in the "Performance Reference Compound Calculator" (available at http://www.serdp.org/Program-Areas/Environmental-Restoration/Contaminated-Sediments/ER-200915). These results are translated to water concentrations using each compound's PE-water partition coefficient, KPEw.

Corresponding samples also were collected for porewater and sediment analyses (Table 4). A ponar dredge was used to collect surface (0"-6") sediment samples from loci having a range of PCB contamination levels at the site. These samples were homogenized at the MIT lab, then a split sample was used to obtain porewater. Pore waters were acquired by placing sediments in glass centrifuge tubes and then centrifuging for 30 to 60 min at 900g to separate the porewaters from the sediment solids. Porewater colloids were removed using alum.

PE, porewater, and sediment were analyzed via previously reported methods (Table 4). Briefly, dichloromethane extracts were analyzed by GC/MS with the chromatography performed as described in EPA Method 8082a.

Table 4. Analytical methods for sample analyses.

Matrix	Analyte	Method	Container	Preservative	Holding Time
PE	PCBs	SOP for PE analysis (see Gschwend et al., 2012c)	Glass vial	Cold	30 days to extract
Pore water	PCBs	EPA 8082a except MS detection instead of electron capture detector	Glass	Cold	7 days to extract
Sediment	PCBs	EPA 8082a except MS detection	Glass	Cold	1 year
Sediment	f_{oc}, f_{BC}	Gustafson et al., 1997	Glass	Cold	1 year

MS = mass spectrometry

6.0 PERFORMANCE ASSESSMENT

6.1 PERFORMANCE OBJECTIVE: DEMONSTRATE PE PASSIVE SAMPLING ACCURATELY PROVIDES MEASURES OF POREWATER CONCENTRATIONS

In light of the initial laboratory testing, two key changes were made in the method. First, more PRCs (Table 5) were used. Also, a graphic user interface called "PRC Correction Calculator" was developed based on the mass transfer model of Fernandez et al. (2009), which allows the investigator to fit the PRC loss data that is deemed analytically dependable (e.g., using only those PRCs showing >10% loss and >10% remaining) and then applied the fit to other HOCs with different mass transfer properties (e.g., K_{PEw}, D_w, D_{PE}). This PRC Correction Calculator is available at https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Sediments/ER-200915/. Testing of these changes shows very good results (Figure 5). To sum, the project team finds that PRC loss data, processed with the PRC-Correction Calculator, accurately evaluated fractional gains of target compounds.

Table 5. List of ^{13}C-labeled PCB congeners used as performance recovery standards in this study. Also shown are the log K_{ow} values from Hawker and Connell (1988) and the log K_{pew} values estimated from log K_{pew} = log K_{ow} – 0.287 from Gschwend et al. (2011).

Performance Reference Compounds			
		log K_{ow}	log K_{pew}
^{13}C PCB 28	2,4,4'-Trichlorobiphenyl	5.67	5.38
^{13}C PCB 54	2,2',6,6'-Tetrachlorobiphenyl	5.21	4.92
^{13}C PCB 47	2,2',4,4'-Tetrachlorobiphenyl	5.85	5.56
^{13}C PCB 97	2,2',3,4',5'-Pentachlorobiphenyl	6.29	6.00
^{13}C PCB 111	2,3,3',5,5'-Pentachlorobiphenyl	6.76	6.47
^{13}C PCB 153	2,2',4,4',5,5'-Hexachlorobiphenyl	6.92	6.63
^{13}C PCB 178	2,2',3,3',5,5',6-Heptachlorobiphenyl	7.14	6.85

