



FINAL REPORT

Standardizing Polymeric Sampling Method for Measuring Freely-Dissolved Organic Contaminants in Sediment Porewater

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LIST OF ACRONYMS

CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
C_{free}	freely-dissolved organic contaminant concentrations in sediment porewater
PRC	performance reference compound
PDMS	polydimethylsiloxane
PAH	polycyclic aromatic hydrocarbon
PCB	polychlorinated biphenyl
RPM	remedial project manager
USEPA	United States Environmental Protection Agency
PE	low density polyethylene
USACE	U.S. Army Corps of Engineers
ERDC	Engineer Research Development Center
QA/QC	quality assurance/quality control
NIST	National Institute of Standards and Technology
HRGC	High Resolution Gas Chromatography
HRMS	High Resolution Mass Spectrometry
LRMS	Low Resolution Mass Spectrometry
RPD	Relative Percent Difference
RPM	Remedial Project Manager
NOAA	National and Oceanic Atmospheric Administration
WHO	World Health Organization
TOC	total organic carbon
DoD	Department of Defense

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The project team wishes to thank Dr. Andrea Leeson and the support staff from the ESTCP program office for their help and guidance throughout this demonstration.

ABSTRACT

The primary purpose of this effort was to demonstrate standardized polymeric sampler procedures for measuring freely-dissolved organic contaminant concentrations (C_{free}) in sediment porewater by multiple academic- and private-sector analytical laboratories, thereby increasing commercial availability, promoting wider acceptance, and increased use. Polymeric samplers consist of hydrophobic polymers (e.g. low-density polyethylene (LDPE), polydimethylsiloxane (PDMS)), which absorb organic compounds present in sediment porewater. Polymeric samplers can be directly inserted into sediment in the laboratory (*ex situ*) or in the field (*in situ*) to yield depth-discreet measures of C_{free} present in sediment porewater. Commercial and academic laboratories participated in three separate tasks to test and validate standard methods for polymeric sampling, culminating in the final task of using the standardized polymeric sampling method to measure C_{free} PAHs and PCBs in a sediment sample. Results showed that (1) LDPE and PDMS polymers yielded equivalent C_{free} results for PAHs and PCBs, regardless of static or active exposures; (2) polymeric samplers provided better quantitation compared to the manual extraction reference method for high molecular weight PAHs and PCBs, which were present at low concentrations; and (3) active exposures achieved equilibrium following continuous mixing for ~ 30 days, suggesting that if polymeric samplers are used to characterize sediment porewater under active exposure conditions for longer than 30 days in the laboratory, performance reference compounds use may be omitted. Due to the unique nature of estimating costs for individual projects, a cost per polymeric sampler is not provided here and should be coordinated directly with the appropriate commercial laboratory supplying these services. Instead, this report features an example scope of work and cost estimate intended to support end users in developing scopes and cost estimates for their sediment porewater characterization projects using polymeric samplers.

EXECUTIVE SUMMARY

Introduction. Bulk sediment contaminant concentrations do not represent the mobile or bioavailable fraction; rather, it is the freely-dissolved contaminant concentrations present in the sediment porewater that provide more useful information for risk assessment. Polymeric samplers consist of hydrophobic polymers (e.g. low-density polyethylene (LDPE), polydimethylsiloxane (PDMS)), which absorb organic compounds present in sediment porewater. Polymeric samplers can be directly inserted into sediment in the laboratory (*ex situ*) or in the field (*in situ*) to yield depth-discreet measures of freely-dissolved organic contaminant concentrations (C_{free}) present in sediment porewater. In comparison to calculations based on concentrations in bulk sediment, C_{free} can be used to predict more accurately chemical toxicity and bioaccumulation in benthic organisms. There is substantial use of polymeric samplers for environmental monitoring, but their acceptance is limited by the lack of standard methods and commercial availability. During this project, multiple university and commercial analytical laboratories worked together to standardize polymeric sampler methods, then validated the standardized method through an interlaboratory method demonstration.

Technology Description. This project featured two common polymeric samplers: solid-phase microextraction (SPME) fibers coated with PDMS and LDPE samplers. PDMS and LDPE can respectively achieve ng/L and pg/L detection limits for polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in porewater with 1 cm depth resolution. PDMS polymeric samplers feature a PDMS sorbent polymer coating (~ 35 μm thick) around a glass core (Figure E1). LDPE samplers feature polymer strips (~ 25-102 μm thick), which are often deployed in metal protective frames (Figure E1) to provide strength for direct insertion into sediment. Organic contaminants partition from the sediment porewater into the organic polymer during exposures; then the polymers may be retrieved, extracted, then the polymer extracts may be analyzed for organic contaminants of interest.

Isotopically-labeled performance reference compounds (PRCs) are pre-loaded into the organic

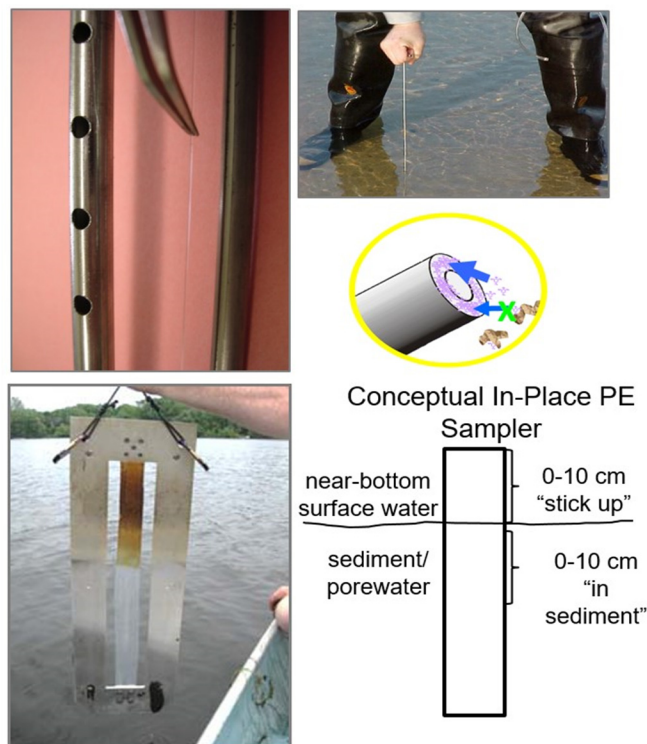


Figure E1. Polymeric sampler images, including schematic of PDMS polymer coating around glass core (upper); LDPE sampler image and schematic of *in situ* deployment (lower)

polymer prior to deployment; the ratio of PRC compound lost to the environment during deployment provides a measure of the polymeric sampler's progress toward reaching equilibrium with target contaminants in the sediment porewater.

Performance Assessment. Demonstration Task 1 involved developing a standardized methodology for LDPE and PDMS polymeric sampler preparation and analysis, including how to: a). prepare polymeric samplers, including cleaning polymers and loading PRCs; b). expose polymeric samplers to sediment in the laboratory (*ex situ*); c). retrieve polymeric samplers from sediment and extract the organic contaminants and PRCs; d). perform chemical analysis of polymeric sampler extracts; and e). interpret results and use them to determine the freely-dissolved organic contaminant concentrations present in the sediment's porewater. Participating laboratories then used the standard method to extract replicate LDPE and PDMS samplers that had been "preloaded" with PRCs by expert academic laboratories. Results showed most labs met accuracy and precisions success criteria established for Task 1; exceedances were occasional, not systematic, and thus supported a "Go" decision to proceed to Task 2. Important lessons learned during Task 1 were (1) LDPE strip area/weight ratios should be measured prior to placing LDPE strips into the PRC loading solution to ensure target PRC loading is uniformly achieved; and (2) solvent type and quantity variations when preparing the PRC loading solution can impact polymer loadings. The standard method was updated to reflect both lessons learned prior to proceeding to Task 2.

Demonstration Task 2 involved participating labs using the standardized polymeric sampling method to independently load PRCs into the polymeric samplers, then extract and quantify PRC concentrations in sampler extracts. All labs achieved good precision with PRC loading; however, varied PRC loading solution solvents and solvent/working solution ratios caused differences in the loaded PRC concentrations achieved between labs. The standard method was updated once more to tighten solvent types and ratios used to prepare PRC loading solutions.

Demonstration Task 3 involved participating labs using the standardized polymeric sampling method to measure PAHs and PCBs in a sediment sample. Each lab used PRC-loaded polymeric samplers in "active" (continuously mixed) and "static" (no mixing) exposures in the laboratory for approximately 30 days. Polymeric sampler results were corrected for progress toward equilibrium as needed using PRC losses. Results between labs were generally in good agreement for target PAH and PCB compounds. Moreover, the polymeric sampler results were in good agreement with the manual porewater extraction method for compounds that could be measured using both methods. Full participation by 4 commercial laboratories and 3 academic laboratories met the minimum interlaboratory method validation study requirement for SW846 method application, thus laying the foundation for a future SW846 application. Section 6 of this final demonstration report describe results in more detail; Appendix B includes the Standard Operating Methods (SOPs) for polymeric sampler use; instruction videos for [LDPE](#) and [PDMS](#) developed under this demonstration are posted online.

Cost Assessment. The original intent of this project was to provide unit costs from each

participating laboratory for polymeric sampler preparation and analysis. However, due to the unique nature of estimating costs for individual project needs, development of a cost per polymeric sampler was not possible. Rather, cost estimates for polymeric sampler preparation and analysis to measure PAHs and PCBs in sediment porewater can be obtained from any of the points of contact listed for the commercial laboratories identified in Table 2-1 of this report. Cost considerations should account for sampler preparation and loading with PRCs, as well as analytical costs for the appropriate analytes. Field blanks and any samplers needed to meet QA/QC requirements should also be accounted for. Calculations to support conversion of extract concentrations to porewater concentrations may be performed by the commercial laboratory or by a separate contractor familiar with passive sampling. Cost savings can be realized through potential compositing of samplers and use of low-resolution methods. While costs can vary by lab, low resolution analysis for PCBs and PAHs can range from \$100 to \$300 per sample, high resolution methods can cost \$600 to \$1,000 per sample. A cost estimate for sediment characterization using polymeric sampler at a hypothetical site is provided in Section 7 of the main report; an example scope of work (Appendix H) for acquiring polymeric sampler sediment characterization services is provided as well.

Implementation Issues. One implementation issue for passive sampling is the need to know approximate concentrations of target analytes present in the sediment porewater so that appropriate PRC concentrations can be loaded into the samplers prior to deployment or use. This can typically be overcome if any existing bulk sediment concentration data is available for a site; guidelines are provided in the final SOPs (Appendix B) and in other references cited in this report.

One of the more costly components of passive sampling is the use of ^{13}C -labeled PRCs. This can be managed by using lower PRC loadings but needs to be balanced with the necessary concentration range needed for the exposure environment and detection limits of analytical method being used. Generally speaking, the PRCs should be present in the post-exposure polymer extract at 10x above the method detection limit so that the post-exposure concentration can be reliably quantified.

Commercial laboratories often prefer to provide polymer extract concentration results, rather than performing the necessary calculations needed to convert extract concentration results to porewater concentrations. As such, an additional contractor or someone else familiar with the mathematical conversion from extract to porewater concentration is needed. The example scope of work (Appendix H) and cost discussion (Section 7) accounts for this need.

1.0 INTRODUCTION

1.1 BACKGROUND

Polymeric samplers absorb hydrophobic organic contaminants present in sediment, whether used passively (i.e., without sediment/polymer mixing) or actively (i.e., with sediment/polymer mixing). The resultant polymer concentrations can be used to calculate freely-dissolved contaminant concentrations (C_{free}) in sediment porewaters. Polymeric samplers may be used as alternatives to (a) Henry samplers and pumping for porewater sample collection or (b) sediment centrifugation with supernatant collection. C_{free} measured by polymeric samplers represents the fraction of contaminants not sorbed to settling solids or associated with dissolved organic carbon and suspended colloidal matter; C_{free} has been linked directly to exposure and risk to sediment-dwelling organisms²⁴. This link has been demonstrated in research supported by numerous organizations including SERDP and ESTCP. For example, a review by Lydy et al.¹ emphasized that polymeric samplers allow the measurement of chemical activity (equivalent to freely dissolved concentration normalized by a contaminant's aqueous solubility), which dictates reactivity and bioavailability of organic hydrophobic sediment contaminants²⁵. Bioaccumulation in rapidly equilibrating deposit feeders has also been directly related to C_{free} . In such cases, the lipid-normalized body burden is approximately equal to the product of the octanol-water partition coefficient and measured C_{free} (e.g., Thomas et al.² or Lu et al.³). Fish and other aquatic organisms that are not directly exposed to sediment may experience bioconcentration from diet or different bioaccumulation than indicated by interstitial porewater for bioaccumulative chemicals because of additional influence from surface water and contaminants in the pelagic diet.

In addition, Greenberg et al.⁴ reviewed the use of polymeric sampling methods to define risk at contaminated sites, recognizing that C_{free} can also be used to quantify bioavailability and, therefore, ultimately exposure and risk. They concluded that use of C_{free} can “better inform risk management decisions made at multiple points in the process of assessing and managing contaminated sediment sites.” Further, C_{free} values have been directly related to final and secondary chronic values (FCVs, SCVs) from U.S. EPA's Ambient Water Quality Criteria (AWQC) that are employed to evaluate the Nation's water quality⁵. These results suggest that C_{free} can provide the best estimate of exposure and risk posed by sediment contaminants. Work by Menzie et al.³⁰ relied on these estimates of exposure and risk to provide a guide for integrating passive sampling methods into management of contaminated sediment sites.

For these applications to be implemented what is needed is the successful commercialization of standardized and accepted passive sampling methods that accurately quantify the C_{free} of contaminants at sites of interest. Polymeric sampling methods, such as those detailed in the joint U.S. EPA and SERDP/ESTCP User's Manual⁶ and in Jonker et al. 2020²⁶ can do this but they have historically been considered a research tool largely used by academic and governmental

researchers (Jonker et al. 2018²⁷). Standardized methods that are accepted by regulatory agencies including the U.S. EPA are necessary at this time but demonstrating the proficiency of commercial laboratories to perform these methods is critical.

The primary purpose of the effort described herein was to demonstrate standardized polymeric sampler procedures⁶ for measuring C_{free} by multiple academic- and private-sector analytical laboratories, thereby increasing commercial availability, promoting wider acceptance, and increased use. U.S. EPA scientists participated in a technical review and advisory capacity for the duration of the study. The approach involved characterization of sediment using standardized polymeric sampling procedures to determine C_{free} in replicates of a large volume sediment sample by all participating laboratories. The C_{free} measurement can be used: (i) to directly assess toxicity where FCVs or SCVs are available in the water phase (e.g., PAH narcosis model), (ii) for estimation of bioaccumulation in benthic organisms, and (iii) for the calculation of site-specific partition constants that can be used in existing fate, bioaccumulation and risk assessment models.

This effort featured *ex situ* laboratory measurements to support method standardization. *In situ* polymeric sampling methods were not demonstrated in this proposed project because *in situ* conditions are inherently variable from site to site, and as such, would not serve the purposes of this method validation/demonstration. This project did, however, demonstrate all technologies necessary for analysis and interpretation of *in situ* polymeric sampling, including the impregnation and analysis of performance reference compounds (PRCs), exposure of samplers to static sediment mimicking some field scenarios, the processing and analysis of passive samplers inserted into sediments, interpretation of performance reference compounds (PRCs) to assess the extent of equilibration, and the calculation of freely-dissolved porewater concentrations (C_{free}) from the measured accumulation of target compounds in the polymeric sampler.

1.2 OBJECTIVES OF THE LABORATORY DEMONSTRATION

Demonstration objectives were as follows.

1. Develop a standardized methodology for polymeric sampler preparation and analysis by multiple private sector contract, government, and academic laboratories. The methodology describes how to:
 - a. Prepare polymeric samplers, including loading PRCs;
 - b. Expose polymeric samplers to sediment in the laboratory (i.e., *ex situ*);
 - c. Retrieve polymeric samplers from sediment and extract the organic contaminants and PRCs;
 - d. Perform chemical analysis on polymeric sampler extracts; and
 - e. Manipulate results to determine contaminant C_{free} in the sediment porewater.
2. Collaborate with government and commercial laboratories to finalize the standardized polymeric sampler methodology, then validated the methodology through a phased

- interlaboratory comparison.
3. Document the standardized methods and interlaboratory method comparison results in a final report consistent with U.S. EPA SW846 method validation guidelines¹¹, in addition to posting a freely available webinar and instructional videos via YouTube and other online platforms.

The project team consulted with multiple federal partners during the project to ensure demonstration outcomes are appropriate and as complete as possible in support of a future SW846 method application. Drs. Robert Burgess and Marc Mills (U.S. EPA Office of Research and Development) and Mr. Matthew Lambert (U.S. EPA Office of Land and Emergency Management) reviewed documents and shared perspectives reflective of their Agency's goal for encouraging private sector laboratories to be more engaged with analyzing passive samplers deployed at Superfund sites. U.S. EPA advisors also provided advice to the project team based on their extensive technical experience working with passive samplers at Superfund sites (and other contaminated sites) around the country. Dr. Janice Willey (NAVSEA) reviewed project documents with an eye toward the future SW846 method approval package submittal and subsequent inclusion in the DoD Environmental Laboratory Accreditation Program (ELAP) and Quality Systems Manual (QSM) for Environmental Laboratories.

1.3 REGULATORY DRIVERS

Polymeric sampling methods are relevant and beneficial to U.S. EPA's authority under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), Superfund Amendments and Reauthorization Act (SARA), and the National Oil and Hazardous Substances Pollution Contingency Plan (NCP) in two ways: (1) freely dissolved concentration measurements (C_{free}) using polymeric sampling methods are substantially more predictive of toxicity to, and bioaccumulation in, both benthic and pelagic invertebrates than established sampling methods, and (2) passive sampling methods provide detection limits sufficiently sensitive to detect very low Applicable, or Relevant and Appropriate Requirements (ARARs), such as the Ambient Water Quality Criteria (AWQC) (i.e., FCVs) for total PCBs (i.e., 64 pg/L water, associated with 1 in a million incremental cancer risk to a population through fish consumption). The NCP requires that remedies selected under CERCLA be protective of human health and the environment and meet all ARARs. Many studies have shown a close log-linear relationship between polymeric sampler measurements and both toxicity and bioaccumulation^{28, 29}. The use of these sampling methods during the Remedial Investigation and the Baseline Ecological Risk Assessment will allow the U.S. EPA to better understand the risk drivers to benthic, freshwater, and marine ecosystems and to have a higher confidence in the protectiveness of CERCLA and SARA remedies with fewer conservative assumptions. Recently, the U.S. EPA Office of Research and Development developed guidance to help the Superfund Program prepare and implement polymeric sampling-based porewater remediation goals to be protective of benthic invertebrates⁶. Additionally, the Record of Decision for Lower Willamette River Superfund Site

did identify the use of passive samplers as a suitable tool for long term monitoring in lieu of fish tissue. However, these methods will require Superfund remedial project managers to have access to commercial laboratories that can provide and analyze passive samplers using well established methods. For example, the AWQC for hydrophobic organic chemicals, such as PCBs, PAHs, DDT, and organochlorine pesticides, are often in the parts per billion, parts per trillion or parts per quadrillion range. Traditional water sampling methods (i.e., grab samples) would require the collection and extraction of several hundred liters of water to meet those detection limits. Polymeric sampling methods can achieve these detection limits with just a few milligrams to a few grams of passive sampler polymer deployed, depending on the contaminant being monitored. This makes it cost-effective to monitor for the attainment of these AWQC and reduces the field work logistics to grab sample surface water and porewater. This example and others, highlight the importance of the evaluation of standardized polymeric methods performed in this ESTCP project.

2.0 TECHNOLOGY

2.1 TECHNOLOGY DESCRIPTION

The project proceeded via phased development of a standard method for *ex situ* analysis of sediments via polymeric sampling. This method was based on a recent guidance document developed as part of a 2012 SETAC Pellston workshop on polymeric sampling⁷ and included additional developments in the field since the workshop. The method included selection of sampler materials and thicknesses, sampler preparation and cleaning, impregnation of PRCs, placement and retrieval from the sediment sample, and analysis of the polymeric sampler results. The analytical approaches selected emphasized existing U.S. EPA methods to aid acceptance of the overall method. The method also included standardized PRCs¹, approaches for introduction of PRCs into the samplers, and the post-sampling measurement of these compounds. The standard method included approaches common to the most-used polymeric porewater sampling sorbents: low density polyethylene (LDPE) and polydimethylsiloxane (PDMS). The procedures for each of these are quite similar but there are differences that were identified in the standard methods. The standard methods were demonstrated and validated through an interlaboratory study that applied the methods to a range of samples – starting simple (analysis of a “calibration check standard” of known composition), building complexity (analysis of PRC-preloaded samplers initially, and then independent PRC loading, extraction, and analysis), and culminated in use of the standardized methods to analyze a homogenized sediment sample prepared for this project. Reproducibility of the method was evaluated at each step. Accuracy of the method was evaluated by comparing polymeric sampler results against results of the academic labs and finally against the manual porewater extraction method^{8,9}.

The interlaboratory effort involved preparation of one large sediment sample that contained concentrations found at a real-world site of PAHs and PCBs. This sample was thoroughly homogenized, split into replicates, and subsamples were analyzed for total organic carbon (TOC), PCBs, and PAHs. Replicates with results within acceptable tolerance limits (defined in Section 5) for homogeneity were used, and subsamples were collected from each replicate and archived for potential future analysis prior to sending replicates to individual labs. The sediment replicates were distributed to (a) academic labs that are proficient in using a particular polymeric sampling approach and that helped develop the polymeric sampler methods (Texas Tech University,

¹ PRCs were typically selected isotopically-labeled versions of the hydrophobic organic contaminants of interest, which are loaded into the samplers prior to deployment. PRC loss from the polymer during deployment provides a measure of its progress toward equilibrium with contaminants in the sediment porewater.

University of Maryland Baltimore County, and Massachusetts Institute of Technology), and (b) environmental analytical labs that had agreed to participate in this project as listed below (Table 2-1). These analyses were performed using the standard methods for *ex situ* porewater analysis. The standard methods require non-depletive changes to the sediments. Mixing (aka "active" sampling) and static polymeric sampling were both included in the standard method, as one may wish to apply the approach *ex situ* (i.e., via active mixing to speed equilibration) or *in situ* (i.e., to capture conditions in the field). PRCs were used to evaluate equilibration or fractional approach to equilibrium. The standard methods are complete and detailed such that future end users can utilize the methods and produce data of similar quality to that achieved by commercial laboratories participating in this demonstration.

Demonstration outcomes were intended to fulfill key requirements of an SW846 method approval package: (a) a complete standard method, and (b) demonstration of interlaboratory method reproducibility ¹¹. Preparation and submittal of the SW846 package was not included in the scope of this demonstration. Development of a standard method is expected to dramatically increase acceptance of polymeric sampler results by the regulatory community for use in sediment site management decisions. With completion of the standard methods and demonstrated method accuracy and reliability, webinars, online seminars and instructional videos were used to disseminate the results to the user community including EPA, DoD, state regulators and remedial project managers.

Table 2-1. Participating commercial laboratories

Participating Commercial Laboratory	Primary Point of Contact	Laboratory Mailing Address
Analytical Resource, Incorporated	Sue Dunnihoo sue@arilabs.com 206-695-6207	ARI Lab 4611 S. 134 th Place, Suite 100 Tukwila, WA 98168
TestAmerica	Bruce Wagner bruce.wagner@testamericainc.com 865-291-3076	TestAmerica Lab 5815 Middlebrook Pike Knoxville, TN 37921
AXYS Enviro	Coreen Hamilton chamilton@axys.com 250-655-5802	AXYS Enviro Lab 2045 Mills Road West Sidney, BC V8L5X2
Vista Analytical Laboratory*	Andrew Patterson anp@vista-analytical.com 916-673-1520	Vista Analytical Lab 1104 Windfield Way El Dorado Hills, CA 95762
Battelle Memorial Institute	Lisa Lefkovitz lefkovitzl@battelle.org 781-681- 5521LEFKOVITZL@battelle.org6 12-607-6387	Battelle Memorial Institute 141 Longwater Dr., Suite 202 Norwell, MA 02061

* Vista Analytical participated in Task 1 only.

2.2 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

Polymeric samplers already have a long history of use in the laboratory and numerous field applications. The LDPE polymeric sampling technology was largely developed with past SERDP and ESTCP support, and these agencies provided substantial support for the development of PDMS polymeric sampling as well. Remedial Project Managers (RPMs) at several contaminated sediment sites are starting to include porewater measurements to refine risk assessments during the remedial investigation/feasibility study phase. A user manual for passive sampling implementation was recently developed through a joint USEPA and ESTCP effort⁶. A number of environmental consulting firms (e.g. ICF International, HDR Engineering, Louis Berger, CH2M-Hill, Geosyntec, Tetra Tech, CDM-Smith, Tierra Solutions, AECOM, Anchor QEA, Integral, Woodward, Ramboll, Wood) are now applying the approach. **Although there is substantial use of the technology, its acceptance remains limited by the lack of standard methods and commercial availability. Outcomes of this demonstration were intended to eliminate these technology transfer barriers and significantly increase polymeric sampler use and promote regulatory acceptance.** Standard methods developed in collaboration with multiple commercial and government laboratories, coupled with an inter-laboratory methods demonstration conducted per U.S. EPA SW846 guidance¹¹, were intended to dramatically enhance commercial availability and acceptance and utilization of polymeric sampling by the regulatory community.

The sampling approach and analysis of LDPE and PDMS samples have been done previously by both contract labs (e.g., AXYS, Columbia, and TestAmerica) and academia. Effective use of the resulting data to manage contaminated sediment sites remains an important topic to develop, although some efforts have already been published online (e.g., [Passive Sampler PRC Calculation Software User's Guide.pdf](#)) and/or described in the peer-reviewed literature^{12, 13}. Current efforts to use polymeric sampling at contaminated sites have involved close coordination with a research lab familiar with the approach. The development of a standardized set of protocols will promote more widespread use, consistent methods, and potentially lower overall cost.