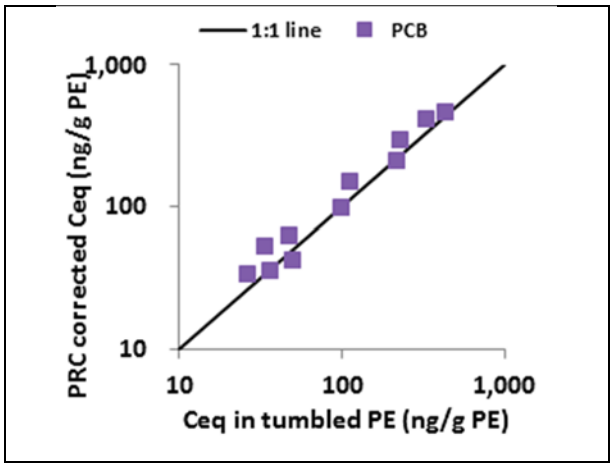


Figure 5. Comparisons between ex situ PE-sampler inferred concentrations using homogenized sediments and PRC corrections with concentrations found by exhaustively mixing PE with lake sediments ("tumbling") in the laboratory until the PCBs in the sediment equilibrated with the PE (Apell and Gschwend, 2014). All PCB target compounds were between PRCs in terms of size causing all corrections to involve interpolations. Results on average to within 15% (N=10), and were at worse within a factor of 1.5 of each other.

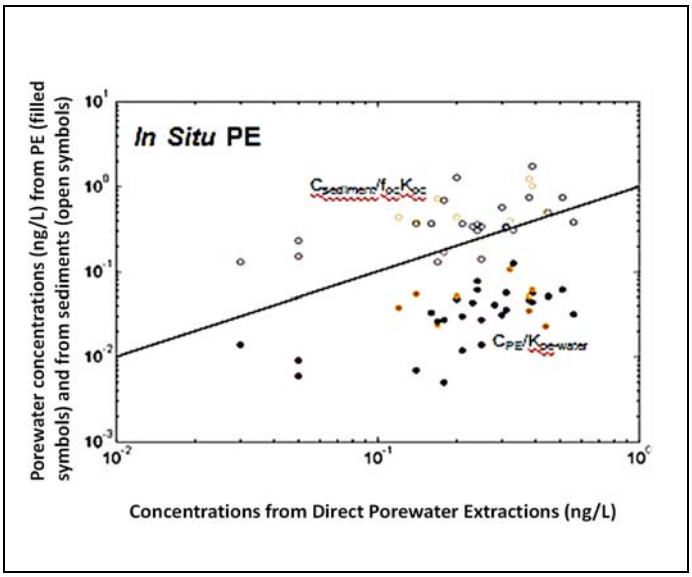


Figure 6. PCB porewater concentrations measured using PE passive samplers (filled circles) were consistently lower when measured in situ as compared to direct porewater extractions and analysis (solid line) while sediment-inferred results were higher that direct porewater analysis.

Next, in situ PE passive sampling consistently showed lower porewater concentrations than corresponding ex situ measurements (Figure 6). This suggested that lake sediments and their porewaters were not at sorptive equilibrium in the field. Various lines of evidence support this, including: a) calculations of the zone of influence of nearby water supply wells implying lake

water infiltration in Pegan Cove; b) temperature profiles in the sediments indicate inflows from the lake at centimeters per day; and c) ratios of PCB congeners in the surface sediment show that less hydrophobic PCBs are depleted relative to more hydrophobic ones as a function of time.

Finally, a comparison of PE passive sampling results with EqP-type calculations was performed (Apell and Gschwend, 2014). In this case, the data from each method was compared to porewater concentrations found by using PE in a solid phase extraction mode from a sediment slurry (after Lohmann et al., 2005). In every case, the ex situ passive sampling results matched the equilibrium results extremely well (Figure 7). Hence, the project team concluded that the PE passive sampling approach obtains accurate porewater concentration data.

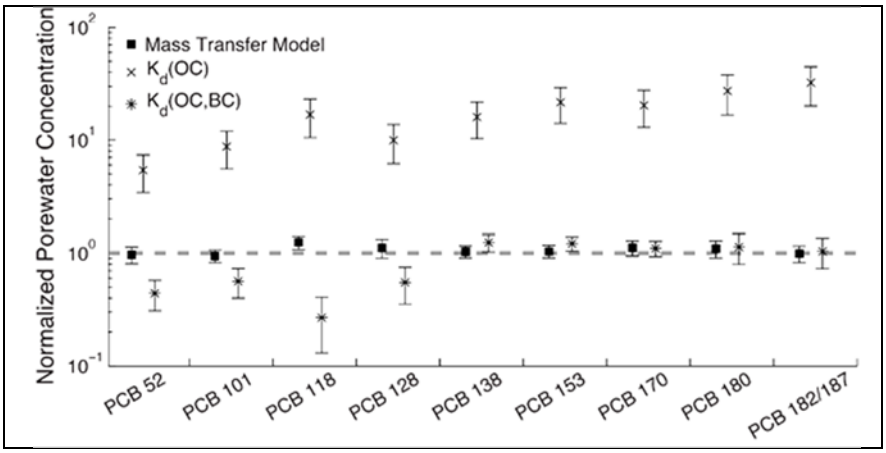


Figure 7. Porewater concentrations deduced from the equilibrated PE (dashed line) compared with (a) the passive sampling (squares), (b) the EqP model accounting for only organic carbon (x) and (c) the EqP model accounting for both organic and black carbon (*). Figure from Apell and Gschwend (2014).

6.2 PERFORMANCE OBJECTIVE: DEMONSTRATE PE PASSIVE SAMPLING IS EFFECTIVE FOR SITE MAPPING.

The PE passive sampling technology allows one to generate maps of the contaminant porewater distributions (Figure 8). Traditionally, this has been done using sediment concentrations (Figure 8 left), but if one accepts that porewater (and water column) concentrations are most suited to calculating sediment bed-to-water column fluxes and biota exposures, then the PE passive sampling map (Figure 8 right) would be much more useful to assessment and remedial design.

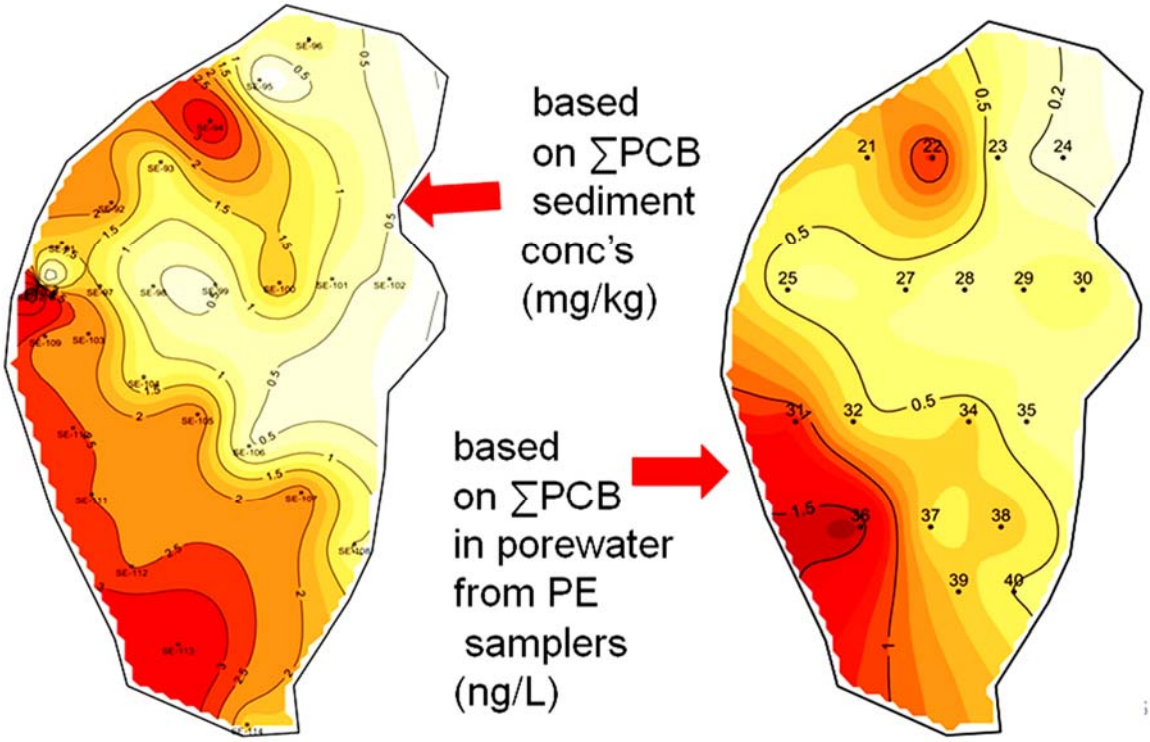


Figure 8. Comparison of maps of total PCB concentrations from: (left) sediment concentrations (mg/kg dry weight) measured from 50 samples before dredging at the site and (right) porewater concentrations (ng/L porewater) obtained using results from 18 in situ PE passive samplers.