There are several limitations that should be acknowledged for passive sampling. First, the method is more appropriate for moderate to high molecular weight compounds for which partitioning to PE and PDMS is strong. Relatively weak sorption by less hydrophobic compounds (i.e., $\log K_{ow} < 3$) can lead to detection limit issues. As such, for certain cases a direct measurement approach or the use of a dialysis system may be more appropriate. Second, the passive sampling approach usually requires a long time for exposure, especially for field deployments where static conditions require more exposure time to allow for sorption. Lastly, the passive sampling approach is currently not suitable for capturing short-term or episodic events, such as concentrations in stormwater. Rather, passive sampling is best used to represent time averaged concentrations.

3.0 PERFORMANCE OBJECTIVES

During this demonstration, multiple laboratories utilized polymeric samplers to quantify freely-dissolved PAHs and PCBs in the porewater of a single sediment sample. Demonstration results were intended to document laboratory accuracy and reproducibility of the polymeric sampler method – a key requirement for future acceptance as a SW-846 Method. The demonstration was designed so that each task reduces sources of variability extraneous to the polymeric sampler method itself prior to proceeding with subsequent tasks. Performance objectives are described in detail below and are summarized in Table 3-1 on the following page.

Table 3-1. Demonstration performance objectives for the microcosm study

Performance Objective	Data Requirements	Success Criteria
Quantitative Performance Objectives		
Interlaboratory analytical variability is low and within acceptable range (Task 1.1)	- Calibration check standards for low- and high-sensitivity methods prepared by one lab - Results of calibration check standard analysis reported as an U.S. EPA Stage 4 data package and Electronic Data Deliverable (EDD)	- Data validator confirms analytical data from each lab meets QC criteria (Section 5.4.4) and is of acceptable quality - Each lab reports $\pm 30\%$ of known concentrations for non-isotopically-labeled analytes; $\pm 50\%$ of known concentrations for isotopically-labeled Performance Reference Compounds (PRCs) - Success constitutes “go” to subsequent task.
Laboratories consistently extract and analyze PRCs from PRC-preloaded polymeric samplers provided by expert academic labs (Task 1.3)	- Results of PRC-loaded polymeric samplers (PDMS and LDPE replicates) from the academic laboratories preparing them - Results of PRC-preloaded polymeric samplers (PDMS and LDPE replicates) extracted and analyzed by all labs - Analytical data submitted as U.S. EPA Stage 4 data package and EDD	- Data validator confirms analytical data from each lab meets QC criteria (Section 5.4.4) and is of acceptable quality - Each lab reports $\geq \pm 50\%$ of known concentrations for the isotopically-labeled PRCs - Percent Relative Standard Deviation (% RSD) $\leq 20\%$ for replicate analyses; tolerance beyond this range will be considered on basis of collective results - Success constitutes “go” to subsequent task.
Laboratories achieve target PRC concentrations in polymeric samplers following standardized methods specific to each polymer (Task 2)	- Extract analysis results from polymeric samplers (PDMS and LDPE replicates) independently loaded by labs following standard method. - Analytical data submitted as U.S. EPA Stage 4 data package and EDD	- Data validator confirms analytical data meets QC criteria (Section 5.4.4) and is of acceptable quality - Each lab achieves within $\pm 50\%$ of target PRC concentrations immediately after loading is complete (i.e. $PRC_{t=0}$); Collective results will be used to establish target $PRC_{t=0}$ concentration criteria for Task 3 %RSD $\leq 20\%$ for replicate analyses performed; tolerance beyond this range will be considered on basis of collective results - Success constitutes “go” to subsequent task.
Laboratories measure target contaminants in homogenized sediment sample using “active” and “passive” sampling/exposure methods (as described in Section 5.3.3) following standardized methods specific to each polymer (Task 3)	- All analytical data from the polymeric sampler measurements submitted as EDD - Analytical data resulting from sediment porewater analysis via polymeric samplers, the Hawthorne method^{8,9}, and the air-bridge method¹⁰ - Analytical data submitted as U.S. EPA Stage 4 data package and EDD	- Data validator confirms analytical data meets QC criteria (Section 5.4.4) and is of acceptable quality - Achieve %RSD $\leq 20\%$ for $PRC_{t=0}$ concentration; tolerance beyond this range will be considered on basis of collective results - Establish intermethod variability by comparing C_{free} estimates determined using polymeric samplers compared to the manual porewater extraction method^{8,9} - Evaluate differences between C_{free} estimates determined via “active” and “passive” exposures; identify to the extent possible contributing sources of interlaboratory variability
Quantitative Performance Objectives		
Meet minimum commercial laboratory participation required to fulfill method validation requirements for SW-846 standardized method application	Responsiveness, flexibility, commitment to identify and resolve technical issues so that maximum participation is retained during demonstration	At least 3 commercial laboratories successfully complete all demonstration tasks

3.1 Interlaboratory analytical variability is low and within acceptable range (Task 1.1).

All participating laboratories agreed to a common suite of PRCs for PAHs and PCBs suitable for high- and low-sensitivity mass spectrometry methods. All labs received “calibration check standards” containing PAHs, PCBs, and select isotopically-labeled PRCs at concentrations known to the Texas Tech University lab of origin. Targeted PAHs were the U.S. EPA 16 Priority PAHs; targeted PCBs were the NOAA 18 congeners¹⁴ plus congeners 126 and 169. All labs used their preferred analytical methods for PAHs and PCBs to ensure that analytical data produced by all labs is of acceptable quality and accuracy.

Data Required: Results of calibration check standards submitted in standard Electronic Data Deliverable (EDD) format for data validation and review.

Success Criteria: Data validation and review confirmed analytical data met QC criteria (Section 5.5.2) and was therefore of acceptable quality. Success was defined as reporting $\pm 30\%$ of known concentrations for non-isotopically-labeled analytes; $\pm 50\%$ of known concentrations for isotopically-labeled PRCs. As described in Section 6, performance metric exceedances were encountered, investigated, and their impact on project path forward was documented.

3.2 Laboratories consistently extract and analyze PRCs from PRC-preloaded polymeric samplers provided by expert academic labs (Task 1.2).

Academic labs prepared PRC-preloaded polymeric samplers (TTU lab for PDMS; MIT for LDPE) and provided them to participating labs for extraction and analysis following standard methods.

Data Required: Multiple PRC-preloaded polymeric samplers (PDMS and LDPE replicates) extract analysis results. Labs submitted the analytical data in EDD format.

Success Criteria: Data validator confirmed that the analytical data met QC criteria and was therefore of acceptable quality. Success for each lab was defined as (1) reported concentration results that were $\pm 50\%$ of known concentrations allowed for isotopically-labeled PRCs; and (2) reported Relative Standard Deviation (%RSD) of $\leq 20\%$ for replicate analyses. As described in Section 6, performance metric exceedances were encountered, investigated, and their impact on project path forward was documented.

3.3 Laboratories achieve target PRC concentrations in polymeric samplers following standardized methods specific to each polymer (Task 2).

Results of Tasks 1.1 and 1.2 confirmed that analytical variability between labs was within acceptable range and that labs could successfully follow the standard method to achieve target accuracy and precision when extracting and analyzing extracts from polymeric samplers – and thus supported a “go” decision to proceed to Task 2. During Task 2, labs were charged with independently loading PRCs into the polymeric samplers, then extracting the lab-loaded samplers and reporting the results.

Data Required: Extract analysis results from polymeric samplers (PDMS and LDPE replicates) independently loaded by labs following standard method. Labs submitted the analytical data in EDD format.

Success Criteria: Data validator confirmed analytical data met QC criteria (Section 5.4.4) and was therefore of acceptable quality. Success for each lab was defined as (1) reported concentration results that were $\pm 50\%$ of the target concentrations for isotopically-labeled PRCs; and (2) reported Relative Standard Deviation (%RSD) of $\leq 20\%$ for replicate analyses. Collective results were used to establish target $PRC_{t=0}$ concentration criteria for Task 3. As described in Section 6, performance metric exceedances were encountered, investigated, and their impact on project path forward was documented.

3.4 Laboratories measure – with quantified accuracy and precision – target contaminants in homogenized sediment sample using “active” and “static” exposure methods (as described in Section 5.3.3) following standardized methods specific to each polymer (Task 3).

At this point in the demonstration, the laboratories had demonstrated that they could independently follow the standard method to produce comparable results. This final objective was intended to demonstrate reproducibility of the standard method for quantifying C_{free} PAHs and PCBs in sediment porewater – and to fulfill the method validation criteria required for a SW846 method application. Resulting C_{free} PAHs and PCBs determined using LDPE and PDMS polymers were compared against (a) values determined using “active” vs. “static” exposures, and (b) C_{free} determined using manual porewater extraction^{8,9} as a reference method.

Data Required: All analytical data from all methods submitted as EDD.

Success Criteria: Data validator confirmed that the analytical data met QC criteria (Section 5.4.4) and was of acceptable quality. A success criterion was established that each lab would achieve a %RSD $\leq 20\%$ for replicate $PRC_{t=0}$ concentrations. This success criterion was achieved for PDMS samplers but not for LDPE samplers, even after trouble shooting as described further in Section 6. Regardless, Task 3 successfully documented interlaboratory variability in C_{free} measurements within and between laboratories and demonstrated no significant difference (1) between C_{free} estimates determined using LDPE or PDMS samplers, (2) between C_{free} estimates determined in “active” vs. “passive” sediment, as both were corrected for progress to equilibrium using PRC results where equilibrium had not been achieved, and (3) between C_{free} estimates determined using polymeric samplers or the manual porewater extraction method; with the caveat that the polymeric samplers were cable of detecting lower concentrations of higher molecular weight PAHs compared to the manual porewater extraction method.

3.5 Meet minimum commercial laboratory participation required to fulfill method validation requirements for SW-846 standardized method application.

EPA’s Guidance for Methods Development and Methods Validation for the RCRA Program¹¹ requires that multiple labs and multiple operators be able to use the standard method and generate comparable performance data – and that this be demonstrated prior to submitting the method for Agency review. Further, the guidance¹¹ requires a minimum of three participants in the multilaboratory method validation study.

Requirement: The project team must be collaborative, responsive, and flexible – and remain

committed to working together to resolve technical issues that may arise at the conclusion of each task. This commitment by all participants ensured that maximum participation was retained during the demonstration.

Success Criteria: Retain at least 3 commercial laboratories – preferably more so that outcomes meet the minimum participation requirements for method validation. We retained a total of 4 commercial laboratories (and 3 academic laboratories) during this study.

4.0 SITE DESCRIPTION

During this demonstration, multiple laboratories utilized polymeric samplers to quantify freely-dissolved PAHs and PCBs in porewater using replicates of a homogenized sediment sample. The sediment sample was selected to contain total PAHs and PCBs in a concentration range that is relevant to pre-remediation characterization and post-remediation sediment monitoring (Table 4-1). Homogenizing multiple sediment samples with different characteristics (e.g. varying contaminant concentrations, geochemistry) to achieve the targeted concentrations could result in diffusive changes over time during the study and was therefore not desired. We therefore pursued two options: (1) collect a large volume sediment sample from an area in the Lower Duwamish Waterway previously found to contain suitable concentrations of PAHs and PCBs, and if found to be unsuitable, (2) utilize an existing large volume sediment sample previously collected from Indiana Harbor and stored at 4°C at the U.S. Army Engineer Research Development Center (ERDC) Environmental Laboratory in Vicksburg, MS.

4.1 LOWER DUWAMISH WATERWAY, RIVERMILE 0.6

The Lower Duwamish Waterway (LDW) in Seattle, Washington (USA), is an estuarine system that receives fresh water from the Green River, and salt water from Elliott Bay. The LDW has been historically polluted by industrial sources, combined sewer overflows, and storm drains discharge¹⁵, which has resulted in elevated concentrations of multiple contaminants. The LDW was declared a Superfund Site in 2001. The 2012 Final Feasibility Study (FFS) for the LDW¹⁶ published site-wide mean sediment concentrations for total high molecular weight PAHs and PCBs of 3.8 and 1.1 ppm dry weight, respectively. The Record of Decision for the LDW Superfund Site¹⁷ was published in 2004 and established Remedial Action Levels for multiple contaminants, including PCBs and PAHs.

The candidate demonstration sediment source from LDW was located at River Mile 0.6 on the west bank. Results of the sediment collection efforts under this project found PAHs were in acceptable range, but PCB concentrations were too low (Appendix A). These results suggest LDW sediment concentrations have decreased over time, which is great news for LDW but was a bit of a disappointment for this demonstration. Accordingly, Indiana Harbor Sediment was pursued as option two.

4.2 INDIANA HARBOR SEDIMENT SCREENING

Since the LDW sediment was unsuitable for this study, an existing large volume sediment sample previously collected from Indiana Harbor was utilized. The Indiana Harbor sediment was stored at 4 °C at the U.S. Army Engineer Research Development Center (ERDC) Environmental Laboratory in Vicksburg, MS. Homogenization and testing of the sediment was performed to determine suitability for this study (see Section 6.3.1 for more details). The average concentration

of total PAHs (1,000 mg/kg dw) and total PCBs (3.3 mg/kg dw) met the minimum concentration requirements threshold, meaning polydimethylsiloxane (PDMS) and low-density polyethylene (LDPE) polymer samplers and standard analytical methods were expected to be capable of reliably quantifying this range of PAHs and PCBs concentrations in the Indiana Harbor sediment samples.

5.0 TEST DESIGN

This section provides an overview of the experimental design and demonstration tasks (Sections 5.1 and 5.2), analytical methods (Section 5.3), as well as data analysis methods (Sections 5.4) used during the demonstration.

5.1 CONCEPTUAL EXPERIMENTAL DESIGN

Multiple laboratories utilized polymeric samplers to quantify freely-dissolved PAHs and PCBs in porewater using a single homogenized sediment during this demonstration. Multiple tasks with multiple go/no-go decision points were included upfront in effort to identify and eliminate sources of inter-laboratory variability extraneous to the polymeric sampler method itself (Figure 5-1). The goal of Task 1 was to ensure all participating labs produce analytical data of acceptable quality that is comparable – and that all labs collaboratively established a standardized method used during subsequent tasks. Tasks 1.1 and 1.2 proceeded in parallel. With satisfactory accomplishment of Task 1.1, the demonstration proceeded to Task 1.3, where labs used the standardized method (outcome of Task 1.2) to extract and quantify PRCs from pre-loaded polymeric samplers supplied by the academic labs. With satisfactory accomplishment of Task 1.3, the demonstration proceeded to Task 2, where labs used the standard method to independently load, extract, and quantify PRCs in “blank” (i.e. not containing PRCs) and PRC pre-loaded polymeric samplers. With satisfactory accomplishment of Task 2, the demonstration proceeded to Task 3, where labs used the unified SOPs to independently complete all steps involved with utilizing polymeric samplers to measure freely-dissolved PAHs and PCBs in sediment porewater using both “active” and “passive” exposure methods. When success criteria at a go/no-go decision point were not fully accomplished, the team worked collaboratively to identify likely causes and to develop corrective actions so that success criteria are achieved by all participants prior to proceeding with the subsequent tasks.

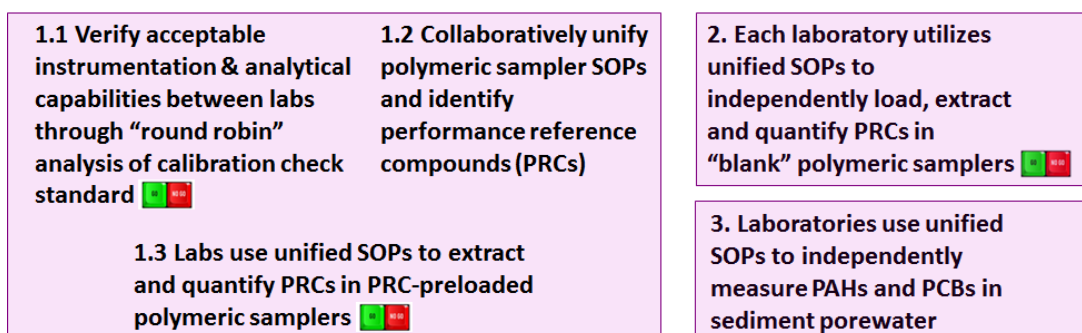


Figure 5-1. Demonstration task phasing with go/no-go decision points

5.2 PHASED INTERLABORATORY DEMONSTRATION TASKS

The following section describes demonstration Tasks 1 – 3.

5.2.1 Task 1: Establish the Standard Method

Task 1 is discussed in more detail in the Task 1 Go/No-Go Memorandum (Appendix D). This task involved compiling polymer handling and processing Standard Operating Procedures (SOPs) for LDPE and PDMS. SOP details that were reviewed and standardized include:

1. Cleaning procedures for the polymer and assembled sampler;
2. Impregnation of the polymeric sampler with PRCs;
3. Extraction of the analytes from the polymeric sampler;
4. Analysis methods building upon existing U.S. EPA analytical methodologies (i.e. identify methods for sample handling to allow use of standard analytical methodologies);

As a first order of business, TTU (PDMS) and MIT (LDPE) shared their respective SOPs with collaborators (UMaryland, USACE, Pyron) for review and input. The PDMS and LDPE SOPs were then provided to the participating commercial labs for review and were revised once more. The updated SOPs and associated commercial lab questions and answers are included in Appendix B. SOP amendments were included as the demonstration progressed so that at the end the SOPs and “FAQ” from commercial laboratories were complete and final at the conclusion of this demonstration. The SOPs include a critically important element required for standardizing the method: prescribed PRCs suitable for both polymers and suitable for “traditional” capillary GC/MS and isotope dilution MS but not for other methods such as GC-FID or GC-ECD.

In this work, the PRCs were isotopically-labeled versions of the organic porewater contaminants of interest, which are loaded into the samplers prior to deployment. PRC loss from the polymer during deployment provides a measure of its progress toward equilibrium with contaminants in the sediment porewater – a key measurement for ensuring a proper conversion of the sediment polymer extract concentration to a porewater concentration. While there are many commercially available isotopically-labeled PAH and PCB candidates for PRCs, commercial laboratories use many of these as their surrogate recovery standards and injection standards. **Establishing a standard suite of PRCs that was acceptable to laboratories using varied analytical methods was crucial to establishing a standardized polymeric sampler method; this was accomplished during demonstration plan development.** The PAH PRCs were independent of the analytical method the laboratories use; thus, there is only one suite of PRCs. We note that ¹³C labelling was only used for six of the carbons in these PAH PRCs (Table 5-1). PCB PRCs varied by analytical method and thus there are two suites of PCB PRCs: one for low resolution mass spectrometry and another one for high resolution mass spectrometry needed for isotope dilution methods.

Table 5-1. Standardized Performance Reference Compounds (PRCs)

Target Contaminant Measured by Polymeric Sampler	Analytical Method	PRC
PAHs	High or Low Sensitivity	¹³ C6-phenanthrene
		¹³ C6-fluoranthene
		¹³ C6-chrysene
		¹³ C6-indeno(1,2,3-cd)pyrene
PCBs	Low Resolution Mass Spectrometry	¹³ C-labled PCB congener 37
		¹³ C-labled PCB congener 47
		¹³ C-labled PCB congener 54
		¹³ C-labled PCB congener 111
		¹³ C-labled PCB congener 138
		¹³ C-labled PCB congener 178
	High Resolution Mass Spectrometry	¹³ C-labled PCB congener 28
		¹³ C-labled PCB congener 47
		¹³ C-labled PCB congener 70
		¹³ C-labled PCB congener 80
		¹³ C-labled PCB congener 111
		¹³ C-labled PCB congener 141
		¹³ C-labled PCB congener 182

The polymeric sampler SOPs (Appendix B) describe preparation, exposure, cleanup, and analysis of the polymeric samplers for measurement of PAHs and PCBs in sediment porewater. The SOPs prescribe PRCs, surrogate (recovery) standards, and injection standards for analysis of PAHs and PCBs in the samplers. Methods for loading PRCs to desired levels were tested and revised as necessary during this demonstration. These SOPs are intended to be suited for use by laboratories analyzing polymers from either *in situ* or *ex situ* sampling studies. The SOPs focus on chemical analysis of polymeric sampler extracts by conventional (and accepted) standard methods for PAHs and PCBs. The proper analysis and PRC-based corrections for equilibrium^{2,18} are included. Options for equilibrium corrections were addressed, including PRCs¹⁹. Quality assurance and quality control (QA/QC) approaches were included in the standard methods as well.

At the beginning of demonstration Task 1, all participating laboratories were sent calibration check standards for analysis using their preferred standard analytical method (details in Section 5). Each calibration check standard was prepared in solvent by TTU using an approach detailed in Appendix B. Two types of check standards were provided to the labs: the first contained select PRCs (Table 5-1) for PAHs and PCBs in solvent (iso-octane); the second contained targeted native PAHs (EPA 16 Priority PAHs) and PCBs (NOAA 18 congeners¹⁴ plus congeners 126 and 169) in solvent (iso-octane). The participating commercial, government, and ESTCP team member laboratories utilized results of the calibration check standards to ensure inter-laboratory analytical variability is within acceptable limits.

At the conclusion of Task 1, all participating laboratories were sent replicate polymeric samplers that were pre-loaded with PRCs by the academic labs, then asked to follow the standardized methods to extract and analyze these polymeric samplers. All laboratories reporting polymeric

sampler mean concentrations within a target value of $\pm 30\%$ of the concentrations established by the academic labs, and a target relative standard deviation (%RSD) of $\leq 20\%$ for replicate analysis, were considered successful. Although these were the expected range of analytical variations, the results from each laboratory were evaluated statistically to define a typical and expected range of variations and to identify laboratories that are outside of the expected range. These results formed the basis for a "go" decision to proceed to Task 2 for specific laboratories as well as the overall project. A visual evaluation of the plotted data was evaluated to pin-point outlying data and laboratories that require corrective action. If analytical variations were greater than expected for all laboratories, efforts were undertaken to evaluate potential variations in sample preparation or variations resulting from sampler transport or processing to determine if the variations could be reduced to acceptable levels. All methodological and/or analytical challenges were identified, documented and resolved before proceeding to Task 2. Any refinement of the consensus PRCs suite identified in Table 5-1 based on results of calibration check standard samples were required prior to proceeding to Task 2.

5.2.2 Task 2: Interlaboratory Preparation and Analysis of Polymeric Samplers

Participating laboratories followed the standardized methods from Task 1 to load and analyze PRCs (Table 5-1) from replicated LDPE and PDMS polymeric samplers. Implementation of Task 2 is discussed in more detail in the Task 2 Go/No-Go Memorandum (Appendix E). Four commercial laboratories and three university research laboratories participated in Task 2.

Isotopically-labeled PRCs were loaded into PDMS and LDPE polymer segments by the participating commercial and university laboratories. Danny Reible's group at TTU and Phil Gschwend's group at MIT, respective subject matter experts for use of PDMS and LDPE samplers, prepared the pre-cleaned samplers in six replicates (plus one sampler as a method blank) for each of the participating laboratories. Laboratories loaded PRCs into the samplers following the standard operating procedures (SOPs) provided by TTU (TTU, 2018) and MIT (MIT, 2017), respectively, for SPME PDMS and LDPE strips. Once the loading was completed (approximately 1 month following PDMS and LDPE insertion into loading solution), PRC-loaded samplers (and the method blank samplers) were extracted per the standardized polymeric sampler SOPs. Each laboratory quantified PAHs using a low resolution mass spectrometry analytical method (EPA Method 8270D-SIM) and PCBs using either a high or low resolution mass spectrometry analytical method (EPA Method 1668C or U.S. EPA Method 8270D-SIM, respectively).

5.2.3 Task 3: Labs Use Standard Methods to Independently Characterize Sediment Porewater using Polymeric Samplers

This task included both actively mixed and static sampling of sediment porewater using polymeric samplers. Active sampling involved inserting the sampler into a sediment and water slurry, followed by continuous mixing/tumbling to ensure maximal contact between the sediment and the sampler. Active sampling accelerates progress toward equilibrium and is therefore faster than static sampling and well suited for estimating bulk contaminant partitioning coefficients. In contrast,

static sampling involves inserting the polymeric samplers into the sediment where hydrophobic contaminants diffuse into the sampler in a static system mimicking some in-situ field conditions with static sediment and porewater. Because desorption from strongly bound sites in sediments can be a slow process, especially for strongly hydrophobic compounds, equilibrium conditions are often not achieved; thus, requiring equilibrium corrections using PRCs or other means as described previously. Because both active and static sampling have significant utility for environmental monitoring, both sampling approaches were included under Task 3. The specific contaminants analyzed for the purposes of the inter-laboratory study were limited to those for which polymer-water partition coefficients exist (e.g. PCBs and PAHs). It is however recognized that these polymeric sampling techniques are applicable to almost any hydrophobic organic compound.

1) Preparation of homogenized sediment for inter-laboratory analysis:

Homogenized sediment samples were prepared at the ERDC lab in Vicksburg, MS, using protocols for sediment homogenization developed for ER-2431. Homogenization and testing of the sediment was performed to determine suitability for this study (see Section 6.3.1 for more details).

2) Task 3 PRC loading: PRC loading for both LDPE and PDMS followed protocols outlined in the respective SOPs (Appendix B). Commercial laboratories performed an initial loading, extraction, and analysis, with remaining LDPE and PDMS polymer segments continuing to soak in the loading solution. A final round of extraction and analysis was performed with remaining polymer segments (n=6) before proceeding to *ex situ* sampling.

3) Protocol for ex situ sampling: Homogenized sediment samples prepared by ERDC were shipped to all participating laboratories, then stored in the refrigerator prior to exposure. The protocol for this sampling largely followed the recently developed draft user manual for passive sampling⁶. Prior to sampler exposure to the sediment, the team determined the polymer and sediment mass required for each of the polymers based on the PCB and PAH concentrations in sediment and expected analytical detection limits. Each participating laboratory portioned out a set mass of sediment into bottles and deployed a PRC-loaded passive sampler into each bottle. At the time of placement of the passive samplers, six samples of PRC-loaded polymer were set aside for initial PRC analyses. Both exposures of polymeric samplers were carried out in the dark or in amber glass bottles to minimize photodegradation. No biocides were added to the bottles. The exposures were carried out at room temperature (22 ± 5 °C). At the conclusion of the 30 day exposure period, laboratories retrieved the polymeric sampler from each bottle, cleaned it based on accepted procedures⁷ (Appendix B), and set it aside for the analysis of PAHs and PCBs.

Active sampling: The bottles were labeled, capped, and placed on either a roller or shaking table for a period of 1 month.

Static sampling: The exposure took place in the static mode (i.e., with the in closed bottles sitting

without motion) for a period of 1 month, largely mimicking *in situ* deployments in sediments.

All commercial laboratory analytical data resulting from Task 3 were submitted along with summaries of instrument calibrations and all method-required quality control (QC) analyses for validation; specific raw data (such as instrument print-outs and sample preparation worksheets) were provided as needed. The data packages from Task 3 (and all Tasks) were reviewed and validated by an independent professional, Mr. Mingta Lin at Pyron Environmental, Inc., to ensure all method requirements were met and data were of good and known quality before any data usage occurred.

4) PRC correction for progress toward equilibrium:

The fraction to steady state (or f_{ss}) results were determined using $C_{PRCt=0}$ and $C_{PRCt=final}$. For PDMS, the f_{ss} values for target analytes were determined according to the procedures described in the final SOPs (Appendix B). For LDPE, the f_{ss} values were determined according to procedures published¹³ as part of previous ESTCP project ER-200915. Software for LDPE PRC calculations is freely available for download from the ER-200915 website at the following URL: <https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Sediments/Bioavailability/ER-200915/ER-200915>.

5.2.4 Manual porewater extraction with colloid separation

The manual porewater extraction method with alum flocculation followed the method used in Ghosh et al 2000 and Khalil et al. 2006^{8,9}. A sediment-water slurry (1:10 ratio) was prepared in 1L glass bottles and 500 mg/L sodium azide was added to inhibit PAH biodegradation. The setup was placed in the dark for 1 month and allowed to equilibrate on a shaker table at room temperature (23 ± 1 °C). The sediment samples were then allowed to settle for one day. This step was followed by the addition of 0.001M alum solution and adjustment of pH back to neutral with NaOH solution. The supernatant water was mixed slowly using a glass pipet for 2 minutes to mix and flocculate the alum without disturbing the settled sediment. The alum floc co-precipitated with suspended particles and settled to the bottom with hours. The supernatant water (about 600 ml) was transferred to a separatory funnel using a 100 ml glass pipette. The pipette was rinsed with 20 ml of hexane which was then used to further used in the separatory funnel for extraction of the water. A total of three sequential extractions were performed followed by the collection of the extract for concentration cleanup, and analysis.

5.2.5 Task 4: Sharing Finalized Standard Methods with Broader Community

The developed finalized standard method for *ex situ* analysis of sediment samples were presented via webinar, online CLU-IN seminar, and YouTube videos. These seminars and webinars focused on the standardized and accepted protocols and feature resulting C_{free} data generated during this study. We note that inclusion of several commercial labs also result in direct communication of the methodology's procedures and capabilities to private sector laboratories and consulting communities.

5.3 ANALYTICAL METHODS

The following section describes the standard analytical methods used by participating laboratories to measure PCBs and PAHs in samples during this project. Appendix F includes quality control criteria for analytical methods.

5.3.1 Analytical Methods: PCB Congeners

PCBs were quantified using high-resolution or low-resolution mass spectrometry methods. Both methods are summarized below.

EPA Method 1668C²⁰ - High-Resolution Gas Chromatography/High Sensitivity Mass Spectrometry (HRGC/HSMS): One methodology used to determine target PCB congeners (i.e., NOAA 18¹⁴ plus congeners 126 and 169 and PRCs) was high-resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS). AXYs-SGS, TestAmerica, and Vista use this methodology for PCB analyses. The laboratories generally follow U.S. EPA Method 1668C with various modifications. The 12-WHO designated PCBs²¹ and the earliest and latest eluted congener at each level of chlorination are determined by the isotope dilution quantitation technique; the remaining congeners are determined by the internal standard quantitation technique.

Modified U.S. EPA Method SW8270D²² – High Resolution Gas Chromatography/Low Sensitivity Mass Spectrometry (HRGC/LSMS): ALS, ARI, and Battelle chose to use HRGC/LRMS methodology modified from U.S. EPA Method 8270D to analyze target PCBs and project-specific PRCs.

5.3.2 Analytical Methods: PAHs

PAHs were analyzed with GC/MS methodology, generally modified from U.S. EPA Method 8270D with selective ion monitoring (SIM) mode to achieve lower detection limits. AXYs-SGS and TestAmerica chose to use isotope dilution technique for analyte quantitation, rather than internal standard technique as stated in U.S. EPA Method 8270D.

EPA Method 1625 Combined with Modified U.S. EPA Method SW8270D²³ (HRGC/MS): AXYs-SGS and Vista chose to combine U.S. EPA Method 8270D and U.S. EPA Method 1625B where a HRGC coupled with mass spectrometry (MS) is used for sample analysis, and isotope dilution technique is applied for analyte quantitation. Vista participated only in Task 1 of this study.

Modified U.S. EPA Method SW8270D (GC/MS): ALS, ARI, and Battelle chose this methodology for PAHs analyses.

5.4 DATA ANALYSIS

Data analysis was performed on analytical results of target analytes and PRCs reported by the commercial laboratories. Various data analysis and evaluation approaches were applied to data generated during Task 1 through Task 3, adhering to the objectives of each task. The data objectives for each task were:

Task 1: Determine if the analytical methodologies and instrumentation proposed by each of the commercial laboratories meet the project required accuracy and reproducibility.

Task 2: Evaluate the commercial laboratories' ability to independently meet the project requirements in LDPE and PDMS sampler loading, processing, extraction and analysis.

Task 3: Assess the inter-laboratory variations and pin-point methodological downsides, if any, in processing, loading, extraction, and analysis of passive sampling devices (PSDs) using real sediment samples in *ex situ* deployments. The analytical data generated in this task is essentially to validate this PSD sampling and analysis protocol.

Table 5-2. Summary of the specific data collected, generated and reviewed

Task	Sample Type	Specific Samples	Data Reported
Task 1	Calibration standard	Target analytes; PRCs	Relative standard deviation (RSD) (%); Difference from true value (%D)
Task 2	Polymeric sampler	Target analytes; PRCs	Relative standard deviation (RSD) (%); Difference from true value (%D)
Task 3	Polymeric sampler	Target analytes; PRCs	Relative standard deviation (RSD)(%), i.e. polymer-specific coefficient of variation (COV) within and across labs for given analytes; average and standard deviations of individual analytes by laboratory and by method

5.4.1 Data Reduction and Laboratory Deliverables

Participating commercial laboratories submitted official laboratory reports for the team project chemist's review. The laboratories followed their standard protocols in processing and reviewing data and then assembling data packages for submission. Data deliverables required for each task included a full data package sufficient for a Level 3 data validation (as defined in U.S. EPA 2009), and a spreadsheet in Excel format that consists of analytical results of sample analysis and associated QC analyses (i.e., method blank, LCS, MS, MSD, surrogate spikes) and information associated with the samples (i.e., sample collection, preparation, and analysis dates, sample types, and laboratory sample identity).

5.4.2 Data Review and Data Validation

General. Data review is independent of the intended use of the information and determines the technical merit of the data by comparing the QC results to method and project-specific criteria. Data are reviewed for traceability, documentation, calculations, check for transcription errors, and evaluation of the data deliverables for contract compliance following all applicable SOPs within

the laboratory.

Prior to any use of the data, the Team project chemist reviewed and validated data packages submitted by participating commercial laboratories. The validation procedures follow the requirements specified in the following documents, as applicable.

- U.S. EPA Contract Laboratory Program National Functional Guidelines for High Resolution Superfund Methods Data Review. Office of Superfund Remediation and Technical Innovation. April 2016. U.S. EPA 542-B-16-001.
- U.S. EPA Contract Laboratory Program National Functional Guidelines for Organic Superfund Data Review. Office of Superfund Remediation and Technical Innovation. January 2017. U.S. EPA 540-R-2017-002.

A Stage 4 (as defined in U.S. EPA 2009) validation was performed on all data reported by commercial laboratories. The numerical QA/QC criteria and the frequency of QA/QC analyses applied to the validation was in accordance with those specified in the analytical methods and the performance-based control limits established by the laboratories (laboratory control limits) provided in the laboratories' SOPs. The validation examined data submitted by the laboratories for methodological compliance with respective laboratory SOPs and determine data quality against project data objectives. Based on the data validation, proper data qualifiers were applied to specific data points to inform data users of the extent of data usability as necessary. The scope and findings of data validation were discussed and documented in a data validation report. Data qualifiers include, but are not limited to: J – The value is an estimate; U – The value is considered not detected at this level; UJ – The analyte was not detected, but the detection limit is an estimate.

5.4.4 Data Reporting and Analysis

Analytical results reported during each task were tabulated and included Appendices D, E, G. The project chemist/data validator produced data validation reports for individual laboratory submittals and also a summary report identifying out-of-tolerance and in-tolerance data issues that could impact comparability of laboratory datasets within a given demonstration task. These data validation reports, along with data summaries, data analysis, lessons learned during the project and other pertinent details are included in this final report and appendices for public release. Raw data deliverables that could be used to identify which labs produced the data were not included in the final report due to lab privacy concerns. However, individual deliverables are retained for private submittal as part of SW846 approval package as needed.

Detailed methods and results of Tasks 1 and 2 are included in Appendices D and E, respectively. Data analysis for Task 3 was similar to Tasks 1 and 2, but was a much larger dataset as the labs independently processed replicated PRC loaded samplers, as well as many replicated sediment samples (n= 6) under both “static” and “active” exposure conditions – and for both LDPE and PDMS polymeric samplers. Accordingly, Task 3 PRC results were systematically screened for potential outliers by preparing box and whisker plots. Outliers, defined here as beyond the 10th and

90th percentiles for a given dataset, were plotted as data points beyond the whiskers on the box plots. No single results outliers were identified; however, visual inspection of the box plots identified a single replicate reported by Lab 84 for the Task 3, LDPE “active” PAHs as being out of range. The before and after replicate removal for that dataset is shown in Appendix G. No other replicates or samples were removed from the Task 3 dataset. As in Tasks 1 and 2, interlab variations were identified by comparing the average and standard deviations of each analyte by method. Method-specific precision was evaluated by computing the coefficient of variation (standard deviation divided by the mean, expressed as a percentage) for each analyte by lab.

6.0 PERFORMANCE ASSESSMENT

This section presents results of the three project tasks, which were designed to identify and eliminate (to the extent practicable) sources of interlab variability extraneous to the polymeric sampler method itself. Section 6.1 describes results of Task 1, which included (a) developing the standardized operating procedures (SOPs) for preparation and use of the polymeric samplers, (b) interlab analysis of calibration check standards intended to establish analytical method comparability between labs, and finally (c) interlab extraction and analysis, per SOPs, of PRC-loaded polymeric samplers, which were prepared by academic laboratories. Section 6.2 describes results of Task 2, which included independent PRC loading, extraction and analysis of the polymeric samplers by all participating labs. Finally, Section 6.3 describes results of Task 3, which included interlab sediment porewater characterization using the standardized polymeric sampling procedures. Each section concludes with a summary of key lessons learned as the project progressed.

6.1 TASK 1 RESULTS

The results of Task 1 are discussed in more detail in the Task 1 Go/No-Go Memorandum (Appendix D). Here we summarize the main results and their implications.

6.1.1 Task 1.1: Calibration Check Standard Preparation and Analysis

Four commercial laboratories and three university research laboratories participated in Task 1. Commercial laboratories participated in this project under the condition of anonymity. Accordingly, identities of laboratories that submitted calibration check standard results were obscured by assigning each a random number (Table 6-1).

Table 6-1. Calibration Standard Analysis by Lab

Test	GC/MS Sensitivity	Check Standard (ng/L)	Laboratory Number (Randomly-Assigned) that Performed Test	
			University	Commercial
PCBs	High Sensitivity	5	40, 75, 84	25, 62, 11
	Regular Sensitivity	50	0, 87, 94	35, 69, 17
PAHs	High Sensitivity	5	58, 82	91
	Regular Sensitivity	100	9, 74, 98	3, 6, 28, 37, 47

Calibration check standard results reported by labs were within acceptable range ($\pm 30\%$ of known concentrations for PCB and PAH natives and $\pm 50\%$ of known concentrations for PCB and PAH PRCs; see Table 3-1) with a few exceptions (Table 6-2). Labs 98 and 28 reported 1 or 2 out of

range results for native PAHs ($\leq \pm 38\%$, Table 6-2). Lab 62 reported 2 out of range results for native PCB congeners ($\leq \pm 36\%$); Lab 11 reported 1 out of range ($\leq \pm 32\%$) result. A significantly out-of-target-range result (-91%) for PAH PRC indeno(1,2,3-cd)pyrene was reported by Lab 74.

Table 6-2. Summary of Task 1.1 Performance

Method	Analyte	Total Labs Performing	Lab Response Rate	Pass	Fail	Pass Rate	Exceedance Summary
EPA 1625B/8270D or EPA 8270D	PAH Natives	10	100%	8	2	80%	Lab 98 ^a achieved +38% for naphthalene
	PAH PRCs	10	100%	9	1	90%	Lab 28 ^b achieved -38% for dibenz[a,h]anthracene and -32% for indeno[1,2,3-cd]pyrene Lab 74 ^c achieved -91% for indeno[1,2,3-cd]pyrene
EPA 8270D	PCB Natives	6	100%	6	0	100%	
	PCB PRCs	6	100%	6	0	100%	
EPA 1668C	PCB Natives	7	100%	5	2	71%	Lab 62 ^d achieved -36% and -32% for PCB-128 and PCB-138, respectively; Lab 11 ^e achieved -32% for PCB-44
	PCB PRCs	7	100%	7	0	100%	
Totals		46		41	5	89%	

a) Naphthalene contamination in lab's internal standard mix, new contaminant-free standard mix prepared; b) check standard solvent (isooctane) likely interfered with lab's internal standard solvent (methylene chloride), issue isolated to Task 1.1; c) suspected column "bleed" for PRC indeno(1,2,3-c,d)pyrene-13C6 on low-resolution GC/MS used by Lab 74, deuterated or fully-labeled PRC would be more appropriate PRC for low-res GC/MS; d&e) apparent experimental error, which were monitored going forward.

Task 1.1. Discussion. Most labs met the acceptance criteria of $\pm 30\%$ for all of the native target analytes and $\pm 50\%$ for all of the PRCs present in the calibration check standard samples (Appendix D). A few labs reported results for a few analytes that were out-of-range (e.g. $\pm 38\%$ for one or two natives; $\pm 58\%$ for one or two PRCs). These exceedances were due to naphthalene contamination in an internal standard and calibration check standard solvent (isooctane) interference with lab standard solvent (methylene chloride); both of which were resolved as of Task 1.1 conclusion. The cause of accuracy exceedances for one or two PCB congeners by Labs 62 and 11 were not identified in QC documents or through data validation. These apparent experimental errors were noted and monitored in subsequent tasks.

A significantly out-of-target-range result (-91%) for PAH PRC indeno(1,2,3-cd)pyrene-13C6 was reported by university Lab 74. Although this consensus PRC choice worked well for all other labs, it did not work well for the low resolution GC/MS method used by Lab 74 because they incorrectly thought the PRC used was indeno(1,2,3-cd)pyrene-13C22 and as a result set their SIM parameters incorrectly. No corrective action was taken as this was simply a limit of Lab 74's instrumentation and SIM parameter error. A key lesson learned: PAH PRC indeno(1,2,3-cd)pyrene-13C6 does not provide sufficient m/z distinction for low resolution GC/MS analysis when there is significant column bleed from a dimethyl siloxane-coated column. Labs performing analysis on a low resolution GC/MS should consider fully-13Clabeled or deuterated indeno(1,2,3-cd)pyrene for use as a PRC instead. Lab 74 continued to use preferred low resolution GC/MS analysis, with

appropriate SIM parameters for PRCs. Task 1.1 acceptance criteria exceedances were occasional, not systemic, and thus supported a “Go” recommendation to move to Task 2.

6.1.2 Task 1.2: Standardization of Polymeric Sampler Procedures

Danny Reible’s group at Texas Technical University (TTU) and Phil Gschwend’s group at the Massachusetts Institute of Technology (MIT) shared their standard operating procedures (SOPs) for the preparation and extraction of PDMS and LDPE samplers with each other and with commercial laboratories to solicit questions and input. The resulting updated polymer-specific SOPs and Frequently Asked Questions (FAQs) from commercial laboratories are included in this report in Appendix B. The final polymer-specific SOPs were utilized by the commercial and university laboratories to complete Task 1.3.

6.1.3 Task 1.3: PRC Pre-Loaded Polymeric Sampler Preparation and Analysis

Identities of laboratories that submitted results for PRC pre-loaded PDMS and LDPE polymeric samplers were obscured by assigning each a random number (Table 6-3). TTU and MIT prepared the PRC pre-loaded polymeric samplers for all labs. Concentrations reported by TTU and MIT were considered the “known” concentrations; accordingly, TTU and MIT identities were not obscured.

Table 6-3. PRC Concentrations in Pre-Loaded Samplers by Receiving Labs

Test	GC/MS Sensitivity	Known Concentration Range for PRC Loaded Samplers (ng/g-LDPE or ng/mL-PDMS)	Laboratory
PDMS PCBs	High Sensitivity	1400 – 1700	76, 85, 93, 10, TTU
	Regular	8700 – 9200	44, 46, 20, TTU
PDMS PAHs	High Sensitivity	600 – 840	14, TTU
	Regular	7000 – 8500	71, 15, 23, 55, 38, 63, 81, TTU
LDPE PCBs	High Sensitivity	31 – 36	93, 18, 72, 60, MIT
	Regular	110 – 160	40, 86, 17, MIT
LDPE PAHs	High Sensitivity	27 – 51	MIT only
	Regular	140 – 200	MIT, 91, 16, 90, 72, 44, 32

Extracted PRC concentrations reported by labs were within $\pm 50\%$ (i.e. between 50% and 150%) of known concentrations for PAH and PCB PRCs loaded in PDMS and LDPE samplers 96% of the time (Table 6-4; Figures 6-1 and 6-2). Lab 38 reported 1 out-of-range result for PAH PRC indeno(1,2,3-cd)pyrene in the PDMS samplers (-58%; Figure 6-1). Lab 86 reported 3 out of range results for PCB PRCs PCB-111, PCB-138 and PCB-178 (respectively, -53%, -60%, and -71%; Figure 6-2).

Table 6-4. Summary of Task 1.3 Performance

Method	Analyte	Total Labs Performing	Lab Response Rate	Pass	Fail	Pass Rate	Exceedance Summary
PDMS	EPA 1625B/8270D or EPA 8270D PAH PRCs	9	100%	8	1	89%	Lab 38 ^a achieved -58% for indeno[1,2,3-cd]pyrene
	EPA 8270D PCB PRCs	4	100%	4	0	100%	
	EPA 1668C PCB PRCs	5	100%	5	0	100%	
LDPE	EPA 1625B/8270D or EPA 8270D PAH PRCs	8	100%	8	0	100%	
	EPA 8270D PCB PRCs	4	100%	3	1	67%	Lab 86 ^b achieved -53%, -60%, 71% for PCB congeners 111, 138, 178
	EPA 1668C PCB PRCs	5	100%	5	0	100%	
Total		35		33	2	94%	

a) detailed investigation identified no explanation for low result; b) not an analytical issue, suspect LDPE material variability in pre-loaded samplers provided to Lab 86, see discussion.

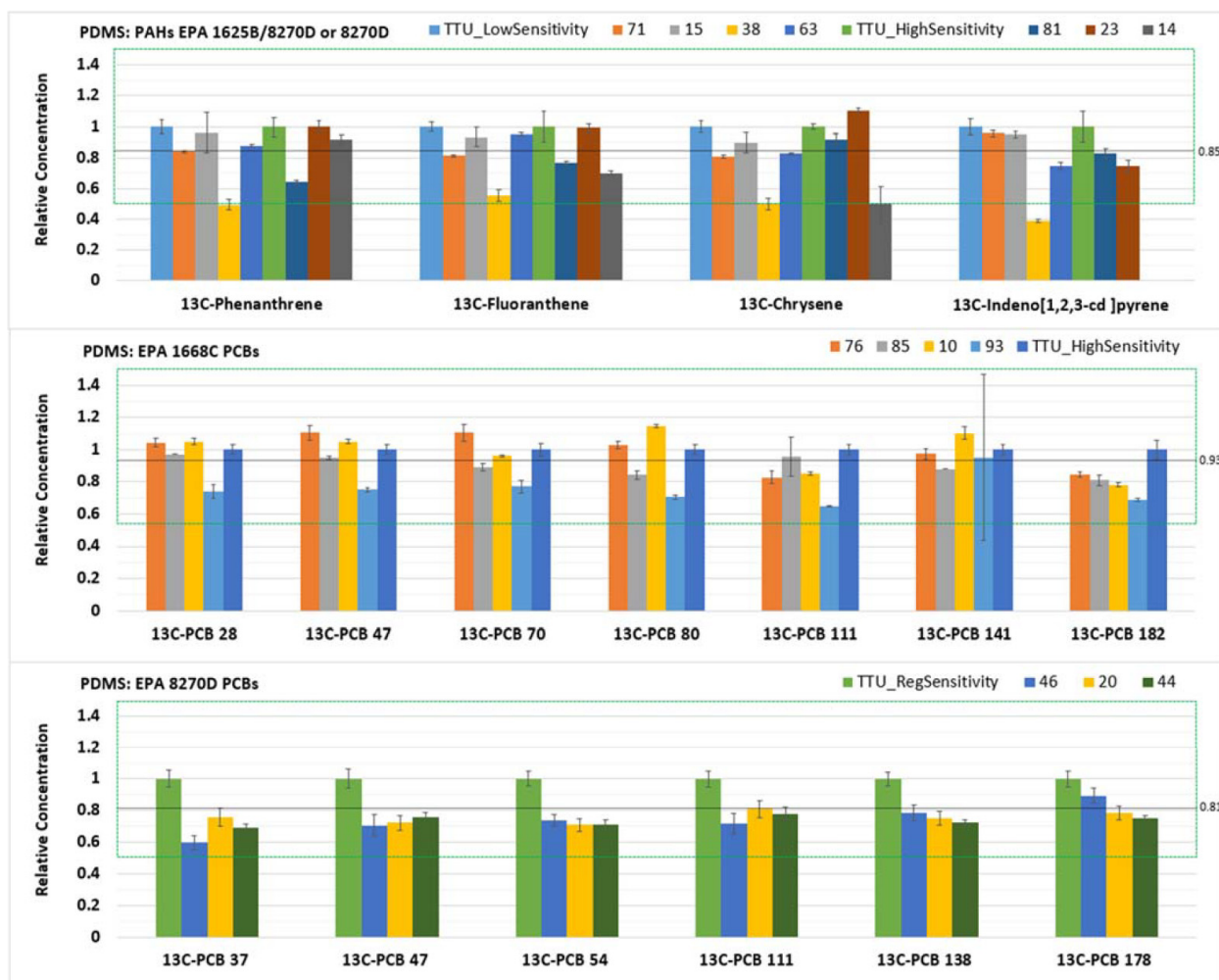


Figure 6-1. PRC Pre-loaded PDMS polymeric sampler results in relative units ($C_{\text{reported}}/C_{\text{known}}$). PCB congeners analyzed by high-sensitivity and regular-sensitivity methods are respectively shown in the middle and bottom; PAHs analyzed by regular- and high-sensitivity methods are shown at the top of the figure. The $\pm 50\%$ of known concentration performance criteria is highlighted in green. Bars and error bars represent the mean and standard deviation of $n=6$ replicates. Average results for each data set are shown as black lines with average values to right.

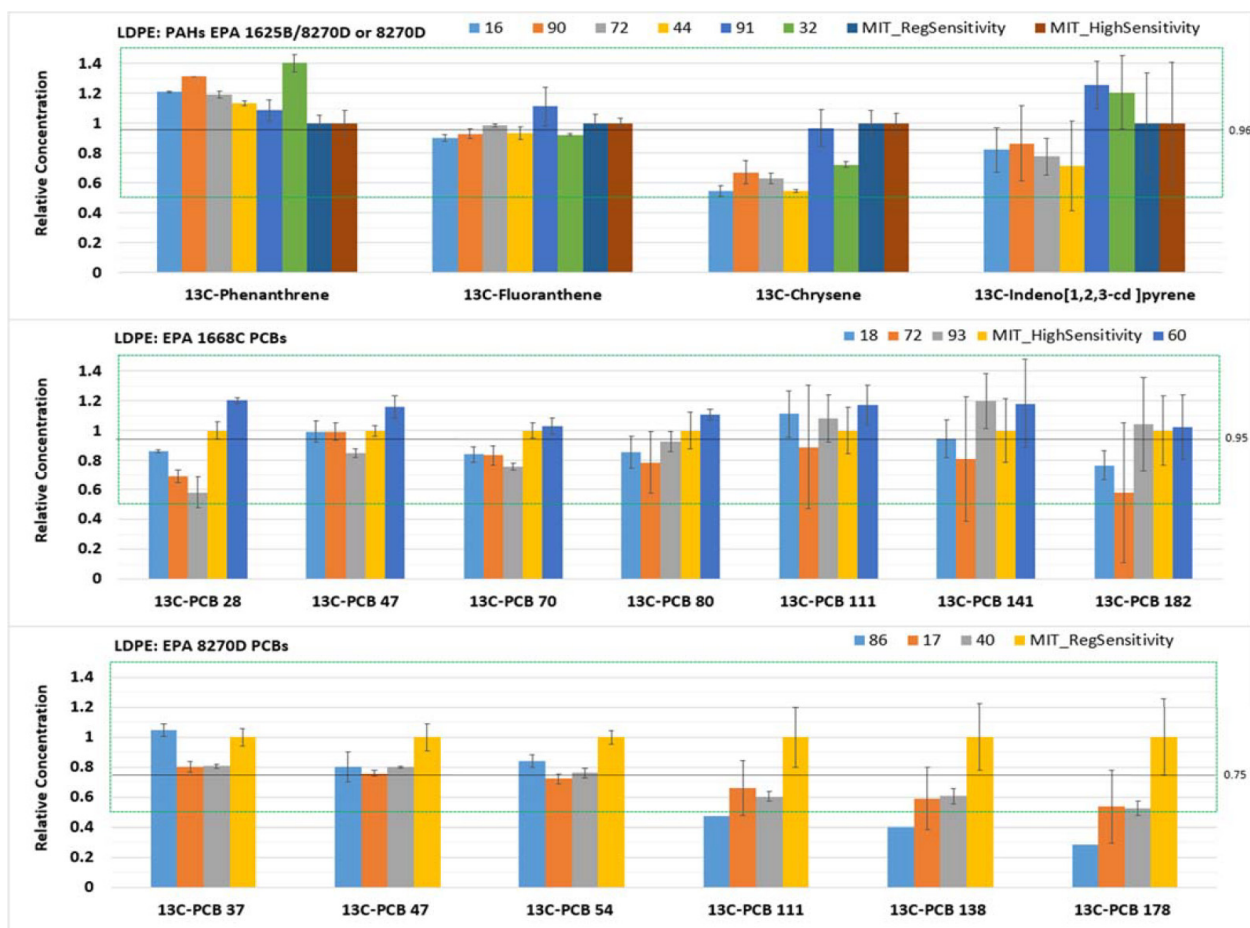


Figure 6-2. PRC Pre-loaded LDPE polymeric sampler results in relative units ($C_{\text{reported}}/C_{\text{known}}$). PAHs analyzed by regular- and high-sensitivity methods are shown at the top of the figure; PCB congeners analyzed by high-sensitivity and regular-sensitivity methods are respectively shown in the middle and bottom panels. The $\pm 50\%$ of known concentration performance criteria is highlighted in green. Bars and error bars represent the mean and standard deviation of $n=6$ replicates. Average results for each data set are shown as black lines with average values to right.