Next, in situ PE passive sampling allowed a 3-dimensional delineation of the extent of contamination. To this end, the in situ PE passive samplers were deployed at locations spread around the demonstration site (Figure 9). Perhaps not surprisingly, the PE sampler uptake of PCB 153 (a major component of the Aroclor 1260 spilled at this site) resulted in similar PE concentrations of ~ 40 ng/g PE throughout the cove. This implies that sites distributed throughout the Pegan Cove area have similarly bioavailable PCB 153 despite very different sediment concentrations.

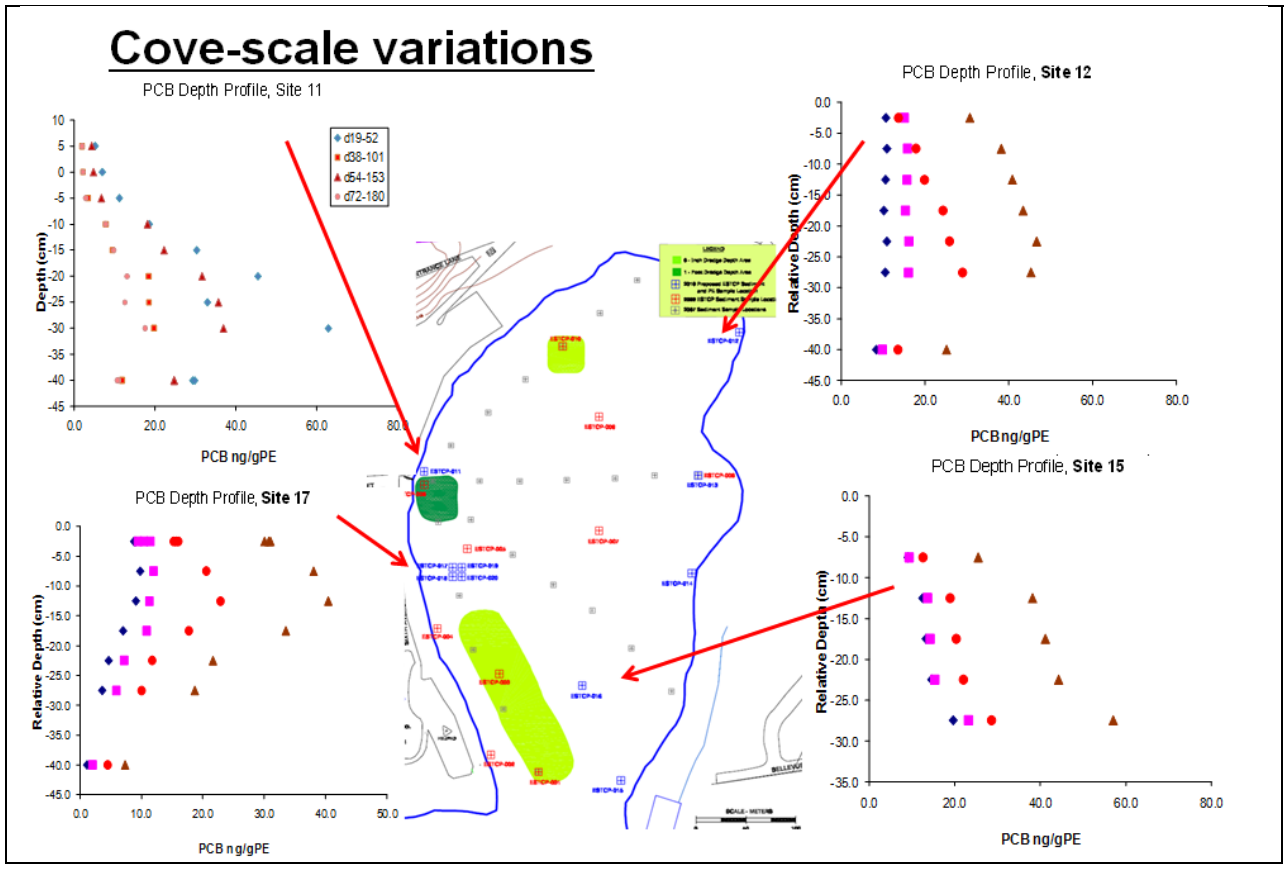


Figure 9. PE depth profiles for four congeners (52, 101, 153, and 180) acquired by in situ PE passive sampling at four locations in Pegan Cove.