Task 1.3. Discussion. Most labs met the $\pm 50\%$ acceptance criteria for PRC pre-loaded samplers analyzed. A single lab reported an exceedance (-58%) for a single PAH PRC (13C6-indeno(1,2,3-cd)pyrene) in PDMS. This exceedance reported by Lab 38 was investigated by the lab chemist and by Mr. Lin (independent data validator). No explanation was found; this anomalous result was deemed insufficient grounds for data or lab exclusion. Lab 86 also reported exceedances for congeners PCB-111, PCB-138, and PCB-178 in LDPE samplers (respectively -53%, -60%, and -71%). These LDPE PCB exceedances appeared not to be actual exceedances by Lab 86, but rather intrinsic variations in the pre-loaded LDPE sampler concentrations. Upon review at MIT where the Task 1.3 samplers were prepared, it was discovered that pre-loaded samplers provided to Lab 86 were a different LDPE material, which contained different steady-state PRC masses. More

specifically two batches of LDPE (one 0.7 mil, the other 1 mil thickness) had been mistakenly stored in the PRC solution together. A key lesson learned: labs preparing PRC-loaded LDPE strips should ensure that the area/weight ratios of the LDPE strips are consistent prior to adding the LDPE strips to the PRC loading solution. Task 1.3 acceptance criteria exceedances were occasional, not systemic, and thus supported a “Go” recommendation to move to Task 2.

6.1.4 Task 1 Discussion and Lessons Learned.

Task 1 results collectively supported a “Go” decision to proceed to Task 2. Results of Task 1.1 showed 89% of lab submittals passed accuracy criteria. Of the 11% that did not, almost all of these were accounted for through corrective actions and lessons learned listed below. In the end only 2 submittals out of 46 had unexplained apparent experimental issues, which resulted in minor acceptance criteria exceedances for Task 1.1. Only 2 out of 35 lab submittals for Task 1.3 failed to meet accuracy criteria, and only 1 was due to unexplained experimental issues. As summarized herein and detailed in Tasks 1.1 and 1.3 data comparability memos (Appendix D), criteria exceedances observed during Task 1 were insufficient to cause data exclusion and were considered suitable for intended use.

Key Lessons Learned:

- Ensure internal standards are free of contaminants that could interfere (co-elute, share key m/z values) with quantifying target analytes.
- Solvent variations can impact method performance; if varied solvent use is being considered as part of new extraction/analysis protocol, be sure to investigate potential interferences ahead of required analysis.
- PAH PRC indeno[1,2,3-cd]pyrene-13C6 does not provide sufficient m/z distinction for low resolution GC/MS analysis when siloxane column bleed may be present late in a GC temperature program; corrective measures associated with use of this PRC (e.g. use indeno[1,2,3-cd]pyrene-13C22) were considered during Task 2/prior to Task 3.
- Labs preparing PRC-loaded LDPE strips should ensure that the area/weight ratios of the LDPE strips are consistent prior to cleaning and adding the strips to the PRC loading solution.
- Surrogate compounds mimic behaviors of target compounds during sample analysis procedures, e.g., sample extraction, extract cleanup, solvent exchange, etc. For analytical methods using injection standards (as opposed to isotope dilution) for analyte quantitation, these standards are added to final extract just prior to instrument analysis so as to assess the fraction of the extract volume analyzed; the injection standard does not reflect potential analyte loss during sample preparation. To quantitate PRC and target analyte concentrations in a sample, the results should be normalized with corresponding surrogate spike recovery. We have taken care during this project to ensure data sets generated by different labs are comparable with respect to surrogate recoveries (i.e., either indistinguishable from 100% recoveries or were recovery corrected).

6.2 TASK 2 RESULTS

The results of Task 2 are discussed in more detail in the Task 2 Go/No-Go Memorandum (Appendix E). Four commercial laboratories and three university research laboratories participated in Task 2. Here we summarize the main results and their implications.

6.2.1 Loading and Analysis of Low-Density Polyethylene (LDPE) Polymetric Samplers

Commercial laboratories participated in this project under the condition of anonymity. Accordingly, participating laboratories that submitted were assigned random numbers for presenting results (Table 6-5).

Table 6-5. LDPE Sampler Tests Performed by Laboratories

PRCs	Method Sensitivity	Target Concentration Range ^(A)	LDPE Laboratory ^(B)	
		LDPE	Commercial	University
PAHs	Low	500, 1000 ^(C)	34, 52, 58, 84	15, 50
PCBs	Low	500, 1000 ^(D)	11, 91	5, 52
	High	500, 1000 ^(E)	86, 93	69

Notes: LDPE results were reported in ng/g-LDPE. (A) Target concentrations were determined by back-calculating from the volumes and concentrations of loading solutions; concentration for each PRC varies and may differ between laboratories, and thus presented as approximate concentration ranges herein. (B) Each laboratory was randomly assigned a number in each type of analysis. (C) For laboratory 84 only. (D) For laboratory 11. (E) For laboratory 86.

PAH PRCs by Low-Sensitivity HRGC/LRMS. Four commercial laboratories (34, 52, 58, and 84) and two university laboratories (15 and 50) loaded and analyzed the PAH PRCs in LDPE samplers with low-sensitivity GC/MS. As illustrated in Figure 6-3, results reported by commercial and university laboratories met the accuracy criteria of -50% to 150% of targeted concentrations, with the following exceptions:

- Commercial laboratory 34: 13C6-phenanthrene (<50% of target concentration),
- Commercial laboratory 52: 13C6-indeno[1,2,3cd]pyrene (>150% of target concentration),
- Commercial laboratory 84: 13C6-phenanthrene 13C6-fluoranthene, 13C6-chrysene (<50% of target concentration) and 13C6-indeno[1,2,3cd]pyrene (>150% of target concentration)
- University laboratory 15: 13C6-phenanthrene 13C6-fluoranthene, and 13C6-indeno[1,2,3cd]pyrene (>150% of target concentration).

All laboratory replicate analysis %RSD values were less than the criterion of ≤20%.

PCB PRCs by High-Sensitivity HRGC/HRMS. Two commercial laboratories (86 and 93) and one university laboratory (69) loaded PCB PRCs in LDPE samplers and analyzed them with high-sensitivity GC/MS methods. As illustrated in Figure 6-3, some PCB PRC recoveries exceeded the upper limit of the accuracy criteria of -50 to 150% target concentrations, as follows:

- Commercial laboratory 86: 13C-PCB 80 and 13C-PCB 111 (>150% of the target

concentration),

- Commercial laboratory 93: 13C-PCB 70, 13C-PCB 141, and 13C-PCB 182 (<50% of the target concentration)
- University laboratory 69: All PCB PRCs (>150% of the target concentration)

All laboratory replicate analysis %RSD values were well less than the criterion of $\leq 20\%$. The overall low %RSD values demonstrated an excellent precision within each of the participating laboratories.

PCB PRCs by Low-Sensitivity HRGC/LRMS. Two commercial laboratories (11 and 91) and two university laboratories (5 and 52) loaded PCB PRCs in LDPE samplers and analyzed them with low-sensitivity GC/MS methods. As illustrated in Figure 6-3, all results reported by commercial and university laboratories met the accuracy criteria of 50-150% target concentrations, except for the following:

- Commercial laboratory 11: 13C-PCB 47 and 13C-PCB 111 (>150% of the target concentration),
- Commercial laboratory 91: 13C-PCB 37, 13C-PCB 47, 13C-PCB 111, 13C-PCB 138, and 13C-PCB 178 All PCB PRCs except 13C-PCB 54 (>150% of the target concentration),
- University laboratory 5: 13C-PCB 37, 13C-PCB 47, 13C-PCB 54, and 13C-PCB 111 All PCB PRCs except 13C-PCB 138 and 13C-PCB 178 (>150% of the target concentration), and
- University laboratory 52: 13C-PCB 37, 13C-PCB 47, 13C-PCB 111, 13C-PCB 138, and 13C-PCB 178 All PCB PRCs except 13C-PCB 54 (>150% of the target concentration).

All laboratory replicate analysis %RSD values were well less than the criterion of $\leq 20\%$, with the exception of university laboratory 5, where the %RSD for 13C-PCB 111 was 42%. The overall low %RSD values demonstrated an excellent acceptable precision within each of the participating laboratories.

In practice, loading of PRCs into LDPE does not have to match a particular concentration goal accurately. Rather, the final PRC concentration achieved must be accurately measured ($C_{\text{PRC},t=0}$ results) before use of that LDPE to characterize sediment porewater. Loaded PRC concentrations should only be a concern if they prove to be far from expected compared to anticipated concentrations corresponding contaminants in the environment. In such cases, sample extracts would need to be run at two dilutions to allow both high concentrations (e.g. contaminant levels) and low concentrations (e.g. PRCs) to be assessed in the same passive sampler. The same applies to PDMS samplers (discussed below).

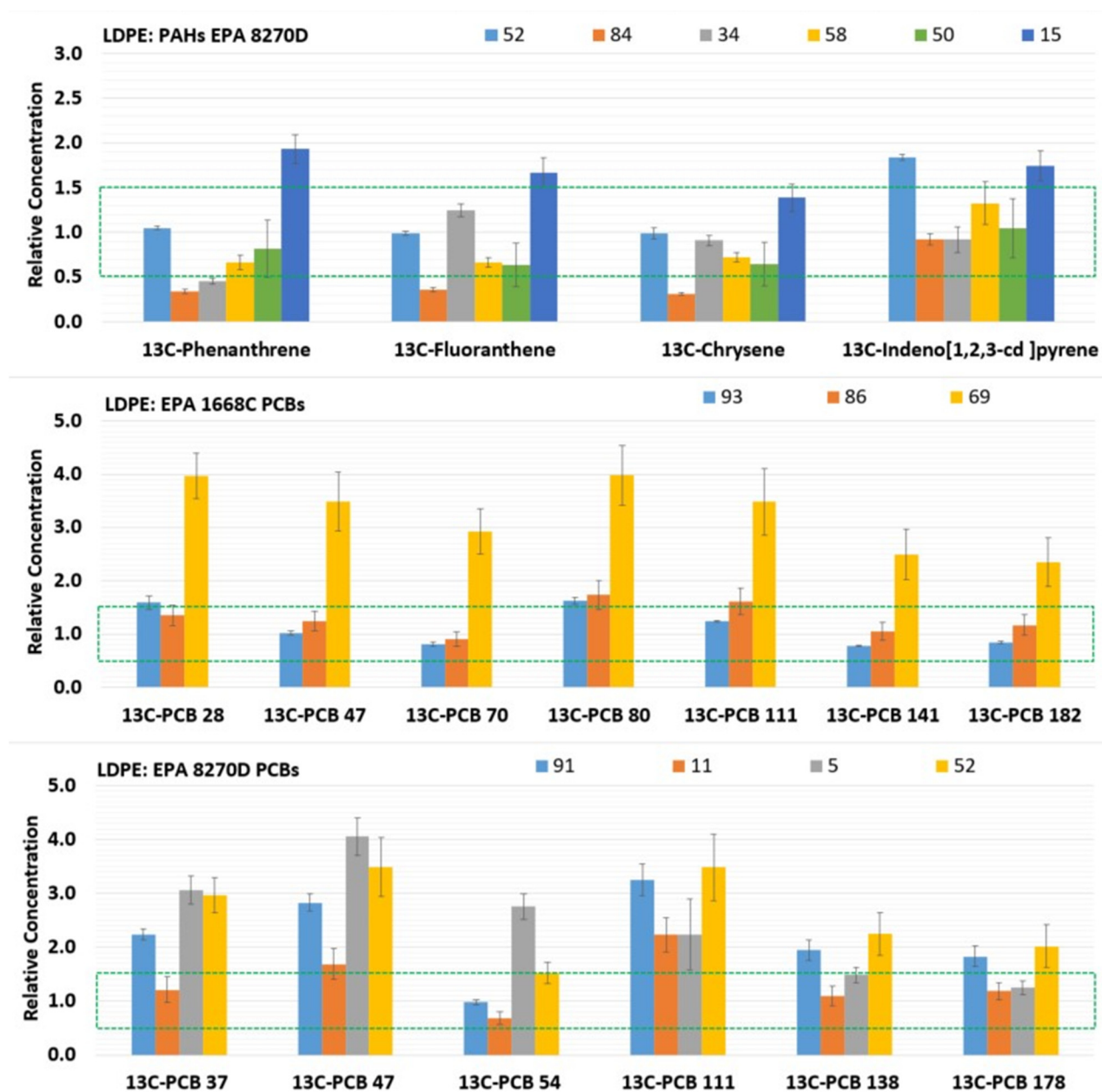


Figure 6-3. LDPE PRC loading and analysis results in relative units ($C_{\text{reported}}/C_{\text{known}}$). PAHs analyzed by the low sensitivity method is shown at the top, PCB congeners analyzed by high-sensitivity and low-sensitivity methods are respectively shown at the middle and bottom of the figure. Bars and error bars represent the mean and standard deviation of $n=6$ replicates. The acceptable range for PRC results ($\pm 50\%$) is highlighted in green.

6.2.2 Loading and Analysis of PRCs in Polydimethylsiloxane (PDMS) Samplers

Commercial laboratories participated in this project under the condition of anonymity. Accordingly, participating laboratories that submitted were assigned random numbers for presenting results (Table 6-6).

Table 6-6. PDMS Samper Tests Performed by Laboratories

PRCs	Method Sensitivity	Target Concentration Range ^(A)	PDMS Laboratory ^(B)	
		PDMS	Commercial	University
PAHs	Low	1184, 5922 ^(C)	19, 48, 83, 98	9, 64
PCBs	Low	1184, 5922 ^(C)	14, 17	4, 55
	High	1184, 1000 ^(D)	37, 95	2

Notes: SPME sampler results were reported in ng/mL-SPME. (A) Target concentrations were determined by back-calculating from the volumes and concentrations of loading solutions; concentration for each PRC varies and may differ between laboratories, and thus presented as approximate concentration ranges herein. (B) Each laboratory was randomly assigned a number in each type of analysis. (C) For laboratories 17 and 83 only. (D) For laboratory 84 only.

PAH PRCs by Low-Sensitivity HRGC/LRMS. Four commercial laboratories (19, 48, 83, and 98) and two university laboratories (9 and 64) analyzed the PAH PRCs loaded in PDMS with low-sensitivity GC/MS. As illustrated in Figure 6-4, all results reported by commercial and university laboratories met the accuracy criteria of -50 to 150% target concentrations with the following exceptions:

- Commercial laboratory 83: 13C6-phenanthrene and 13C6-indeno[1,2,3-cd]pyrene,
- Commercial laboratory 98: 13C6-phenanthrene, and
- University laboratory 9: 13C6-fluoranthene.

All laboratory replicate analysis %RSD values (n=6) were well less than the criterion of $\leq 20\%$, which demonstrated acceptable precision within each laboratory.

PCB PRCs by High-Sensitivity HRGC/HRMS. Two commercial laboratories (37 and 95) and one university laboratory (2) analyzed the PCB PRCs loaded in PDMS with high-sensitivity GC/MS. As shown in Figure 6-4, all results reported by commercial and university laboratories met the accuracy criteria of -50 to 150% target concentrations, indicating a satisfactory accuracy. All laboratory replicate analysis %RSD values (n=6) were well less than the criterion of $\leq 20\%$, demonstrating an excellent acceptable precision within each of the participating laboratories.

PCB PRCs by Low-Sensitivity HRGC/LRMS. Two commercial laboratories (14 and 17) and two university laboratories (4 and 55) analyzed the PCB PRCs loaded in PDMS with low-sensitivity GC/MS methods. As illustrated in Figure 6-4, all results reported by commercial and university laboratories met the accuracy criteria of -50 to 150% target concentrations with the following exceptions:

- Commercial laboratory 19: 13C-PCB 37
- Commercial laboratory 17: 13C-PBs 54, 111, 138, and 178, and
- University laboratory 4: 13C-PCB 54.

All laboratory replicate analysis %RSD values (n=6) were well less than the criterion of $\leq 20\%$, with the only minor exception of university laboratory 4, where the %RSD for 13C-PCB 47 was

21%. The overall low %RSD values demonstrated an excellent acceptable precision within each of the participating laboratories.

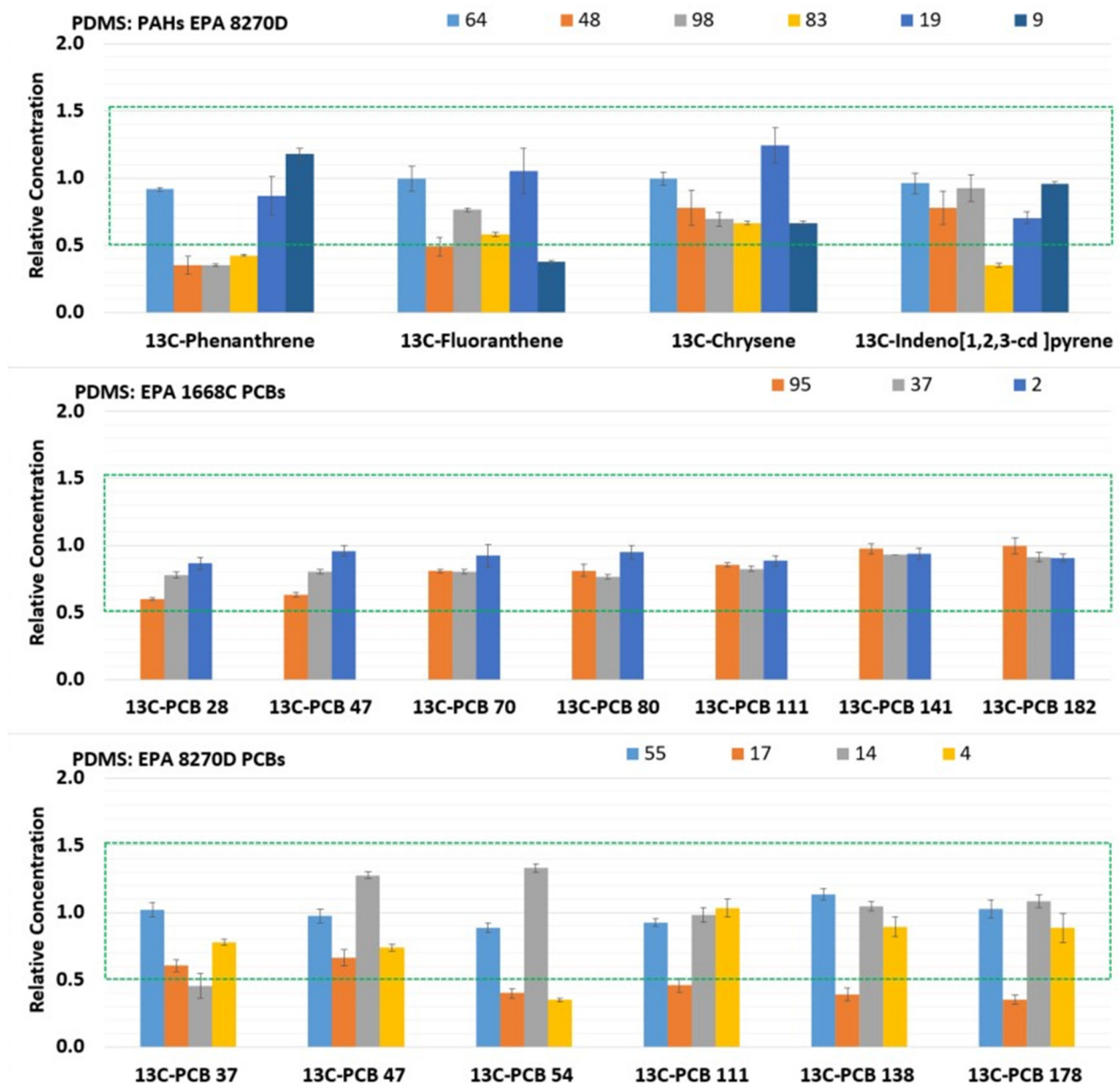


Figure 6-4. PDMS PRC loading and analysis results in relative units ($C_{\text{reported}}/C_{\text{known}}$). PAHs analyzed by the low sensitivity method is shown at the top, PCB congeners analyzed by high-sensitivity and low-sensitivity methods are respectively shown at the middle and bottom of the figure. Bars and error bars represent the mean and standard deviation of $n=6$ replicates. The acceptable range for PRC results ($\pm 50\%$) is highlighted in green.

6.2.3 Task 2 Discussion

ALL laboratories achieved measurable loading and acceptable precision ($\leq 20\%$ RSD in replicated PRC-loaded samplers) during Task 2. Achieving acceptable precision in the PRC concentrations loaded into the polymeric samplers prior to deployment (i.e. $C_{\text{PRC}, t=0}$) is critical because this value is used to correct measured concentrations of PAHs and PCBs in sediment porewater for their progress towards equilibrium during field deployments. As long as the $C_{\text{PRC}, t=0}$ result precision is quantified and is acceptable, and the loaded PRC concentration is readily detectable (high enough to allow as much as 80% loss during deployment and still be measureable, i.e. $>10\times$ MDL post-deployment) by the analytical method being used, the PRCs may be used to correct for equilibrium conditions.

Variations in solvent type and volumetric proportions used to prepare the PRC loading solution led to variations in loaded PRC concentration achieved by different laboratories. All laboratories prepared their PRC loading solutions (referred to below and in the SOPs as the “working standard”) in 80:20 methanol:water for LDPE and in 20:80 methanol:water for PDMS, consistent with the polymeric sampler SOPs. However, compositions of the “spiking standard” varied for each lab. The spiking standard contained high concentrations of PRCs in a solvent (e.g. nonane if solvent exchange was not performed), which was then “spiked” into the working standard solvent (e.g. methanol) to spike the final PRC concentrations in the PRC loading solutions (mixes of methanol and water). Varied PRC concentrations in the spiking standard solution caused variations in the spike standard volume added to the working standard between labs; varied volumes added coupled with varied solvent types used to prepare the spiking standard resulted in differences in final loaded PRC concentrations achieved by the different labs. Spiking standards with high nonane content (i.e., solvent used by the vendor to store and ship the PRCs) were particularly problematic. It is important to ensure spiking standard and working standard solvent miscibility and also best to minimize the ratio of nonane to solvent in the working standard. We recommended acetone as the spiking standard solvent; problems were encountered when alternative solvents were used (e.g. hexane with PDMS). As a result, the LDPE and PDMS SOPs were updated (Appendix B) to feature more stringent requirements regarding spiking standard solvent types and proportions. Acceptable method performance across laboratories were obtained so long as laboratories follow updated SOPs to ensure: (1) use of miscible carrier solvents to form a uniform PRC loading solution, (2) use of an appropriate volume of loading solution per mass of polymeric samplers being prepared, (3) the samplers have sufficient time in the loading solution to achieve equilibrium, and (4) analysis of replicate PRC-loaded samplers after the samplers have equilibrated to ensure acceptable precision on the PRC-loaded sampler $C_{t=0}$ measurement *before* using the PRC-loaded samplers to characterize sediment porewater concentrations.

Acceptable precision in the $C_{\text{PRC}, t=0}$ results reported by all laboratories during Task 2, coupled with refined SOPs and corrective actions described below, supported a GO! decision to proceed with Task 3. All laboratories were provided copies of the updated SOPs, which featured more

stringent PRC loading solution requirements, and they agreed to follow the revised requirements during PRC loading of blank samplers during Task 3. Further, participating laboratories were required to provide their Task 3 $C_{\text{PRC}, t=0}$ results for ER201735 team review and approval so that acceptable accuracy and precision could be verified prior to proceeding with the Task 3 interlab sediment measurements.

6.3 TASK 3 RESULTS

Task 3 consisted of four components: preparation of the homogenized large-quantity sediment sample that was apportioned to the laboratories, laboratory preparation of PRC-loaded polymeric samplers, laboratory exposure of the polymeric samplers to the sediment, and finally polymeric sampler recovery, extraction and analysis for PAHs and PCBs. Supporting information for Task 3 in Appendix G includes the following: PRC loading conditions by lab; polymer extract concentrations by lab; data validation findings by lab; box and whisker plots for Task 3 PRC concentrations as well as final f_{ss} -corrected polymer-based sediment porewater concentrations; and finally tabulated final f_{ss} -corrected polymer-based sediment porewater concentration for all Task 3 replicates.

6.3.1 Homogenization of the Large-Quantity Sediment Sample

Sediment from Indiana Harbor available at ERDC in cold storage (4 °C) was used. The available sediment was composited in two drums by adding 50% volume of each bucket into each drum (Figure 6-5). The sediment in each drum was homogenized with an overhead 1/3 horsepower Lightnin Impellor mixer (11 inch prop). The homogenized material was then distributed into 15, 5-gallon buckets, with a total of 2.25 gallons from each drum placed in each bucket. The sediment was then homogenized in each bucket.

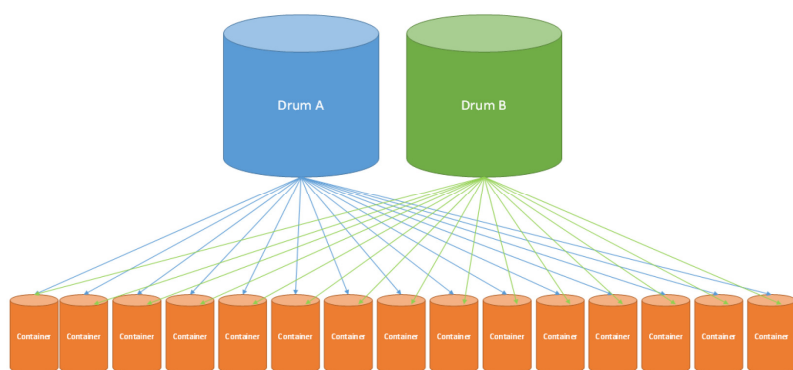


Figure 6-5. Sediment Compositing and Homogenization. Indiana Harbor sediment was homogenized in two drums, then split into 15 buckets and homogenized again. Sediment from each bucket was composited a final time before filling sample jars for the laboratories.



Sediment samples were then collected from the 15 buckets and submitted for total organic carbon (TOC) analysis as an indicator of homogeneity among the buckets. Buckets #1, #2, and #4 were excluded from further consideration because TOC concentrations in those buckets exhibited greater than 20% relative difference from the global mean TOC concentration value (Table 6-7).

Table 6-7. Total Organic Carbon (TOC) in Indiana Harbor Sediment Samples

Sample	TOC, mg/kg	% moisture	% solids	Relative Percent Difference (RPD) from mean value, %
IHC Bucket #1	120,000	69	31	71%
IHC Bucket #2	85,000	64	36	21%
IHC Bucket #3	63,000	64	36	10%
IHC Bucket #4	52,000	64	36	26%
IHC Bucket #5	80,000	67	33	14%
IHC Bucket #6	65,000	63	37	7%
IHC Bucket #7	62,000	64	36	12%
IHC Bucket #8	72,000	64	36	3%
IHC Bucket #9	64,000	66	34	9%
IHC Bucket #10	58,000	64	36	17%
IHC Bucket #11	57,000	64	36	19%
IHC Bucket #12	58,000	66	34	17%
IHC Bucket #13	56,000	64	37	20%
IHC Bucket #14	79,000	63	37	13%
IHC Bucket #15	80,000	63	37	14%
mean	70,067	65	35	
standard dev.	17,240	2	2	

PAHs and PCB congeners were measured in sediment samples (Buckets #3 and #5-#15) and the results are shown in Table 6-8. Target analytes included the 16 U.S. EPA Priority pollutant PAHs and the NOAA 18 congeners suite plus congeners 126 and 169 (congeners 195, 206 were not measured for this task). The average total concentration of PAHs (1,000 mg/kg dw) and PCBs (3.3 mg/kg dw) met the minimum concentration requirements threshold, meaning

polydimethylsiloxane (PDMS) and low-density polyethylene (LDPE) polymer samplers and standard analytical methods were capable of reliably quantifying this range of PAHs and PCBs concentrations expected in the polymeric samplers. Furthermore, the level of homogeneity achieved in the sediment between buckets was deemed acceptable, with $\leq 11\%$ RSD values for all PCB congeners and $\leq 15\%$ RSD values for all PAHs except acenaphthene and fluorene.

Table 6-8. Average PAHs and PCB Congeners Concentrations Across Selected Subsamples (Buckets #3 and #5 - #15)

PAHs	Average, ug/kg dry weight	Standard Deviation	Relative Standard Deviation	PCBs	Average, ug/kg dry weight	Standard Deviation	Relative Standard Deviation
Naphthalene	415,750	64,385	15%	PCB 8	327	19	6%
Phenanthrene	29,500	4,241	14%	PCB 101	123	8	7%
Anthracene	55,075	3,164	6%	PCB 105	50	3	7%
Fluoranthene	20,483	3,090	15%	PCB 118	73	6	8%
Pyrene	17,575	2,615	15%	PCB 126	ND	--	--
Benzo (a) anthracene	44,267	2,963	7%	PCB 128	ND	--	--
Chrysene	57,058	4,023	7%	PCB 18	689	63	9%
Benzo (b) fluoranthene	32,833	2,186	7%	PCB 138	52	4	8%
Benzo (k) fluoranthene	48,017	6,006	13%	PCB 153	54	5	9%
Benzo (a) pyrene	48,275	3,195	7%	PCB 28	951	69	7%
Indeno (1,2,3-cd) pyrene	20,533	2,110	10%	PCB 169	ND	--	--
Dibenz (a,h) anthracene	6,465	902	14%	PCB 170	19	2	11%
Benzo (g,h,i) perylene	22,625	2,492	11%	PCB 180	44	4	8%
Acenaphthylene	3,724	369	10%	PCB 187	22	2	9%
Acenaphthene	110,508	25,743	23%	PCB 44	309	21	7%
Fluorene	67,550	21,170	31%	PCB 52	275	21	8%
				PCB 66	270	21	8%
Sum, mg/kg dw	1,000			PCB 77	47	4	9%
				Sum, mg/kg dw	3.3		

The sediment from buckets #3 and #5 - #15 was again dispensed into a large container, remixed, then apportioned into jars for the participating laboratories. The sediment was sent to participating laboratories for the future Task 3 sediment exposure, and the laboratories stored the sediment at 2-6 °C until use.

6.3.2 Task 3 PRC Loading Results

The first step in conducting the Task 3 sediment porewater characterization involved all participating laboratories following the SOPs (Appendix B) to load PRCs into LDPE strips and PDMS fiber segments. The loading procedure was designed to achieve a uniform concentration of each PRC in the polymers (CPRCt=0), which were then compared to the post-exposure PRC concentration to determine extent of equilibration. After loading, the PRC Ct=0 concentrations were evaluated for each laboratory. Variations in the absolute PRC concentrations were noted across the labs as a result of scale up of the methods during Tasks 1 and 2; these are summarized in Figures 6-6 and 6-7 below. Although Lab 34 PCBs were biased low for PDMS, all other PRCs

accuracy and precision performance criteria were acceptable (Figure 6-6).

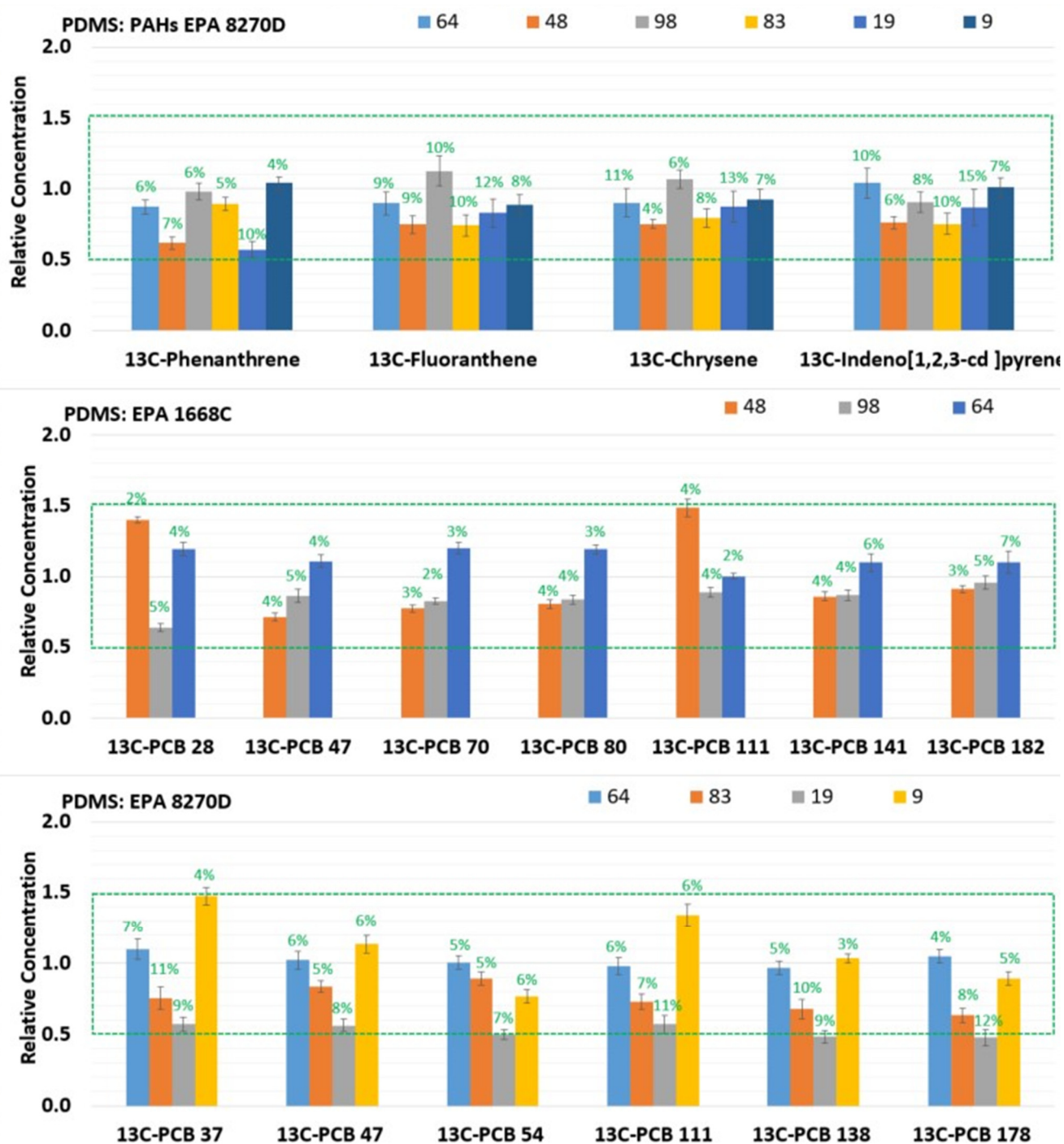


Figure 6-6. PDMS Task 3 PRC loading analysis results (C_{avg}/C_{target}). PAHs analyzed by the low sensitivity method are shown at the top, PCB congeners analyzed by high-sensitivity and low-sensitivity methods, respectively, are shown at the middle and bottom of the figure. Bars and error bars represent the mean and standard deviation of $n=6$ replicates.

In contrast to favorable PRC loading results obtained initially for PDMS, multiple labs reported accuracy and precision performance criteria exceedances for PCB and PAH PRC loading in LDPE (Figure 6-7). Accordingly, Task 3 was paused to accommodate LDPE PRC loading trouble shooting. PRC loading solution composition and exposure conditions are summarized in Appendix G.

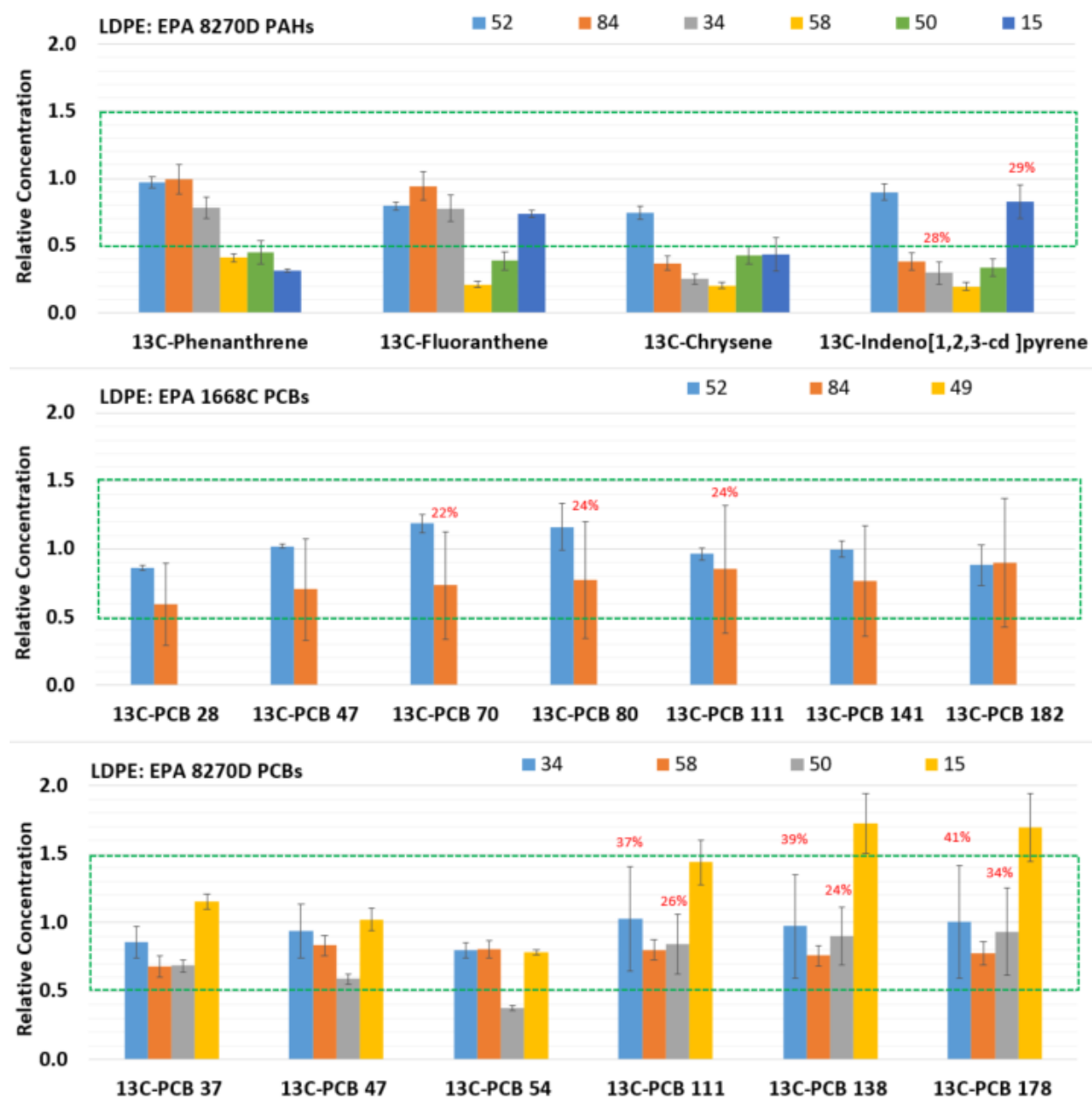
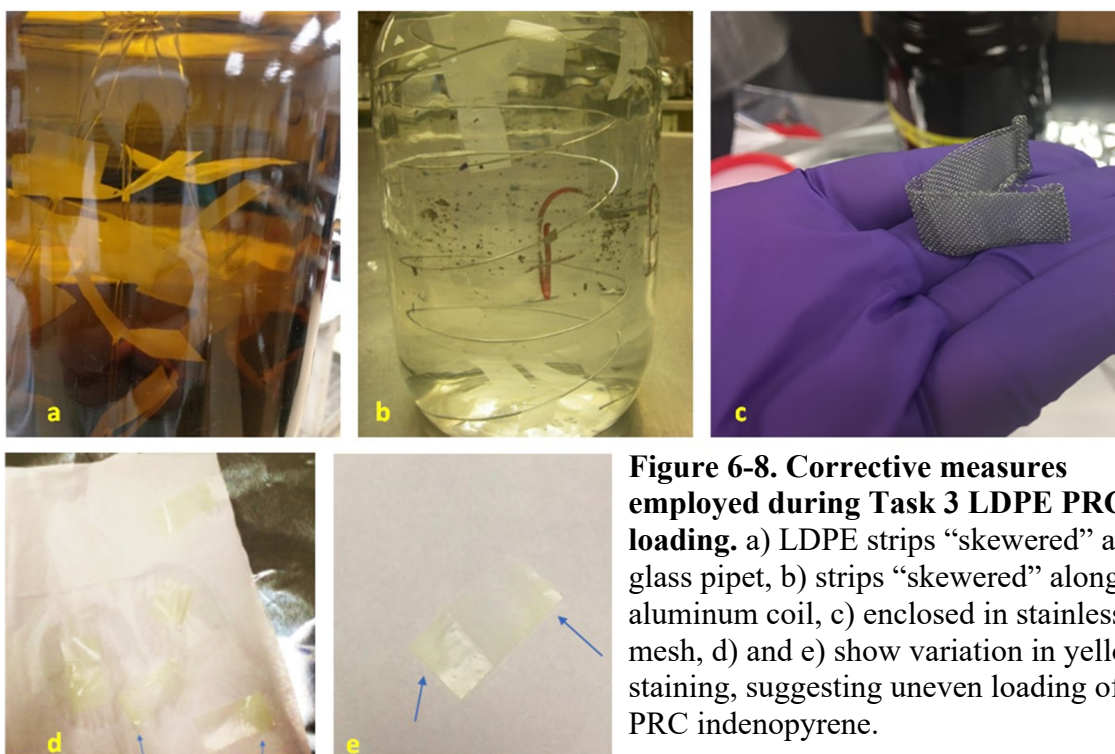


Figure 6-7. Initial LDPE Task 3 PRC loading analysis results ($C_{avg,n=6}/C_{target}$). PAHs analyzed by the low sensitivity method is shown at the top, PCB congeners analyzed by high-sensitivity and low-sensitivity methods are respectively shown at the middle and bottom of the figure. Bars and error bars represent the mean and standard deviation of $n=6$ replicates. Several percent coefficient

of variation (red text) values were greater than 20%, which was established as the precision target for precursor tasks.

PRC loading solutions featured in Task 3 (Appendix B, G) reflected learnings from Task 2, i.e. the SOPs were updated a final time following Task 2 to tighten requirements for solvent ratios in effort to prevent phase separation from impacting PRC loading results in Task 3. Accordingly, we anticipated phase separation during loading was not the primary cause of the variability observed in the LDPE initial PRC loading results (Figure 6-7).

Likely causes of variability in the LDPE results were identified as polyethylene sheets sticking to each other and/or floating to the top of the PRC loading solution, potentially exposing some samplers to the air-liquid interface in the jar. Corrective steps were taken to ensure uniform loading of LDPE strips, followed by continued soaking in the same PRC loading solution. Corrective measures included suspending LDPE strips by “stabbing” them along glass pipet tubes (Figure 6-8a) or along aluminum coils (Figure 6-8b); inserting the LDPE strips into stainless steel mesh (Figure 6-8c). Even following these corrective measures, some labs observed visual and varied staining of the LDPE in the PRC solutions, with some strips appearing “tie dyed” with bright yellow stains (Figure 6-8d, 6-8e), suggesting non-uniform loading of the yellow-colored PRC indenopyrene.



The LDPE strips were allowed to “soak” in the PRC loading solutions for at least an additional 30 days following trouble shooting efforts identified in Figure 6-8. Lab-specific PRC loading conditions are provided in Appendix G – both for PDMS, as well as for LDPE before and after trouble shooting (referred to as PRC loading #1, and PRC loading #2 in Appendix G). After at least 30 days, a new set of replicate LDPE segments were retrieved from the loading solution for computing new PRC,Ct=0 measurements. As illustrated in Figure 6-9, even following troubleshooting efforts to improve exposure uniformity to the PRC loading solution, precision of the PRC,Ct=0 measurement, as indicated by the percent coefficient of variation of the measurement, was still well above the desired $\leq 20\%$ value. Since the PRC information is only used to evaluate the extent of equilibrium during the polymeric sampling, differences in handling that lead to PRC concentration variations between labs (that is, interlab variability) is not important except to identify potential handling differences. What is critical is that each laboratory has a good estimate of PRC loading for their laboratory (that is, the intralab variability) in the PRCs. Accordingly, with PRC,Ct=0 measurement precision and accuracy for both PDMS and LDPE established, the project proceeded on to the Task 3 sediment exposures.

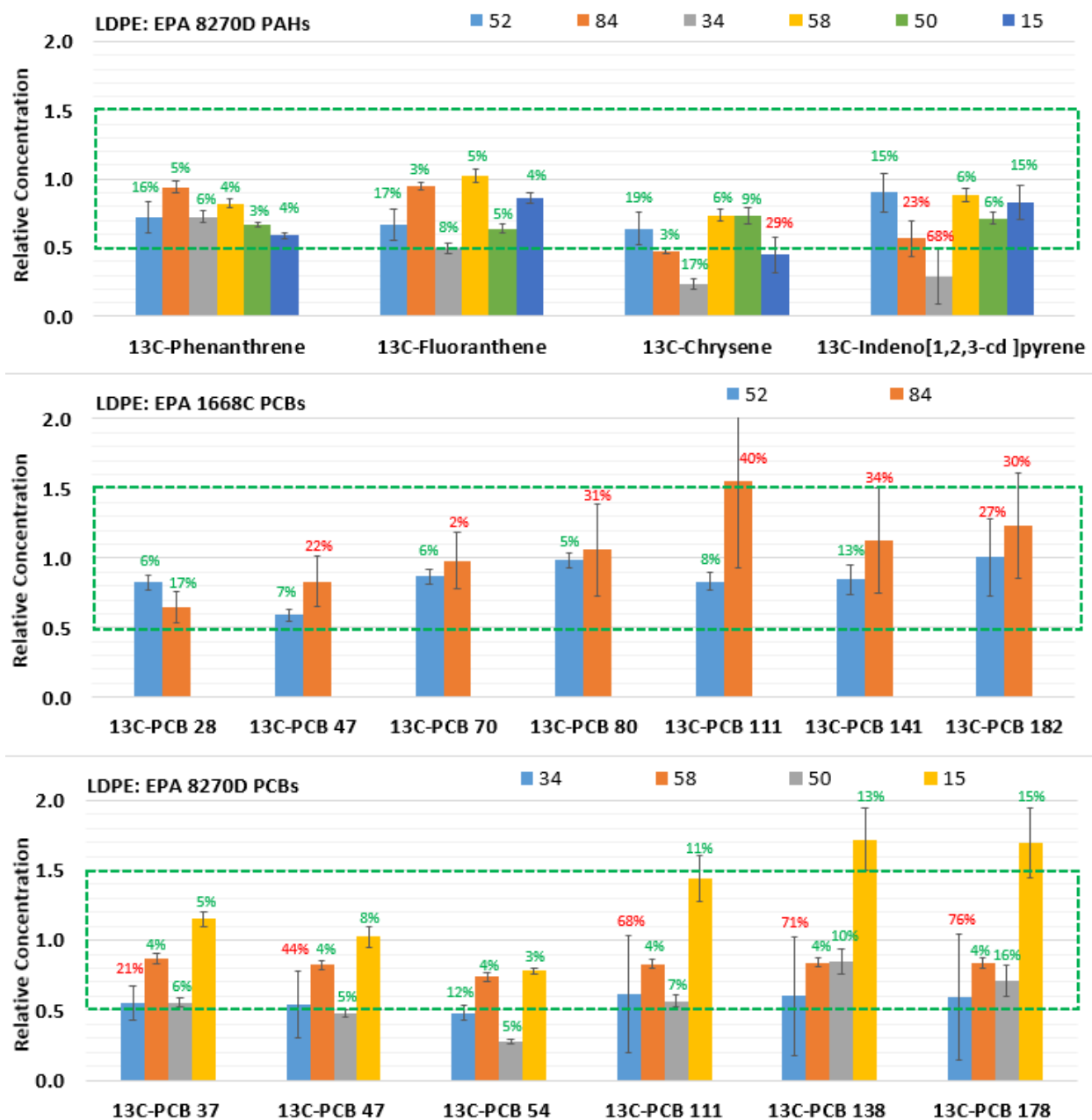


Figure 6-9. Final LDPE Task 3 PRC loading analysis results (C_{avg}/C_{target}). PAHs analyzed by the low sensitivity method is shown at the top, PCB congeners analyzed by high-sensitivity and low-sensitivity methods are respectively shown at the middle and bottom of the figure. Bars and error bars represent the mean and standard deviation of $n=6$ replicates. Several percent coefficient of variation (red text) values remained at greater than 20% following trouble shooting.

6.3.3 Task 3 Sediment Porewater Characterization Results.

Sediment porewater concentrations were measured via PDMS and LDPE polymer following procedures described in the finalized SOPs (Appendix B) and per exposure conditions detailed in Appendix G. Sediment measurements were performed using both polymers over a period of ~ 30 days under static conditions (where the polymers were not anticipated to reach equilibrium with sediment porewater PCBs and PAHs) and under actively mixed conditions (where equilibrium was a possibility).

Porewater Results for PDMS “Active” Sampling.

Sediment porewater concentrations of PCBs and PAHs measured using PDMS polymer were fairly consistent across labs (Figure 6-10). Precision of the porewater concentration results measured using PDMS polymer, as indicated by the percent coefficient of variation (COV) on replicate measurements, ranged from 3 – 71% for PCBs and 1 – 85% for PAHs across all labs (Tables 6-9, 6-10). The COV was less than 20% for most labs for all compounds except the volatile naphthalene and the low concentration (sometime below detection) dibenzoanthracene.

Some deviations were noted. Laboratory 38, which analyzed PCBs using both low and high (respectively 38 and 38* in Figure 6-10) reported consistently lower and more variable results when using the high sensitivity method. Although PCB congeners 77, 126, 128, 169, 195, and 206 were initially identified as PCB analytes of interest for this demonstration, the Indiana Harbor sediment featured non-detect concentrations or low concentrations of these congeners (congener 195 and 206 was not measured in the sediment); accordingly, results of these congeners are not presented for comparison here. Interlab results were variable for higher molecular weight congeners (PCB-153 and above), which were present at lower concentrations in the sediment. In practice, larger polymer segments could have been extracted to provide additional sensitivity for these low concentration, higher molecular weight congeners.

A similar level of interlab consistency was observed in the PDMS-based porewater estimated concentrations of PAHs (Figure 6-10). The largest variability between labs was observed for the most volatile PAH naphthalene and dibenzoanthracene, which was present at very low concentrations and not detected by some labs. Differences in sediment processing direct volatile loss from the thin layers of PDMS could account for the naphthalene differences. Similar to higher molecular weight PCBs, variability in results for the higher molecular weight PAHs could have been overcome by exposing a larger mass of polymer than was done for this study.