6.3 PERFORMANCE OBJECTIVE: DEMONSTRATE PE PASSIVE SAMPLING IS SUITED TO LONG TERM MONITORING (LTM) AFTER SITE REMEDIATION

The in situ PE passive samplers were also used for LTM. The PE samplers enabled measurements of both the porewater and the overlying bottom water, a useful combination in LTM (Figure 10). Focusing on the data for one representative congener, the project team saw as much change in PCB 101 presence in the bottom water as was seen in the porewater. For example, PCB 101 was about 10x higher at site 11 at our demonstration site in the fall of 2012 as compared to the winter of 2010. This was also noted at site 43 in fall 2012 compared to fall 2011. Clearly, one can use such porewater and bottom water concentrations to ascertain whether exposures of biota in the area are substantially changing over time. To sum, these initial stages of LTM were readily completed using passive samplers.

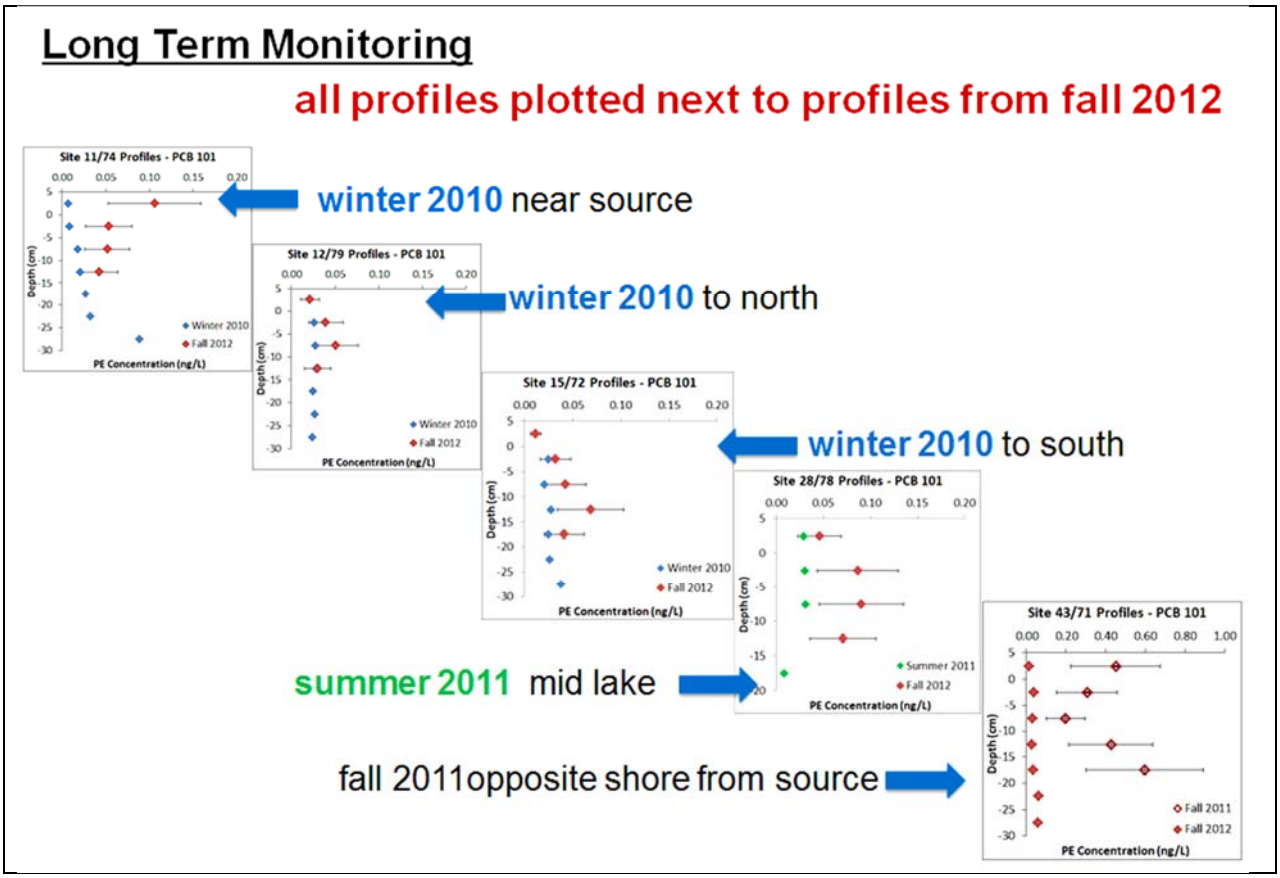


Figure 10. Results for PCB 101 using in situ PE passive samplers for long term monitoring at the Pegan Cove site. Each profile is co-plotted with results from the fall of 2012 (diamonds). Also note that results above depth = 0 represent the bottom water concentrations.

6.4 PERFORMANCE OBJECTIVE: DEMONSTRATE PE PASSIVE SAMPLING COMMERCIALLY VIABLE BASED ON QA/QC METRICS, EASE OF USE, AND COSTS

The project was performed in collaboration with colleagues from ICF International, a "commercial" entity. Notably, ICF International participants led the field sampling efforts and the cost performance assessments. Second, an environmental contract laboratory, Pace Analytical, was involved in the program. Colleagues at Pace helped identify key methodological choices such as which compounds to use as PRCs so as to avoid interfering with surrogate and injection standards used in standard protocols (e.g., EPA Method 1668 for congener specific analysis of PCBs). Finally, QA/QC parameters were established allowing commercial planning of PE passive sampling implementation. First, using the typical PE sample sizes (1 mil sheet cut to 5 cm long and 5 cm wide yielding about 60 mg of PE) and final extract volumes (~100 µL), for PCB analyses using high resolution capillary chromatography combined with low-resolution mass spectrometry, the detection limits are near 1 pg/L for individual PCBs and PAHs. Notably, the SOP for PE preparation (Gschwend et al., 2012a) gives guidance on how to make the PE samplers so as to accomplish the necessary sensitivities. At no time did a trip blank sampler show detectable PCB contamination corresponding to >1 pg/L_{water}.

Next, the project team showed that the precisions associated with PE-inferred porewater concentrations are dependent on the site of interest and the investigator's choice of sample deployment duration. Within a single lab, Fernandez et al. (2009) and Apell and Gschwend (2014) show relative standard deviations on resultant porewater concentrations, correcting for surrogate recoveries and after PRC adjustments, are generally better than a factor of two. More importantly, this project work found that the PE passive sampling approach yields porewater concentration accuracies that are much better than current EqP (Follett, 2011; Gschwend et. al., 2011; Apell and Gschwend, 2014).

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7.0 COST ASSESSMENT

7.1 SYSTEM COST

This section presents a simple cost model that reflects the cost elements that would be required for implementing the PE sampling technology at a real site.

Cost Elements. The costs associated with passive PE sampler deployment and ponar dredge sampling were broken down into the following five cost elements:

1. Expendable items: including materials such as stainless steel mixing bowls/spoons, decontamination supplies (buckets, brushes, distilled water, detergent), Nitrile gloves, aluminum foil, plastic sheeting, rope, paper towels, garbage bags, bubble wrap, Ziplock bags, and ice.
2. Non-expendable items: including materials such as the ponar dredge, PE frames and hardware, sink rope, vehicle rental, and handheld GPS rental.
3. Field labor: developed from actual field events for PE deployment and ponar dredge sampling. The project team assumed field campaign involving the collection of 12 traditional ponar dredge sediment samples and 12 PE samples.
4. Sample shipment: costs based on FedEx priority overnight shipping from a FedEx drop off location near the demonstration site in Framingham, Massachusetts, to a contract analytical laboratory in Minneapolis, Minnesota (Pace Analytical). This is the commercial laboratory that was used for both sediment and PE analyses during the project. Shipment costs also include packing tape to secure sample coolers.
5. Analytical costs: include average per sample costs charged by commercial laboratories for PCB analysis via EPA Method 1668A for sediment and PE samples (average of unit costs provided by Pace Analytical and AXYS Analytical). Also includes costs for PE preparation supplies (e.g., PE strips, solvents, labeled PRCs, surrogates, glassware, nitrogen), and labor associated with PE preparation (e.g., cutting, cleaning, and PRC loading of PE) and calculating PRC corrections.