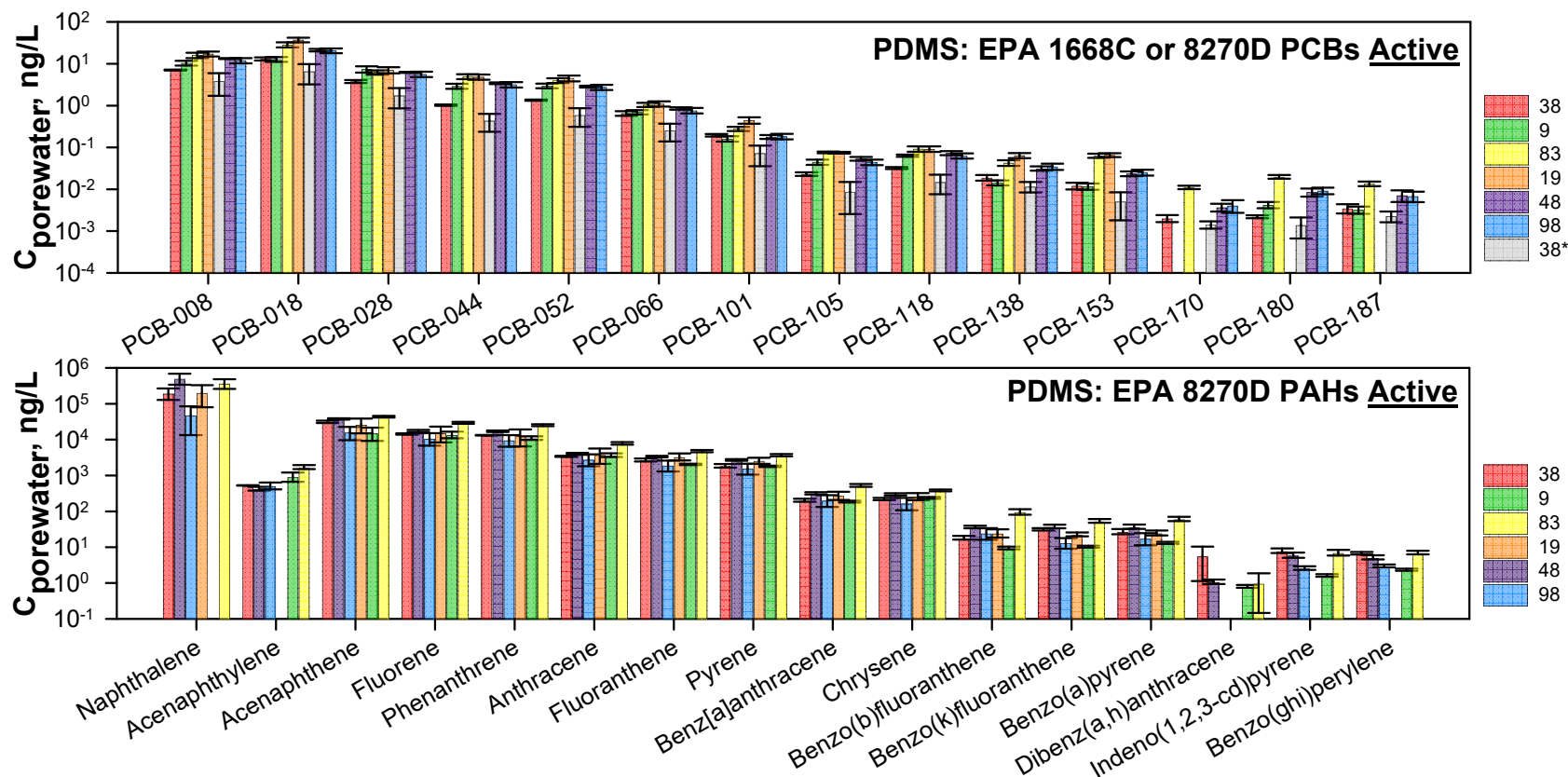


Figure 6-10. Task 3 PDMS active results for PCBs (upper) and PAHs (lower). Bars represent average results for individual labs and compounds; error bars represent one standard deviation for replicate measurements. For all labs n=6 except lab 38 where n=3 and lab 9 where n=5 for PCBs.

Table 6-9. Coefficient of variation (COV) for Task 3 PDMS PCBs Active Results

PDMS: U.S. EPA 1668C or 8270D PCBs Active (Corresponds with data shown in Figure 6-10)							
Lab:	38	9	83	19	38*	48	98
Method^a:	LR	LR	LR	LR	HR	HR	HR
PCB-008	3%	13%	14%	14%	<u>55%</u>	3%	15%
PCB-018	9%	13%	14%	12%	51%	7%	13%
PCB-028	8%	17%	12%	17%	51%	3%	15%
PCB-044	3%	14%	14%	14%	46%	5%	14%
PCB-052	3%	13%	13%	16%	47%	5%	14%
PCB-066	13%	12%	11%	14%	45%	7%	15%
PCB-101	7%	14%	12%	17%	51%	11%	15%
PCB-105	10%	14%	4%	4%	71%	10%	16%
PCB-118	5%	6%	15%	15%	49%	11%	14%
PCB-138	16%	14%	16%	14%	28%	12%	17%
PCB-153	18%	17%	11%	11%	65%	13%	16%
PCB-170	19%	nd	9%	nd	20%	21%	<u>34%</u>
PCB-180	8%	17%	11%	nd	52%	22%	17%
PCB-187	<u>25%</u>	20%	13%	nd	29%	<u>31%</u>	28%
minimum	3%	6%	4%	4%	20%	3%	13%
maximum	25%	20%	16%	17%	71%	31%	34%
where maximum >20%, new maximum with <u>largest</u> COV value removed	16%				55%	22%	28%

*laboratory performed both high and low resolution methods; ^a LR=low resolution and HR=high resolution method used for analysis; nd=analyte reported as non-detect in replicate samples by laboratory

Table 6-10. Coefficient of variation (COV) for Task 3 PDMS PAHs Active Results

PDMS: U.S. EPA 8270D PAHs Active (Corresponds with data shown in Figure 6-10)						
Lab:	38	48	84	19	9	83
Naphthalene	35%	<u>34%</u>	<u>73%</u>	<u>61%</u>	nd	30%
Acenaphthylene	1%	12%	22%	nd	29%	13%
Acenaphthene	8%	5%	40%	44%	<u>40%</u>	5%
Fluorene	4%	7%	38%	47%	21%	6%
Phenanthrene	2%	4%	36%	50%	12%	6%
Anthracene	3%	6%	37%	46%	12%	8%
Fluoranthene	9%	5%	33%	22%	4%	7%
Pyrene	11%	5%	34%	19%	4%	7%
Benz(a)anthracene	9%	7%	36%	26%	6%	9%
Chrysene	8%	7%	37%	23%	6%	6%
Benzo(b)fluoranthene	12%	8%	35%	26%	8%	17%
Benzo(k)fluoranthene	8%	12%	33%	12%	6%	12%
Benzo(a)pyrene	17%	14%	37%	16%	7%	14%
Dibenz(a,h)anthracene	<u>80%</u>	14%	nd	nd	9%	<u>85%</u>
Indeno(1,2,3-cd)pyrene	15%	16%	11%	nd	8%	18%
Benzo(ghi)perylene	8%	14%	9%	nd	7%	11%
minimum	1%	4%	9%	12%	4%	5%
maximum	80%	34%	73%	61%	40%	85%
maximum with <u>largest</u> COV value removed	35%	16%	40%	50%	29%	30%

nd=analyte reported as non-detect in replicate samples by laboratory

Porewater Results for LDPE “Active” Sampling.

Sediment porewater concentrations of PCBs and PAHs measured using LDPE polymer under “active” exposure were fairly consistent across labs (Figure 6-11). Laboratory 58, which analyzed PCBs using both low sensitivity methods was typically biased high compared to other labs.

Interlab consistency was observed in the LDPE-based porewater estimated concentrations of PAHs as well (Figure 6-11). As with PDMS, most variability between labs was observed for the more volatile PAHs naphthalene and acenaphthene, which may be attributed to handling of the sediment sample itself as opposed to a polymeric sampler-specific issue. Variability in results for the higher molecular weight PAHs could have been overcome by exposing a larger mass of polymer than was done for this study.

Precision of the porewater concentration results measured using LDPE under “active” exposure, as indicated by the percent COV on replicate measurements, ranged from 4 – 71% for PCBs and 3 - 133% for PAHs across all labs (Tables 6-11, 6-12). A single analyte commonly skewed the COV range for a given lab. With those values removed, the COV on replicate PDMS porewater estimates ranged from 4 – 33% for PCBs and 3 - 88% for PAHs across all labs.

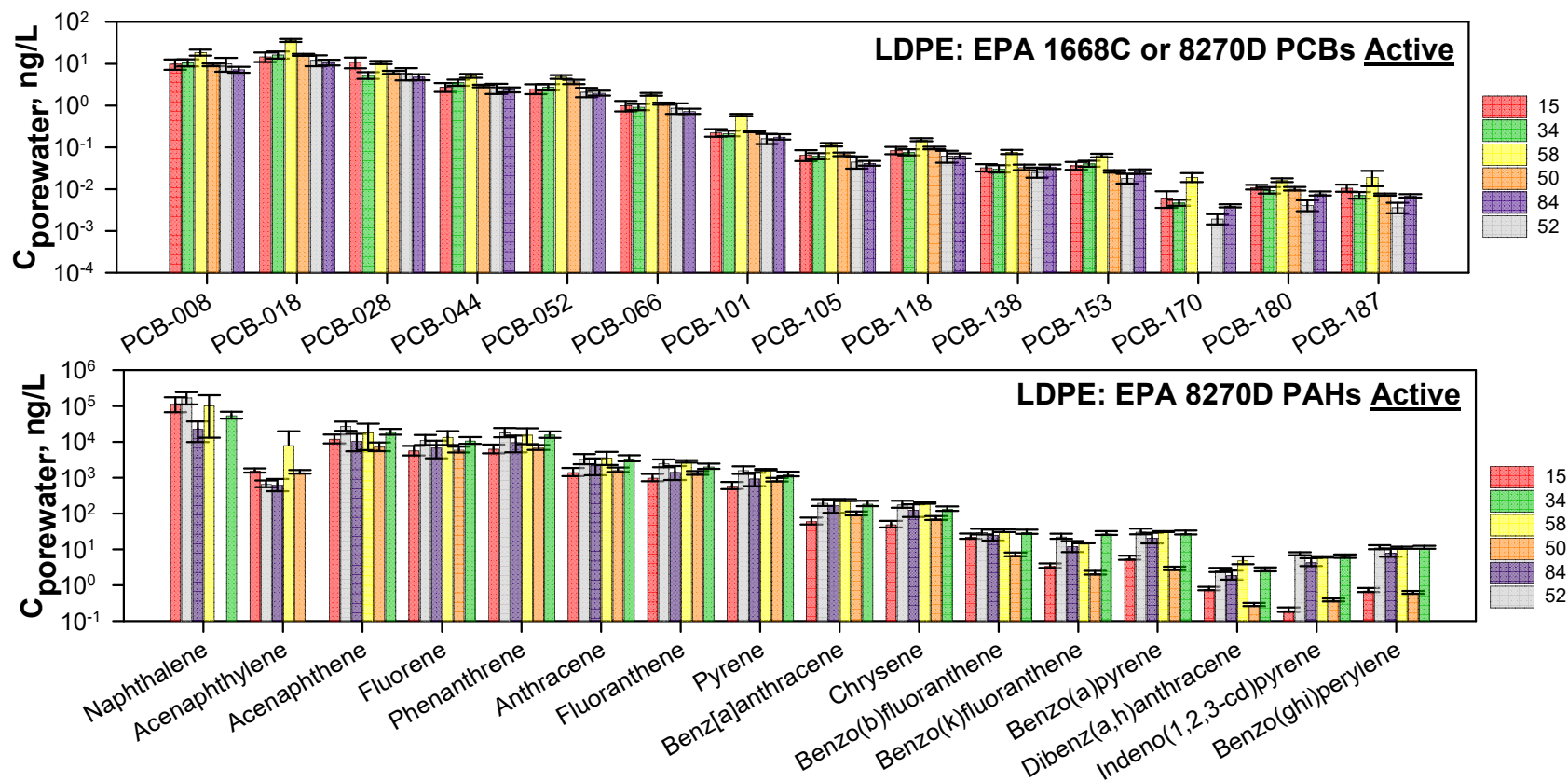


Figure 6-11. Task 3 LDPE active exposure results for PCBs (upper) and PAHs (lower). Bars represent average results for individual labs and compounds; error bars represent one standard deviation. For all labs $n=6$ except lab 15 where $n=7$ for PCBs

Table 6-11. Coefficient of variation for Task 3 LDPE PCBs Active Results

LDPE: U.S. EPA 1668C or 8270D PCBs Active (Corresponds with data shown in Figure 6-11)						
Lab:	15	34	58	50	52	84
Method^a:	LR	LR	LR	LR	HR	HR
PCB-008	27%	19%	16%	7%	<u>36%</u>	16%
PCB-018	26%	19%	8%	5%	29%	15%
PCB-028	28%	18%	9%	8%	<u>33%</u>	16%
PCB-044	24%	17%	11%	7%	27%	13%
PCB-052	26%	17%	10%	12%	25%	14%
PCB-066	28%	17%	8%	6%	29%	14%
PCB-101	20%	15%	6%	4%	27%	14%
PCB-105	29%	17%	9%	10%	32%	13%
PCB-118	20%	16%	8%	7%	32%	14%
PCB-138	20%	20%	11%	15%	27%	12%
PCB-153	22%	16%	10%	7%	26%	12%
PCB-170	<u>43%</u>	16%	24%	nd	28%	9%
PCB-180	13%	17%	10%	10%	29%	11%
PCB-187	19%	18%	<u>40%</u>	6%	28%	9%
minimum	13%	15%	6%	4%	25%	9%
maximum	43%	20%	40%	15%	36%	16%
where maximum >20%, new maximum with <u>largest</u> COV value removed	29%		24%		33%	

*laboratory performed both high and low resolution methods; ^a LR=low resolution and HR=high resolution method used for analysis; nd=analyte reported as non-detect in replicate samples by laboratory

Table 6-12. Coefficient of variation for Task 3 LDPE PAHs Active Results

LDPE:U.S. 8270D PAHs Active (Corresponds with data shown in Figure 6-11)						
Lab:	15	52	84	58	50	34
Naphthalene	45%	37%	58%	88%	nd	<u>22%</u>
Acenaphthylene	13%	21%	37%	<u>133%</u>	11%	nd
Acenaphthene	28%	29%	50%	69%	27%	19%
Fluorene	30%	31%	51%	42%	18%	21%
Phenanthrene	28%	29%	49%	47%	15%	20%
Anthracene	26%	31%	49%	40%	15%	19%
Fluoranthene	23%	25%	42%	8%	12%	16%
Pyrene	22%	23%	41%	4%	12%	15%
Benz(a)anthracene	22%	22%	41%	6%	12%	17%
Chrysene	21%	22%	39%	5%	12%	14%
Benzo(b)fluoranthene	17%	18%	33%	9%	12%	14%
Benzo(k)fluoranthene	15%	16%	34%	3%	12%	12%
Benzo(a)pyrene	13%	18%	33%	3%	11%	13%
Dibenz(a,h)anthracene	11%	13%	28%	25%	10%	13%
Indeno(1,2,3-cd)pyrene	14%	10%	25%	5%	9%	11%
Benzo(ghi)perylene	13%	13%	26%	7%	9%	10%
minimum	11%	10%	25%	3%	9%	10%
maximum	45%	37%	58%	133%	27%	22%
maximum with <u>largest</u> COV value removed	30%	31%	51%	88%	18%	21%

*laboratory performed analysis on 10x dilution, many results were flagged with E flag, indicating results exceeded calibration range; nd=analyte reported as non-detect in replicate samples by laboratory; n/a=not applicable, two or fewer results were reported by the laboratory for this analyte

Porewater Results for PDMS “Static” Sampling.

Sediment porewater concentrations of PCBs and PAHs measured using PDMS polymer under “static” exposure were fairly consistent across labs (Figure 6-12). Laboratory 83, which analyzed PCBs using low sensitivity methods was typically biased high compared to other labs for higher molecular weight PCBs.

Interlab consistency was observed in the PDMS-based porewater estimated concentrations of PAHs as well (Figure 6-12). Again, most variability between labs was observed for the more volatile PAHs naphthalene and acenaphthene, which may be attributed to handling of the sediment sample or the polymer. Variability in results for the higher molecular weight PAHs could have been overcome by exposing a larger mass of polymer than was done for this study.

Precision of the porewater concentration results measured using PDMS under “static” exposure, as indicated by the percent COV on replicate measurements, ranged from 3 – 38% for PCBs and 2 - 59% for PAHs across all labs (Tables 6-13, 6-14). A single analyte commonly skewed the COV range for a given lab. With those values removed, the COV on replicate PDMS porewater estimates ranged from 3 – 19% for PCBs and 2 – 34% for PAHs across all labs.

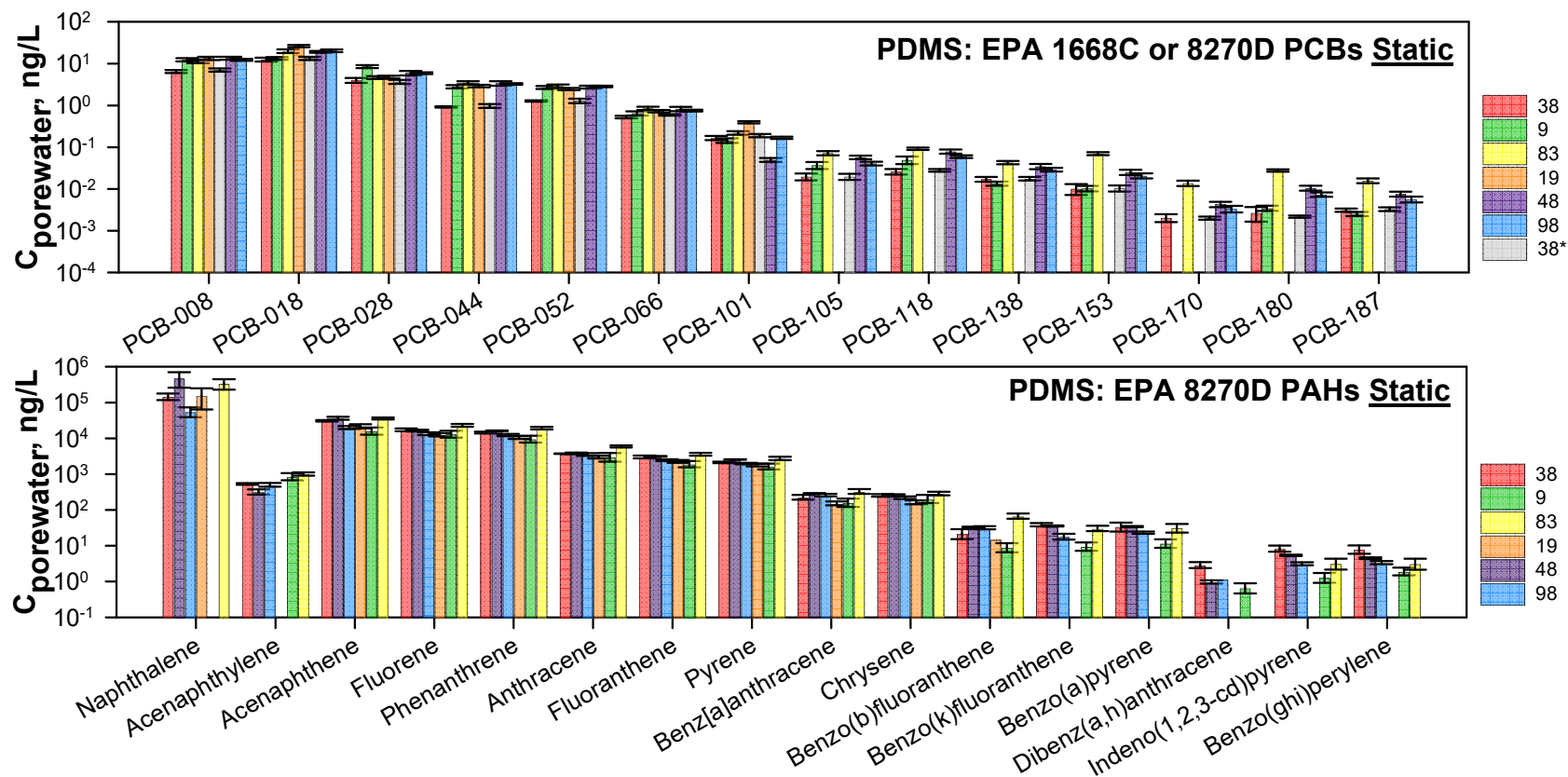


Figure 6-12. Task 3 PDMS static exposure results for PCBs (upper) and PAHs (lower). Bars represent average results for individual labs and compounds; error bars represent one standard deviation. For all labs $n=6$ except lab 38 where $n=3$ and lab 9 where $n=7$.

Table 6-13. Coefficient of variation for Task 3 PDMS PCBs Static Results

PDMS: U.S. EPA 1668C or 8270D PCBs Static (Corresponds with data shown in Figure 6-12)							
Lab:	38	9	83	19	38*	48	98
Method ^a :	LR	LR	LR	LR	HR	HR	HR
PCB-008	8%	9%	10%	9%	9%	8%	5%
PCB-018	10%	7%	10%	6%	9%	5%	7%
PCB-028	13%	8%	8%	8%	11%	12%	5%
PCB-044	3%	9%	8%	7%	11%	12%	5%
PCB-052	4%	8%	10%	6%	12%	8%	4%
PCB-066	7%	11%	9%	7%	4%	12%	5%
PCB-101	11%	13%	10%	6%	9%	11%	6%
PCB-105	18%	19%	12%	nd	17%	10%	10%
PCB-118	15%	21%	7%	nd	8%	11%	7%
PCB-138	13%	11%	9%	nd	9%	14%	10%
PCB-153	29%	15%	8%	nd	17%	15%	14%
PCB-170	22%	nd	15%	nd	9%	15%	18%
PCB-180	38%	14%	7%	nd	6%	13%	12%
PCB-187	9%	11%	13%	nd	11%	14%	16%
Minimum	3%	7%	7%	6%	4%	5%	4%
Maximum	38%	21%	15%	9%	17%	15%	18%
where maximum >20%, new maximum with <u>largest</u> COV value removed	29%	19%					

laboratory performed both high and low resolution methods, only n=3 replicates were analyzed for 38 all other labs analyzed n=6 replicates; ^a LR=low resolution and HR=high resolution method used for analysis; nd=analyte reported as non-detect in replicate samples by laboratory

Table 6-14. Coefficient of variation for Task 3 PDMS PAHs Static Results

PDMS: U.S. 8270D PAHs Static (Corresponds with data shown in Figure 6-12)						
Lab:	38	48	84	19	9	83
Naphthalene	21%	46%	31%	59%	nd	32%
Acenaphthylene	5%	17%	11%	nd	23%	10%
Acenaphthene	5%	10%	10%	14%	22%	6%
Fluorene	9%	6%	9%	11%	21%	9%
Phenanthrene	5%	2%	7%	9%	22%	8%
Anthracene	1%	5%	9%	9%	27%	7%
Fluoranthene	9%	2%	6%	9%	20%	9%
Pyrene	5%	2%	5%	8%	18%	11%
Benzo(a)anthracene	15%	2%	8%	12%	26%	16%
Chrysene	8%	6%	8%	12%	26%	12%
Benzo(b)fluoranthene	31%	4%	10%	na	29%	17%
Benzo(k)fluoranthene	10%	3%	18%	nd	26%	17%
Benzo(a)pyrene	28%	4%	7%	nd	27%	27%
Dibenz(a,h)anthracene	19%	11%	na	nd	31%	nd
Indeno(1,2,3-cd)pyrene	20%	4%	10%	nd	31%	34%
Benzo(ghi)perylene	26%	6%	10%	nd	25%	34%
minimum	1%	2%	5%	8%	18%	6%
maximum	31%	46%	31%	59%	31%	34%
maximum with <u>largest</u> COV value removed	28%	17%	18%	14%	31%	34%

nd=analyte reported as non-detect in replicate samples by laboratory; n/a=not applicable, two or fewer results were reported by the laboratory for this analyte

Porewater Results for LDPE “Static” Sampling.

Sediment porewater concentrations of PCBs and PAHs measured using LDPE polymer under “static” exposure were fairly consistent across labs (Figure 6-13) but variability increased with congener hydrophobicity. Laboratories 34 and 58, which both used low sensitivity methods, reported biased high results for higher congeners (PCB-153 and above) compared to other labs.

Interlab consistency was observed in the LDPE-based porewater estimated concentrations of PAHs as well (Figure 6-13). Again, most variability between labs was observed for the more volatile PAHs naphthalene and acenaphthene, which may be attributed to handling of the sediment sample itself as opposed to a polymeric sampler-specific issue. Variability in results for the higher molecular weight PAHs could have been overcome by exposing a larger mass of polymer than was done for this study.

Precision of the porewater concentration results measured using LDPE under “static” exposure, as indicated by the percent COV on replicate measurements, ranged from 4 - 123% for PCBs and 9 - 79% for PAHs across all labs (Tables 6-15, 6-16). A single analyte commonly skewed the COV range for a given lab. With those values removed, the COV on replicate LDPE porewater estimates ranged from 4 - 120% for PCBs and 9 - 63% for PAHs across all labs.