Costs that were equally associated with both sampling techniques were not included in the cost analysis. These included costs such as the preparation of planning and health and safety documents, the use of a boat, personal protection equipment (PPE), permitting, baseline characterization (i.e., hydraulic or bathymetry assessment), and reporting.

A percent cost savings by using the PE sampling method instead of the traditional ponar dredge method was calculated using the following equation:

$$\%\ \text{Savings} = \frac{\$\,Traditional\ Method - \$\,PED\ Method}{\$\,Traditional\ Method} * 100\%$$

7.2 COST DRIVERS

The costs to execute a sediment sampling program using PE samplers will vary to a degree from site to site. The key cost drivers are discussed below with a brief discussion of their cost impact.

Fresh Water versus Marine Environment. Costs were developed based on sampling in a fresh water environment using PE samplers constructed of aluminum sheet metal and zinc-coated hardware. Sampling in a marine environment could potentially increase the material costs for the PE frame and hardware if corrosion resistant materials (e.g., stainless steel) are required.

Water Depths. Costs were developed using PE deployment equipment designed for water depths of less than 20 feet, working from a small skiff, and in an area with only wind driven water currents. If it is anticipated that water depths are greater than 20 feet, it may be necessary to find other deployment and retrieval options, such as using certified divers to install the PE samplers by hand or using a larger boat to increase stability when installing the PE samplers.

River or Tidal Currents. Some sites may have slow- to fast-moving currents. If this is the case, a larger boat may be required and could increase labor and fuel costs. Water currents could also increase the level of difficulty for field personnel and could increase labor costs.

Site Access. Site access complexity can increase project costs significantly. If straightforward access to the site is not available, it may require field teams to physically carry supplies to the site and sampling locations. This would increase labor costs by increasing field deployment times. There would be significantly more equipment to transport using traditional sediment sampling equipment compared to PE samplers.

Investigation Derived Waste (IDW). IDW includes both solid wastes (e.g., Nitrile gloves, plastic sheeting, aluminum foil, etc.) and non-hazardous/hazardous wastes (excess sediment, decontamination fluids). Non-hazardous/hazardous waste generated from PE samplers is expected to be minimal. Traditional sediment sampling, however, could generate larger volumes of contaminated sediment depending on the number of sampling locations. Additionally, decontamination fluids associated with traditional sediment sampling may require special handling and disposal.

Rental Equipment versus Purchasing Equipment. It is difficult to evaluate the cost/benefit of renting PE samplers versus purchasing them because the sampling device and sampling protocols have not yet been commercially developed. Equipment costs under this demonstration study were developed based on the capital costs of materials for both the PE sampler and the ponar dredge. The capital cost of PE samplers was approximately $66.50 per sampler. Excluding the costs for the sink rope and PE deployment tool (which could be reused in future sampling programs), each PE sampler frame and associated hardware was calculated at $53 per PE sampler. The approximate capital cost for the purchase of a ponar dredge is $810 (based on a 2013 price from Cole Palmer).

7.3 COST ANALYSIS

Costs were developed assuming 12 samples would be collected. Table 6 summarizes the total costs incurred for each cost element, including the percent cost savings.

Table 6. Cost comparison of PE samplers and traditional sediment sampling technique.

Cost Element	PE Sampling Technique Cost	Ponar Dredge Sampling Technique Cost	% Cost Savings of PE Technique
Expendable Items	$37	$169	78%
Non-Expendable Items	$948	$960	1%
Field Labor	$1,240	$1,530	19%
Sample Shipment	$104	$243	57%
Total Field Sampling Cost	**$2,330**	**$2,902**	**20%**
Total Analytical Cost	**$11,022**	**$10,080**	**-9%**

Notes: Assumes collection and analysis of 12 samples with a ponar dredge and 12 PE sampler deployments.