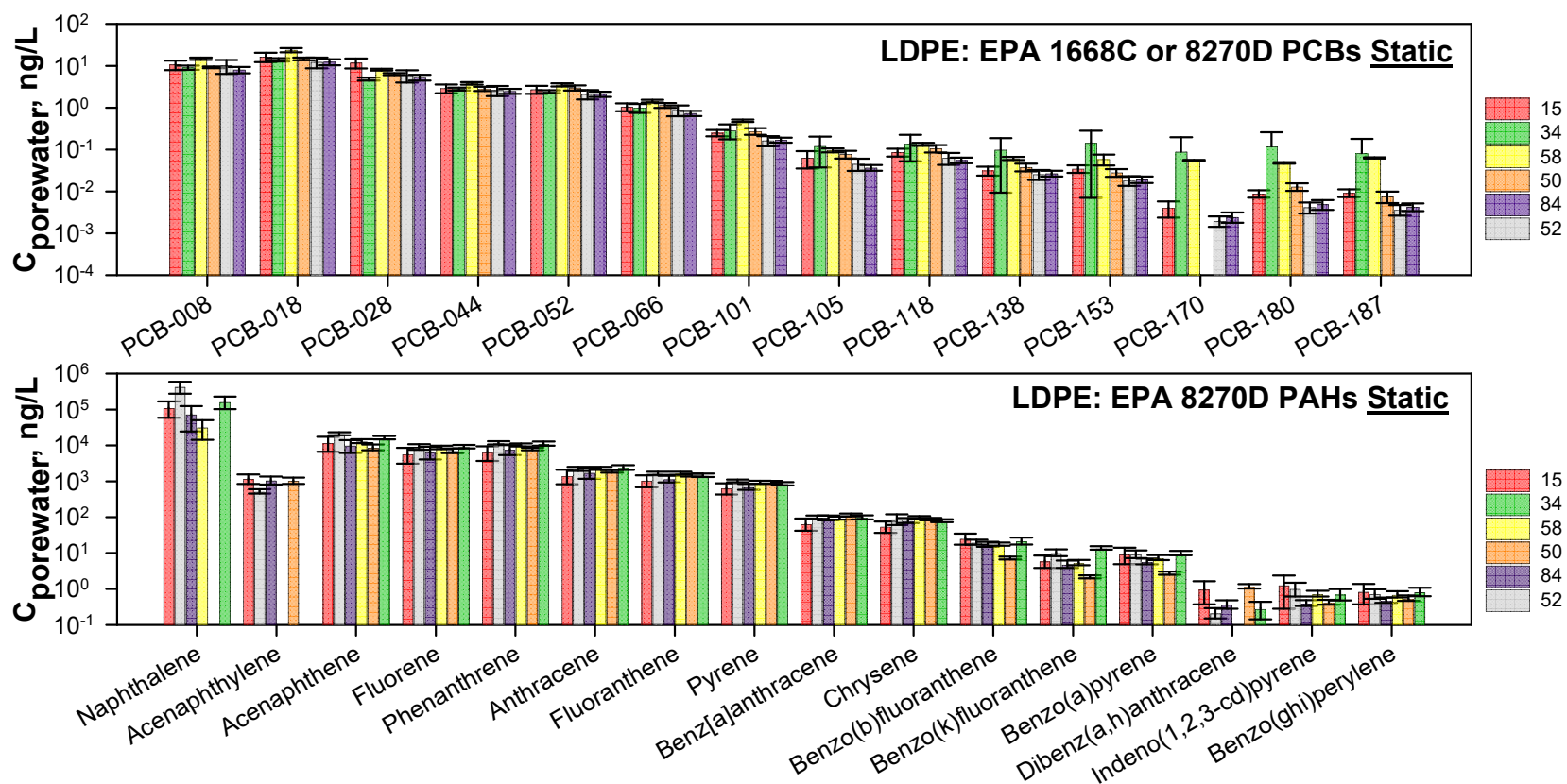


Figure 6-13. Task 3 LDPE static exposure results for PCBs (upper) and PAHs (lower). Bars represent average results for individual labs and compounds; error bars represent one standard deviation. For all labs $n=6$ except lab 50 where $n=7$.

Table 6-15. Coefficient of variation for Task 3 LDPE PCBs Static Results

LDPE: U.S. EPA 1668C or 8270D PCBs Static (Corresponds with data shown in Figure 6-13)						
Lab:	15	34	58	50	52	84
Method^a:	LR	LR	LR	LR	HR	HR
PCB-008	25%	12%	6%	5%	<u>36%</u>	18%
PCB-018	25%	9%	12%	8%	29%	17%
PCB-028	27%	9%	5%	6%	33%	16%
PCB-044	24%	8%	7%	12%	27%	14%
PCB-052	22%	8%	9%	14%	25%	14%
PCB-066	22%	24%	7%	14%	29%	14%
PCB-101	18%	39%	6%	18%	27%	14%
PCB-105	<u>44%</u>	69%	11%	21%	32%	16%
PCB-118	21%	62%	9%	20%	32%	15%
PCB-138	24%	90%	8%	21%	27%	16%
PCB-153	20%	95%	<u>29%</u>	21%	26%	18%
PCB-170	41%	<u>123%</u>	4%	nd	28%	<u>27%</u>
PCB-180	20%	118%	4%	20%	29%	26%
PCB-187	21%	120%	4%	<u>31%</u>	28%	21%
Minimum	18%	8%	4%	5%	25%	14%
Maximum	44%	123%	29%	31%	36%	27%
maximum with <u>largest</u> COV value removed	41%	120%	12%	21%	33%	26%

^a LR=low resolution and HR=high resolution method used for analysis; nd=analyte reported as non-detect in replicate samples by laboratory;

Table 6-16. Coefficient of variation for Task 3 PAHs Static Results

LDPE: U.S. 8270D PAHs Static (Corresponds with data shown in Figure 6-13)						
Lab:	15	52	84	58	50	34
Naphthalene	48%	36%	<u>67%</u>	<u>56%</u>	nd	38%
Acenaphthylene	30%	14%	25%	nd	<u>20%</u>	nd
Acenaphthene	44%	10%	39%	13%	18%	11%
Fluorene	47%	17%	39%	12%	15%	11%
Phenanthrene	44%	10%	31%	10%	8%	13%
Anthracene	43%	13%	34%	10%	8%	15%
Fluoranthene	36%	10%	21%	9%	9%	11%
Pyrene	34%	9%	18%	10%	9%	11%
Benz(a)anthracene	37%	11%	15%	10%	9%	13%
Chrysene	35%	33%	16%	11%	8%	9%
Benzo(b)fluoranthene	34%	16%	15%	11%	9%	22%
Benzo(k)fluoranthene	38%	21%	23%	17%	10%	12%
Benzo(a)pyrene	49%	24%	18%	16%	10%	14%
Dibenz(a,h)anthracene	63%	30%	27%	nd	14%	<u>51%</u>
Indeno(1,2,3-cd)pyrene	<u>79%</u>	<u>42%</u>	19%	18%	16%	35%
Benzo(ghi)perylene	57%	29%	16%	20%	18%	27%
minimum	30%	9%	15%	9%	8%	9%
maximum	79%	42%	67%	56%	20%	51%
maximum with <u>largest</u> COV value removed	63%	36%	39%	20%	18%	38%

*One of six replicates was identified as outlier and deleted, results of n=5 replicates shown; nd=analyte reported as non-detect in replicate samples by laboratory; n/a=not applicable, two or fewer results were reported by the laboratory for this analyte

6.3.4 Equality of PRC-corrected “Active” vs. “Static” Porewater Measures.

With the exception of LDPE “active” samplers, which did achieve equilibrium, all other polymeric sampler-based porewater estimates were corrected for progress toward steady-state/equilibrium using PRC losses measured during exposure. We therefore hypothesized that porewater concentrations estimated from “active” and “passive” exposures would be equivalent after appropriate correction for nonequilibrium. Equivalence of “active” and “static” porewater measurements was assessed for both polymers by performing a linear regression on the average porewater estimates for all PCB and PAH compounds across labs. Results illustrated in Figure 6-14 below show insignificant proportional differences (i.e. slope is not significantly different from 1), as well as quite small systematic differences (intercept also near zero).

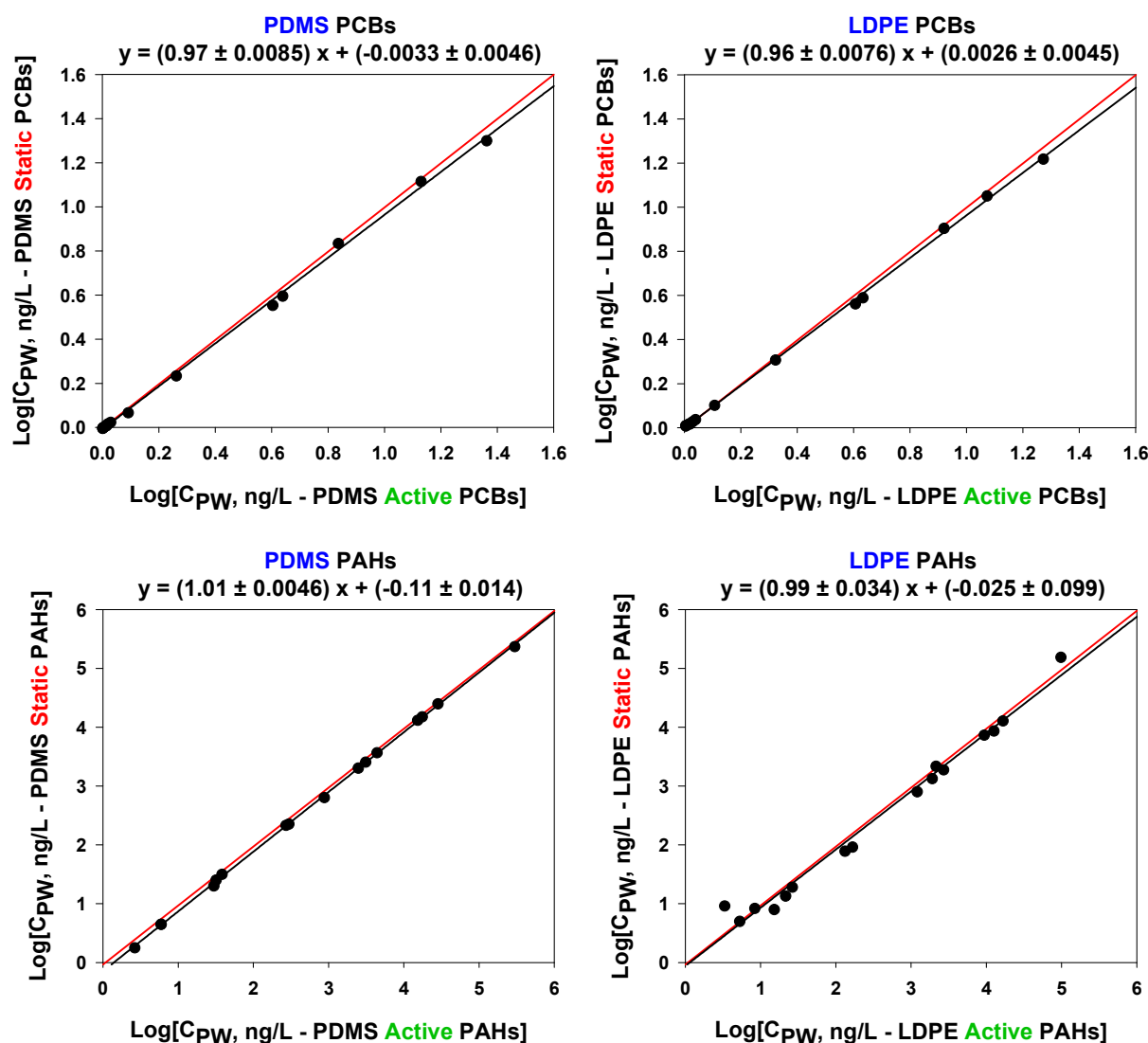


Figure 6-14. Polymer-based porewater results in static vs. active exposures for PCBs (upper) and PAHs (lower). Data points represent the average result for all participating labs, for a given PAH or PCB analyte, under static or active exposure.

6.3.5 Differences between polymeric sampler-based porewater estimates and reference method.

Finally, we compared polymeric sampler-based porewater concentration estimates with those yielded by the manual porewater extraction reference method. In this porewater extraction method, the sediment is allowed to equilibrate with water for 1 month in a shaker, followed by gravity settling of sediment and further settling of colloidal particles using alum flocculation. The clarified water equilibrated with sediment is then extracted with hexane to measure the PAHs and PCBs. Remaining DOC-associated PAHs and PCBs are corrected based on the approach provided in Section 5.2.4. Because “active” and “static” polymeric sampling exposures provided equivalent results (Figure 6-14), we featured average PDMS and LDPE “active” porewater concentration estimates only for this final method comparison.

Here the average over all sediment porewater estimate replicates for each PCB and PAH compound, along with the standard deviation of this estimate, was plotted with results of the manual porewater extraction reference method. The manual porewater extraction method was performed in triplicate and by one academic laboratory only. As summarized in Figure 6-15 below, results of this comparison show:

1. PDMS and LDPE provided estimates of concentrations in the sediment porewater that were similar to the concentrations measured using manual porewater extraction for the low molecular weight PCB congeners. The direct porewater extraction method is not sensitive enough to provide reliable measurements of ultra-low concentrations of C_{free} for high molecular weight compounds but provides reasonable measurements for the low molecular weight more soluble congeners.
2. PDMS and LDPE provided estimates of PAH concentrations in sediment that were similar to the concentrations measured using direct porewater extraction for all the PAH compounds that were detectable (up to benzo(k)fluoranthene). The three highest molecular weight PAH compounds could not be detected using the direct porewater extraction method.
3. Polymer-based measurements provide increase sensitivity for higher molecular weight compounds compared to the manual porewater extraction method.

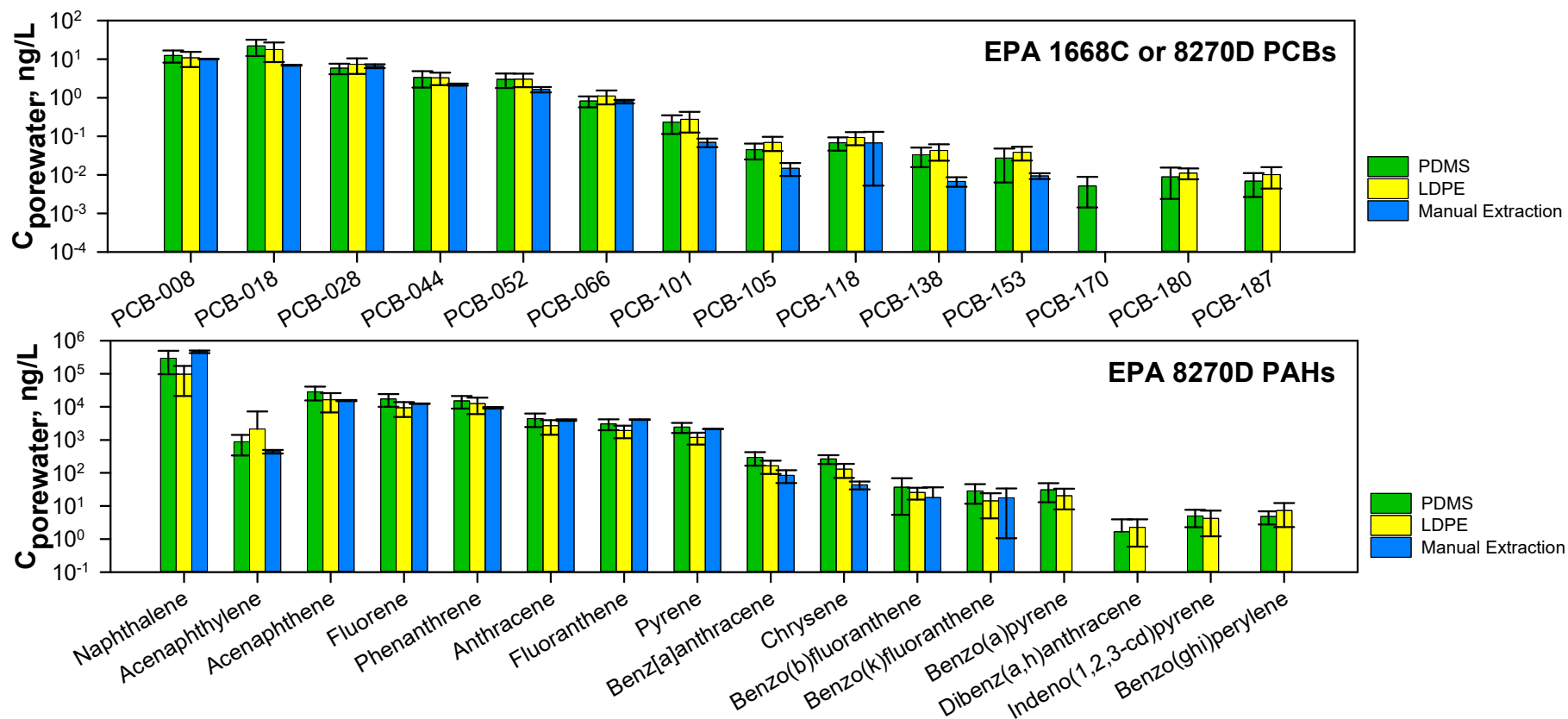


Figure 6-15. Inter-method comparison of PCBs and PAHs porewater concentration results. Bars represent average results for all participating labs for listed analytes; error bars represent one standard deviation.

7.0 COST ASSESSMENT

7.1 COST MODEL

The original intent of this project was to provide unit costs from each laboratory for polymeric passive sampling preparation and analysis. However, due to the unique nature of estimating costs for individual project needs, development of a cost per polymeric sampler was not possible. Rather, cost estimates for polymeric sampler preparation and analysis to measure PAHs and PCBs in sediment porewater can be obtained from any of the points of contact listed for the commercial laboratories identified in Table 2-1. Cost considerations should account for sampler preparation and loading with PRCs, as well as analytical costs for the appropriate analytes. Field blanks and any samplers needed to meet QA/QC requirements should also be accounted for. Calculations to support conversion of extract concentrations to porewater concentrations may be performed by the commercial laboratory or by a separate contractor familiar with passive sampling. Cost savings can be realized through potential compositing of samplers and use of low resolution methods. While costs can vary by lab, low resolution analysis for PCBs and PAHs can range from \$100 to \$300 per sample, high resolution methods can cost \$600 to \$1,000 per sample.

7.2 COST ANALYSIS

Following the template scope of work provided in Appendix H, an example cost estimate was developed (Table 7-1). The cost estimate was developed for a fictitious site, assumed to be simple in complexity and small in size. The cost estimate was developed assuming a contractor provides technical expertise in scoping and execution of the field effort, with analytical support from a commercial laboratory. This scope does not account for contracting fees, profit, or other cost markups. The complexity and size of a site serve as a primary factor in driving the cost estimate, influencing the preparation, number of samplers, and scale of analysis required. No dive team or boat rental was assumed in developing the cost estimate. While some field deployment/retrieval efforts may be performed in shallow water without the support of a dive team, a commercial dive crew is often needed to support both deployment and retrieval of samplers. The cost of other generic field supplies was also not captured in this estimate. For the sampler preparation and analysis covered in Tasks 2 and 3, either LDPE or PDMS can be represented by this estimate. Both PCB and PAH analysis are assumed. PRCs for both compounds can be included on a single sampler. There may be instances where collocated sediment is also collected alongside passive samplers, which should be incorporated into the cost estimate if that is of interest. Another consideration for the field effort and number of samplers identified for deployment is the duration required for passive sampler deployment (typically 30 days) and the potential for loss of samplers during that time. For this reason, it may be beneficial to deploy additional sampler beyond the minimum number needed for characterization to account for inevitable field losses.

**Table 7-1. Conceptual cost model for sediment porewater characterization
using polymeric samplers**

Cost Element	Details	# Units	Cost Per Unit	Estimated Costs
Task 1. Project Kickoff and Work Plan/QAPP Finalization Support				
Kickoff meeting	Labor	8	\$150 per hr	\$1,200
Work Plan Development Support	Labor	40	\$150 per hr	\$6,000
QAPP Development Support	Labor	60	\$150 per hr	\$9,000
Quality Control Plan Development Support	Labor	20	\$150 per hr	\$3,000
Health and Safety Plan Development Support	Labor	20	\$150 per hr	\$3,000
Subtotal				\$22,200
Task 2. Passive Polymeric Sampler Preparation and Field Deployment/Retrieval				
Polymeric passive sampler preparation including PRC loading	Materials	35	\$75 per sample	\$2,625
	Labor	80	\$150 per hr	\$12,000
field work kick-off/field readiness review meeting	Labor	8	\$150 per hr	\$1,200
Contractor travel for sampler deployment and retrieval – 2 staff	Airfare	4	\$500 round trip	\$600
	Hotel & Per Diem	20	\$200 per day	\$3,000
Field Deployment	Labor	80	\$150 per hr	\$12,000
Field Retrieval	Labor	80	\$150 per hr	\$12,000
Overnight shipment of samplers to and from site	Materials	2	\$50 per shipment	\$300
Subtotal				\$43,725
Task 3. Chemical Analysis of Polymeric Passive Samplers				
Unit cost of polymeric sampler analysis by commercial lab for low resolution PCBs	Unit cost	30 samples + 2 trip blanks + 3 QC sample	\$200 per sample	\$7,000
Unit cost of polymeric sampler analysis by commercial lab for low resolution PAHs	Unit cost	30 samples + 2 trip blanks + 3 QC sample	\$200 per sample	\$7,000
Reporting & Data Management	Labor	40	\$150 per hr	\$6,000
Subtotal				\$20,000
Task 4. Final Report				
Field Report	Labor	20	\$150 per hr	\$3,000
Data validation (assume Stage 2A or equivalent)	Labor	40	\$150 per hr	\$6,000
Data analysis – converting polymeric extract concentrations into porewater concentrations	Labor	40	\$150 per hr	\$6,000
Draft Report	Labor	100	\$150 per hr	\$15,000
Discussion Meetings	Labor	8	\$150 per hr	\$1,200
Final Report	Labor	20	\$150 per hr	\$3,000
Subtotal				\$34,200
Project Management	Labor	-	10%	\$12,000
TOTAL				\$132,125

A template scope of work/performance work statement is provided in Appendix H to assist projects seeking to implement passive sampling at a site. The template scope of work outlines services to be performed by a contractor in the following tasks:

1. Preparation [or support of preparation] of a Work Plan and Quality Assurance Project Plan (QAPP).
2. Preparation and supply of polymeric passive samplers loaded with the appropriate performance reference compounds for a project.
3. Field support for polymeric passive sampler and retrieval at the site.
4. Extraction and laboratory analysis of recovered polymeric passive samplers and calculation of equilibrium porewater concentrations using PRCs.
5. Reporting of equilibrium concentrations of the target analytes based on analysis of the polymeric passive samplers and PRC performance corrections.

8.0 IMPLEMENTATION ISSUES

One implementation issue for passive sampling is the need to know approximate concentrations of target analytes present in the sediment porewater so that appropriate PRC concentrations can be loaded into the samplers prior to deployment or use. This can typically be overcome if any existing bulk sediment concentration data is available for a site and following guidelines in the final SOPs (Appendix B) and other references^{6, 7}.

One of the more costly components of passive sampling is the use of ¹³C-labeled PRCs and quantities required to prepare the loading solution. This can be managed by using lower PRC loadings, but needs to be balanced with the necessary concentration range needed for the exposure environment and detection limits of analytical method being used. Generally, the PRCs should be present in the post-exposure polymer extract at 10x above the method detection limit.

Commercial laboratories often prefer to provide polymer extract concentration results, rather than performing the necessary calculations needed to convert extract concentration results to porewater concentrations. As such, an additional contractor or someone else familiar with the mathematical conversion from extract to porewater concentration is needed. The example scope of work (Appendix H) and cost discussion in Section 7 accounts for this need.

8.1 RECOMMENDATIONS AND LESSONS LEARNED FOR IMPLEMENTING A PASSIVE SAMPLING STUDY

Numerous lessons learned during this study provided useful information for planning, implementing, and interpreting data from a passive sampler investigation. Starting simply with a “round robin” analysis of a defined calibration check standard, then slowly building in complexity through a series of go/no-go decision points, provided a chance to identify methodological challenges and improve the standard method SOPs as this project progressed. Three key lessons learned are described below.

First, as detailed in depth in the Task 1 Go Memo (Appendix D), we found that variability existed within and between labs, even when the sample being analyzed was a calibration standard dissolved in clean solvent. This was great perspective to have when comparing interlaboratory sediment porewater results! Task 1 results also showed that PAH PRC ¹³C6-indeno(1,2,3-cd)pyrene was not distinguishable from column bleed on low resolution mass spectrometry instruments. Labs using low resolution methods should consider use of fully labeled indeno(1,2,3 cd)pyrene.

Second, Task 2 results (Appendix E) showed how variations in solvent type and proportions used to prepare the PRC loading solutions can significantly influence the PRC loading on the polymers.

This observation prompted revisions to the SOPs so that requirements for solvents used were more stringent. The effects of solvents involves both working solutions and the actual loading solution as follows:

- (a) The kinetics of PRC loading changes with the type of loading solution with faster loading in solvent (100% methanol) or solvent-water mixtures (methanol-water mixtures) although the equilibrium amount of loading is quantitatively easier to define with 100% water loading solution. A convenient balance between quantitative control and speed of loading is with an 80% water- 20% methanol loading solution.
- (b) The availability of PRCs in low volatility solvents such as nonane makes preparation of working solutions and loading solutions challenging. It is always important to create a working solution that is full soluble in the loading solution and this applies to both the solvent and the PLC to be loaded. Use of insoluble solvent such as hexane as a working solution can lead to phase behavior in the loading solution leading to nonuniformities in loading and potential delamination of PDMS fibers during PRC loading. The use of evaporation of low-volatility PRCs to dryness or near-dryness to remove the initial solvent and the use of working solution solvents such as acetone that are miscible in both organic and water phases can reduce this problem

Third, achieving precision targets during PRC-loading of LDPE strips in Task 3 was a challenge. Because participating labs had adopted the more stringent solvent use requirements for preparing PRC loading solution at this point in the project, we suspect the variability was simply not due to solvent choices but also due to floating/clumping of the many LDPE strip replicates present in the Task 3 PRC loading solution. Various corrective measures were used by labs in efforts to ensure even exposures of passive sampling media to achieve uniform loading and reduce variability between LDPE replicate PRC loaded concentrations. However, variability persisted following corrective measures. As per the final SOPs, the Task 3 LDPE PRC loading solution was prepared using a water:methanol ratio of 80:20. Using a “water only” LDPE PRC loading solution (i.e. no methanol) may be advantageous as it reduces the possibility of solvent-related interferences and requires lower mass amounts of costly isotopically-labeled PRCs to achieve the target loading. But one should note that “water only” PRC loading requires an extended loading timeframe, which was not possible to accommodate within the timeline in Task 3 of this project. Readers are encouraged to review Appendices D and E for more details on these lessons learned.

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APPENDIX A
Lower Duwamish sediment screening results

ESTCP sediment collection for concentration confirmation

Methods. Reconnaissance was conducted during daylight hours on 29 January to assess site access for sampling. It was noted that access to Site 2 (Terminal 105) was only during daylight hours and a gate to the site was closed from dusk to dawn. As such, a decision was made to prioritize sampling at Site 1 (Herring House Park).