Expendable Items. The calculated percent cost savings related to expendable items for the PE sampling method is 78 percent ($169 for ponar dredge sampling versus $37 for PE samplers). This savings is contributed largely to the fact that PE samplers do not require decontamination of field equipment or the transfer of sample media from a sampling device to a sample container, as is the case with traditional sediment sampling.

Non-Expendable Items. Based on the material costs, it is believed that rental costs for one dozen PE samplers could be comparable to the costs of renting a ponar or Ekman dredge. Because the percent difference in non-expendable costs associated with the two sampling methods is only 1 percent, this cost element is considered negligible as it relates to the overall cost analysis.

Field Labor. The PE sampling labor hours used in the cost comparison are for two mobilizations. The first mobilization includes 4 hours to install 12 PE samplers. The second mobilization includes a total of 6 hours to retrieve those same 12 PE samplers, remove the PE strip from the sampler frame, place the PE strips into sample containers, and pack the containers in a cooler for shipment to the laboratory. The traditional sediment sampling labor hours used in the costing are for one mobilization. A conservative estimate of 60 minutes per sample was used to collect the sample, homogenize the sample, place in a sample container, decontaminate the equipment, and pack the samples in a cooler with ice for shipment to the laboratory.

Sample Shipment. The difference in shipping costs between the two sampling methods is driven by the much lower weight of a PE sample versus a sediment sample, as well as the analytical requirement of having to cool sediment samples to less than 4 degrees Celsius, while PE samples do not currently require this.

Analytical Cost. An average unit cost of $840 per sample was used in the cost comparison, for both the traditional sediment and PE sample analysis. In addition to the unit cost for PCB analysis, PE preparation supplies were estimated at approximately $62 per sample (based on

MIT analytical laboratory costs) and included the material costs for the PE strips, solvents, labeled PRCs, surrogates, glassware, and nitrogen. The labor associated with PE preparation (including cutting, cleaning, and PRC loading of PE) was estimated at 1.5 hours per sample, while the labor associated with performing PRC corrections was estimated at 1 hour per sample (based on MIT analytical laboratory costs). It is these additional PE preparation labor and supply costs that cause the total analytical cost of the PE samples to be approximately 9 percent higher than the traditional sediment sample analysis.

7.4 COST ASSESSMENT SUMMARY

Results of this cost assessment indicate that overall field sampling costs using PE samplers is approximately 20 percent less than traditional sediment sampling techniques using a ponar dredge, while current analytical costs are somewhat higher of the PE samplers. Combined, this cost model indicates PE sampling costs about 3% more than traditional sediment work; largely driven by analysis expenses.

8.0 IMPLEMENTATION ISSUES

One impediment to adoption of PE passive sampling may be the unfamiliarity of environmental consultants and contract laboratories with using this approach. To help mitigate this implementation issues, SOPs documents were developed as part of this project describing the preparation of PE passive samplers, means for their deployments, and chemical analyses after their recovery (Gschwend et. al., 2012a; 2012b; and 2012c). In addition, a graphic user interface, called the PRC-Correction Calculator (Tcaciuc et. al; 2014) was developed based on the mass transfer model described in Fernandez et al. (2009). This calculator substantially assists in the analysis of data for contaminants like PCBs, PAHs, or DDTs in PE samplers.

Perhaps a second key issue limiting the ability of commercial entities to adopt PE passive sampling is that the regulations are still written and often enforced in terms of total PCB concentrations in sediments. Hence, the commercial entity must utilize methods that allow them to translate the PCB results in PE into such metrics for the regulators. This can be done in various ways. First, because the PE measures can be directly converted to concentrations in porewater, then perhaps water quality standards could be applied to assess such porewater results (∑PCBs Maximum Contaminant Level in drinking water = 0.5 µg/L). Alternatively, one may use the porewater concentrations to estimate equilibrium (lipid normalized) tissue concentrations (e.g., Gschwend et. al., 2011); regulators could use such tissue concentration results to estimate risks to humans who consume such shellfish or finfish. Finally, this latter process may require employing a food web model, which is driven by measures of contaminants in the water column and porewater (not sediment) to estimate tissue concentrations in biota of interest.

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APPENDIX A

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