The sampling team (Kristen Kerns and Nate Malmborg) arrived on site for sampling at approximately 2100 and established a grid at LDW_1 in the approximate location of a previous sample (NOAA SiteChar (WIT282)) collected during the Lower Duwamish Waterway Remedial Investigation. The exact grid location was dictated where visible debris was minimal or could be easily removed from the sampling area. The centroid of the grid was captured on a handheld Tremble GPS unit. The 6x6ft grid was established with stakes and marked out with neon line to demarcate nine 2x2ft squares in a 3x3 orientation.

Hand cores were collected from the centroid of each of the individual quadrants. If refusal was met, the core was repositioned in a different area within the same quadrant. Hand cores were driven to a depth of 30cm then homogenized in a stainless steel bowl with other discrete samples from the same row. This resulted in 3 30cm cores homogenized together into a single composite for each row, yielding a total of 3 composites for the sampling location. Sample IDs, time collected, and field conditions are noted in the table below.

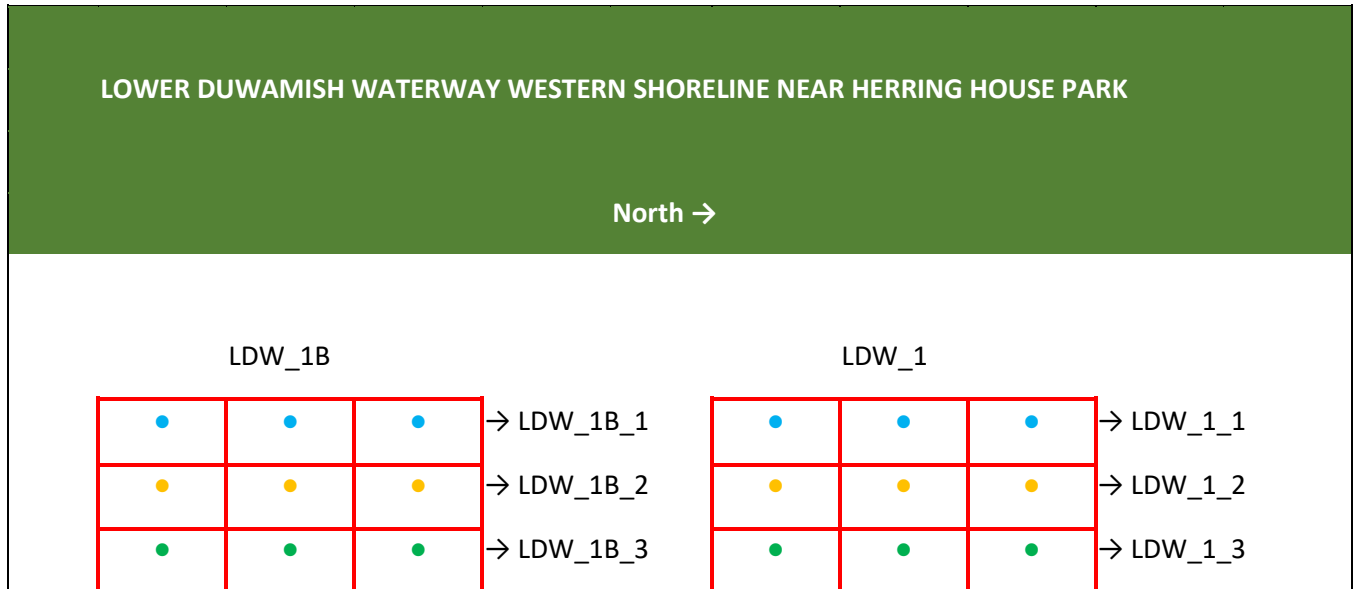
After completing sample collection at LDW_1, sampling supplies were decontaminated with Alconox and DI water before moving to LDW_1B. The location of LDW_1B was based on reoccupying a previous sample (LDWRI-SurfaceSedimentRound3 (LDW-SS312)) collected during the Lower Duwamish Waterway Remedial Investigation. Similar methods were conducted at location LDW_1B similar to those at LDW_1. One deviation from the collection methods was for 2 of the 3 discrete hand cores in composite LDW_1B_1 could only be driven to a depth of approximately 20cm despite multiple attempts to reposition the core in different areas of the quadrant. Samples were brought back to the USACE lab, placed in the freezer, and then shipped via FedEx on ice overnight to the ERDC lab.

Table 1. Sample IDs, time collected, and sample notes

Sample ID	Time Collected	Notes
LDW_1_1	2110	Sediment in plot LDW_1 was silty and cohesive. Primarily surface debris consisting of brick, logs, netting.
LDW_1_2	2135	-
LDW_1_3	2150	-
LDW_1B_1	2232	2 of the 3 discrete samples in this composite could only be penetrated to ~20cm, despite multiple attempts within the sample quadrant. Significant wood debris at depth. Sediment in plot LDW_1B had significant amount of small wood chips at depth.
LDW_1B_2	2244	-
LDW_1B_3	2258	-

Table 2. GPS coordinates

LDW RI Sample ID	Sample Coordinates (X,Y State Plane)	ESTCP Sample ID	Sample Coordinates
NOAA SiteChar (WIT282)	1265967, 208217	LDW_1	1265966, 208247
LDWRI-SurfaceSedimentRound3 (LDW-SS312)	1265998, 208009	LDW_1B	1265977, 207961

**Figure 1.** Schematic of sampling grids

Chain of Custody Record—US Army Corps of Engineers

Project: ESTCP Location: Lower Duwamish Waterway Lab: ESTCP DOE: Long Beach Sampling Team: Parsons, Parsons (DNR, BSA, etc.) Project No.: 1265998 Report Period: 12/15/16 to 12/15/16 Report No.: 1265998		Sampling Method and Frequency: (Handwritten: 1265998, 1265998)		Additional Lab Instructions:
Sample Identification				
Sample ID	Sample Date	Sample Time	Sample Location	Sample Status
LDW_1_1	12/15/16	11:15	1265998	✓
LDW_1_2	12/15/16	11:15	1265998	✓
LDW_1_3	12/15/16	11:15	1265998	✓
LDW_1B_1	12/15/16	11:15	1265998	✓
LDW_1B_2	12/15/16	11:15	1265998	✓
LDW_1B_3	12/15/16	11:15	1265998	✓
ESTCP Sample Tracking Numbers: (Handwritten: 1265998, 1265998, 1265998, 1265998, 1265998, 1265998)				
Signatures: (Handwritten signatures and dates)				

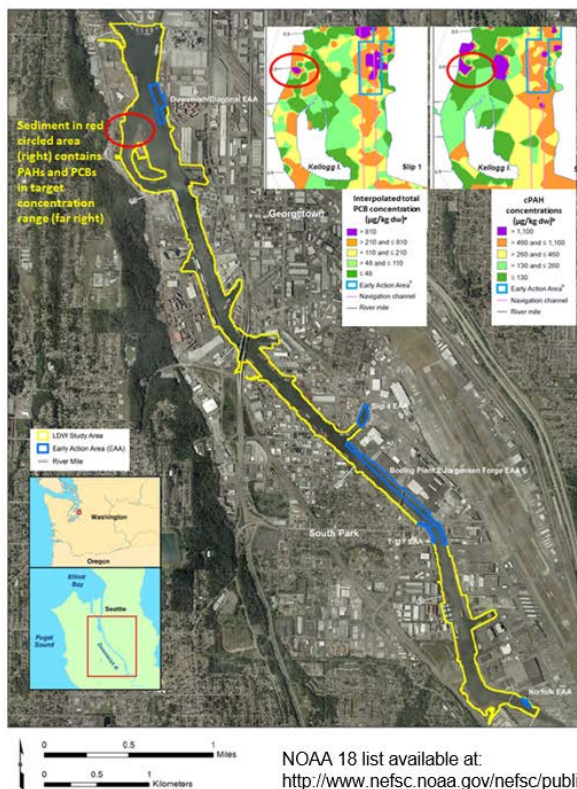
Photo 1. Chain of custody form.

Results. Concentrations of Total PAHs and Total PCBs in sediment samples collected from both LDW field plots are summarized in Table 3 below. Detailed analytical results are included as attachment. Minimum acceptable sediment concentrations of Total PAHs and Total PCBs was established as 10 and 0.1 mg/kg-dw, respectively (Figure 2). PAHs were in acceptable range but PCBs were too low in LDW sediment to meet demonstration objectives.

Table 3. Total PAHs and total PCBs for field plots LDW_1 and LDW_1B

Sample ID	mg/kg-dw		Sample ID	mg/kg-dw	
	Total PAHs	Total PCBs		Total PAHs	Total PCBs
LDW_1_1	74	0.088	LDW_1B_1	37	0.12
LDW_1_2	6.5	10	LDW_1B_2	68	0.087
LDW_1_3	2.6	0.082	LDW_1B_3	45	0.13
avg ± std	28 ± 40	3.3 ± 5.6	avg ± std	50 ± 16	0.11 ± 0.023

Lower Duwamish Waterway Superfund Site



Targeted Total PAHs and PCBs sediment concentrations for demonstration, mg/kg dry weight

Contaminant	Target Sediment Concentration Range	Lowest Acceptable Sediment Concentrations
Total PAHs	30 – 100	10
Total PCBs	1 – 5	0.1 – 0.5

Target PCBs NOAA 18
Target PAHs EPA Priority 16

Figure 2. Target sediment concentrations for demonstration

																			REC																
																			SUM, ug/kg																
CLIENT	PROJECT	PROJECTNUM	LabName	SAMPLENAME	LABSAMPID	MATRIX	RPTMATRIX	SAMPDATE	PREPDATE	ANALDATE	BATCH	METHODCODE	METHODNAME	REFNAME	ANALYTE	CASNUMBER	SURROGATE	TIC	Result	RL	RL	UNITS	RPTMODL	BASIS	DILU	SPEL	UPEL	LOW	ANALYST	PSOLDS	ANOTE	ANALYTE ORDER			
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_1_1	18A3102-01	Soil/Sediment	Soil/Sediment	01/29/2018 21:10:00	02/08/2018 08:24:00	02/08/2018 08:25:00	18B880	Solids, Dry Weight	% Calculation	*** DEFAULT PREP * % Solids	Naphthalene	91-20-3	FALSE	FALSE	63.3	0.500	0.500	% Solids	FALSE	NA	1								1		
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_1_1	18A3102-01	Soil/Sediment	Soil/Sediment	01/29/2018 21:10:00	02/06/2018 09:46:00	02/26/2018 10:56:14	18B880	PAH SM&2	EPA 8270C	EPA 3545	Anthracene	120-12-7	FALSE	FALSE	5030	91.1	303	ug/kg dry	TRUE	NA	10								2-03	1	
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_1_1	18A3102-01	Soil/Sediment	Soil/Sediment	01/29/2018 21:10:00	02/06/2018 09:46:00	02/26/2018 10:56:14	18B880	PAH SM&2	EPA 8270C	EPA 3545	Phenanthrene	85-01-8	FALSE	FALSE	12690	91.1	303	ug/kg dry	TRUE	NA	50								2-03	12	
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_1_1	18A3102-01	Soil/Sediment	Soil/Sediment	01/29/2018 21:10:00	02/06/2018 09:46:00	02/26/2018 10:56:14	18B880	PAH SM&2	EPA 8270C	EPA 3545	Fluoranthene	206-44-0	FALSE	FALSE	13900	91.1	303	ug/kg dry	TRUE	NA	50								2-03	17	
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_1_1	18A3102-01	Soil/Sediment	Soil/Sediment	01/29/2018 21:10:00	02/06/2018 09:46:00	02/26/2018 10:56:14	18B880	PAH SM&2	EPA 8270C	EPA 3545	Pyrene	129-00-0	FALSE	FALSE	14600	91.1	303	ug/kg dry	TRUE	NA	50								2-03	18	
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_1_1	18A3102-01	Soil/Sediment	Soil/Sediment	01/29/2018 21:10:00	02/06/2018 09:46:00	02/26/2018 10:56:14	18B880	PAH SM&2	EPA 8270C	EPA 3545	2-Methylnaphthalene	91-57-6	FALSE	FALSE	579	18.6	60.5	ug/kg dry	TRUE	NA	10								2-03	2	
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_1_1	18A3102-01	Soil/Sediment	Soil/Sediment	01/29/2018 21:10:00	02/06/2018 09:46:00	02/26/2018 10:56:14	18B880	PAH SM&2	EPA 8270C	EPA 3545	Benzo (a) anthracene	56-55-3	FALSE	FALSE	4110	93.1	303	ug/kg dry	TRUE	NA	50								2-03	21	
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_1_1	18A3102-01	Soil/Sediment	Soil/Sediment	01/29/2018 21:10:00	02/06/2018 09:46:00	02/26/2018 10:56:14	18B880	PAH SM&2	EPA 8270C	EPA 3545	Chrysene	218-01-9	FALSE	FALSE	4780	93.1	303	ug/kg dry	TRUE	NA	50								2-03	22	
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_1_1	18A3102-01	Soil/Sediment	Soil/Sediment	01/29/2018 21:10:00	02/06/2018 09:46:00	02/26/2018 10:56:14	18B880	PAH SM&2	EPA 8270C	EPA 3545	Benzo (b) fluoranthene	205-99-2	FALSE	FALSE	1280	18.6	60.5	ug/kg dry	TRUE	NA	10								2-03	27	
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_1_1	18A3102-01	Soil/Sediment	Soil/Sediment	01/29/2018 21:10:00	02/06/2018 09:46:00	02/26/2018 10:56:14	18B880	PAH SM&2	EPA 8270C	EPA 3545	Benzo (k) fluoranthene	207-08-9	FALSE	FALSE	3930	18.6	60.5	ug/kg dry	TRUE	NA	10								2-03	28	
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_1_1	18A3102-01	Soil/Sediment	Soil/Sediment	01/29/2018 21:10:00	02/06/2018 09:46:00	02/26/2018 10:56:14	18B880	PAH SM&2	EPA 8270C	EPA 3545	Benzo (g,h,i) perylene	50-32-8	FALSE	FALSE	5160	18.6	60.5	ug/kg dry	TRUE	NA	10								2-03	29	
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_1_1	18A3102-01	Soil/Sediment	Soil/Sediment	01/29/2018 21:10:00	02/06/2018 09:46:00	02/26/2018 10:56:14	18B880	PAH SM&2	EPA 8270C	EPA 3545	1-Methylnaphthalene	90-12-0	FALSE	FALSE	558	18.6	60.5	ug/kg dry	TRUE	NA	10								2-03	3	
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_1_1	18A3102-01	Soil/Sediment	Soil/Sediment	01/29/2018 21:10:00	02/06/2018 09:46:00	02/26/2018 10:56:14	18B880	PAH SM&2	EPA 8270C	EPA 3545	Indeno (1,2,3-cd) pyrene	193-39-5	FALSE	FALSE	1610	18.6	60.5	ug/kg dry	TRUE	NA	10								2-03	30	
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_1_1	18A3102-01	Soil/Sediment	Soil/Sediment	01/29/2018 21:10:00	02/06/2018 09:46:00	02/26/2018 10:56:14	18B880	PAH SM&2	EPA 8270C	EPA 3545	Dibenz (a,h) anthracene	53-70-3	FALSE	FALSE	447	18.6	60.5	ug/kg dry	TRUE	NA	10								2-03	31	
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_1_1	18A3102-01	Soil/Sediment	Soil/Sediment	01/29/2018 21:10:00	02/06/2018 09:46:00	02/26/2018 10:56:14	18B880	PAH SM&2	EPA 8270C	EPA 3545	Benzo (a) anthracene	56-55-3	FALSE	FALSE	1380	18.6	60.5	ug/kg dry	TRUE	NA	10								2-03	32	
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_1_1	18A3102-01	Soil/Sediment	Soil/Sediment	01/29/2018 21:10:00	02/06/2018 09:46:00	02/26/2018 10:56:14	18B880	PAH SM&2	EPA 8270C	EPA 3545	2-Fluorobiphenyl	321-40-8	TRUE	FALSE	40	18.6	60.5	ug/kg dry	TRUE	NA	10	93.13	42.7	105	40	CHL	63.3	2-03	33		
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_1_1	18A3102-01	Soil/Sediment	Soil/Sediment	01/29/2018 21:10:00	02/06/2018 09:46:00	02/26/2018 10:56:14	18B880	PAH SM&2	EPA 8270C	EPA 3545	Terphenyl-d4	1718-51-0	TRUE	FALSE	78	18.6	60.5	ug/kg dry	TRUE	NA	10	93.13	83.8	125	30	CHL	63.3	2-03	34		
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_1_1	18A3102-01	Soil/Sediment	Soil/Sediment	01/29/2018 21:10:00	02/06/2018 09:46:00	02/26/2018 10:56:14	18B880	PAH SM&2	EPA 8270C	EPA 3545	Acenaphthylene	208-66-8	FALSE	FALSE	679	18.6	60.5	ug/kg dry	TRUE	NA	10								2-03	7	
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_1_1	18A3102-01	Soil/Sediment	Soil/Sediment	01/29/2018 21:10:00	02/06/2018 09:46:00	02/26/2018 10:56:14	18B880	PAH SM&2	EPA 8270C	EPA 3545	Acenaphthene	83-32-9	FALSE	FALSE	1280	18.6	60.5	ug/kg dry	TRUE	NA	10								2-03	8	
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_1_1	18A3102-01	Soil/Sediment	Soil/Sediment	01/29/2018 21:10:00	02/06/2018 09:46:00	02/26/2018 10:56:14	18B880	PAH SM&2	EPA 8270C	EPA 3545	Fluorene	86-73-7	FALSE	FALSE	1190	74047	18.6	60.5	ug/kg dry	TRUE	NA	10							2-03	9	
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_1_1	18A3102-01	Soil/Sediment	Soil/Sediment	01/29/2018 21:10:00	02/06/2018 09:46:00	02/26/2018 13:30:56	18B880	PCBs	EPA 8082	EPA 3545	PCB-1016	12674-11-2	FALSE	FALSE	ND	1.30	3.96	ug/kg dry	TRUE	NA	1								2-03	U 1	
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_1_1	18A3102-01	Soil/Sediment	Soil/Sediment	01/29/2018 21:10:00	02/06/2018 09:46:00	02/26/2018 13:30:56	18B880	PCBs	EPA 8082	EPA 3545	PCB-1254	11097-69-1	FALSE	FALSE	30.9	1.30	3.96	ug/kg dry	TRUE	NA	1								2-03	U 11	
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_1_1	18A3102-01	Soil/Sediment	Soil/Sediment	01/29/2018 21:10:00	02/06/2018 09:46:00	02/26/2018 13:30:56	18B880	PCBs	EPA 8082	EPA 3545	PCB-1260	11096-82-5	FALSE	FALSE	19.0	1.30	3.96	ug/kg dry	TRUE	NA	1								2-03	U 12	
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_1_1	18A3102-01	Soil/Sediment	Soil/Sediment	01/29/2018 21:10:00	02/06/2018 09:46:00	02/26/2018 13:30:56	18B880	PCBs	EPA 8082	EPA 3545	2,4,5,6-Tetrachloro-m-xylene	877-09-8	TRUE	FALSE	5.9	7.54	24.5	ug/kg dry	TRUE	NA	1	9.313	63.3	125	40	CHL	63.3	2-03	U 13		
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_1_1	18A3102-01	Soil/Sediment	Soil/Sediment	01/29/2018 21:10:00	02/06/2018 09:46:00	02/26/2018 13:30:56	18B880	PCBs	EPA 8082	EPA 3545	Decachlorobiphenyl	2053-24-3	TRUE	FALSE	8.47	7.54	24.5	ug/kg dry	TRUE	NA	1	9.313	90.9	125	40	CHL	63.3	2-03	U 14		
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_1_1	18A3102-01	Soil/Sediment	Soil/Sediment	01/29/2018 21:10:00	02/06/2018 09:46:00	02/26/2018 13:30:56	18B880	PCBs	EPA 8082	EPA 3545	PCB-1221	11104-28-2	FALSE	FALSE	ND	1.30	3.96	ug/kg dry	TRUE	NA	1								2-03	U 3	
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_1_1	18A3102-01	Soil/Sediment	Soil/Sediment	01/29/2018 21:10:00	02/06/2018 09:46:00	02/26/2018 13:30:56	18B880	PCBs	EPA 8082	EPA 3545	PCB-1222	11104-28-2	FALSE	FALSE	ND	1.30	3.96	ug/kg dry	TRUE	NA	1								2-03	U 4	
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_1_1	18A3102-01	Soil/Sediment	Soil/Sediment	01/29/2018 21:10:00	02/06/2018 09:46:00	02/26/2018 13:30:56	18B880	PCBs	EPA 8082	EPA 3545	PCB-1242	53469-21-9	FALSE	FALSE	ND	1.30	3.96	ug/kg dry	TRUE	NA	1								2-03	U 7	
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_1_1	18A3102-01	Soil/Sediment	Soil/Sediment	01/29/2018 21:10:00	02/06/2018 09:46:00	02/26/2018 13:30:56	18B880	PCBs	EPA 8082	EPA 3545	PCB-1248	12672-29-6	FALSE	FALSE	15.6	87.6	1.30	3.96	ug/kg dry	TRUE	NA	1								2-03	U 9
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_1_2	18A3102-02	Soil/Sediment	Soil/Sediment	01/29/2018 21:35:00	02/08/2018 08:24:00	02																									

CLIENT	PROJECT	PROJECT/CONT	LabName	SAMPLENAME	LABSAMPID	MATRIX	RPTMATRIX	SAMPDATE	PREPDATE	ANALDATE	BATCH	METHODCODE	METHODNAME	PREPNAME	ANALYTE	CASNUMBER	SURROGATE	TIC	Result	SUM, ug/kg		DL	UNITS	RPT/MOL	BASIS	DILU SPECK	UPPER	LOW	ANALYST	PSOLIDS	ANOTE	ANALYTE ORDER			
																				dw	RL														
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_18_1	18A3102-04	Soil/Sediment	Soil/Sediment	01/29/2018 22:32:00	02/06/2018 09:46:00	02/26/2018 10:56:14	18B08018	PAH SM2	EPA 8270C	EPA 3545	1-Methylnaphthalene	90-12-0	FALSE	FALSE	104	20.3	65.8	ug/kg dry	TRUE	NA	10					CHL	58.3	3			
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_18_1	18A3102-04	Soil/Sediment	Soil/Sediment	01/29/2018 22:32:00	02/06/2018 09:46:00	02/26/2018 10:56:14	18B08018	PAH SM2	EPA 8270C	EPA 3545	Indeno (1,2,3-cd) pyrene	193-39-5	FALSE	FALSE	968	20.3	65.8	ug/kg dry	TRUE	NA	10					CHL	58.3	30			
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_18_1	18A3102-04	Soil/Sediment	Soil/Sediment	01/29/2018 22:32:00	02/06/2018 09:46:00	02/26/2018 10:56:14	18B08018	PAH SM2	EPA 8270C	EPA 3545	Dibenz (a,h) anthracene	53-70-3	FALSE	FALSE	154	20.3	65.8	ug/kg dry	TRUE	NA	10					CHL	58.3	31			
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_18_1	18A3102-04	Soil/Sediment	Soil/Sediment	01/29/2018 22:32:00	02/06/2018 09:46:00	02/26/2018 10:56:14	18B08018	PAH SM2	EPA 8270C	EPA 3545	Benzo (g,h,i) perylene	191-24-2	FALSE	FALSE	662	20.3	65.8	ug/kg dry	TRUE	NA	10					CHL	58.3	32			
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_18_1	18A3102-04	Soil/Sediment	Soil/Sediment	01/29/2018 22:32:00	02/06/2018 09:46:00	02/26/2018 10:56:14	18B08018	PAH SM2	EPA 8270C	EPA 3545	2-Fluorobiphenyl	321-60-8	TRUE	FALSE	51	20.3	65.8	ug/kg dry	TRUE	NA	10	101.3	50.0	105	40			CHL	58.3	45	
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_18_1	18A3102-04	Soil/Sediment	Soil/Sediment	01/29/2018 22:32:00	02/06/2018 09:46:00	02/26/2018 10:56:14	18B08018	PAH SM2	EPA 8270C	EPA 3545	Terphenyl-d	1718-51-0	TRUE	FALSE	100	20.3	65.8	ug/kg dry	TRUE	NA	10	101.3	99.1	125	30			CHL	58.3	46	
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_18_1	18A3102-04	Soil/Sediment	Soil/Sediment	01/29/2018 22:32:00	02/06/2018 09:46:00	02/26/2018 10:56:14	18B08018	PAH SM2	EPA 8270C	EPA 3545	Acenaphthylene	208-96-8	FALSE	FALSE	154	20.3	65.8	ug/kg dry	TRUE	NA	10					CHL	58.3	7			
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_18_1	18A3102-04	Soil/Sediment	Soil/Sediment	01/29/2018 22:32:00	02/06/2018 09:46:00	02/26/2018 10:56:14	18B08018	PAH SM2	EPA 8270C	EPA 3545	Acenaphthene	83-32-9	FALSE	FALSE	286	20.3	65.8	ug/kg dry	TRUE	NA	10					CHL	58.3	8			
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_18_1	18A3102-04	Soil/Sediment	Soil/Sediment	01/29/2018 22:32:00	02/06/2018 09:46:00	02/26/2018 10:56:14	18B08018	PAH SM2	EPA 8270C	EPA 3545	Fluorene	86-73-7	FALSE	FALSE	463	37017	20.3	65.8	ug/kg dry	TRUE	NA	10					CHL	58.3	9		
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_18_1	18A3102-04	Soil/Sediment	Soil/Sediment	01/29/2018 22:32:00	02/06/2018 09:46:00	02/26/2018 13:30:56	18B08018	PCBs	EPA8082	EPA 3545	PCB-1016	12674-11-2	FALSE	FALSE	ND	1.42	4.30	ug/kg dry	TRUE	NA	1							CHL	58.3	U	
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_18_1	18A3102-04	Soil/Sediment	Soil/Sediment	01/29/2018 22:32:00	02/06/2018 09:46:00	02/26/2018 13:30:56	18B08018	PCBs	EPA8082	EPA 3545	PCB-1254	11097-69-1	FALSE	FALSE	36.1	1.42	4.30	ug/kg dry	TRUE	NA	1							CHL	58.3	11	
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_18_1	18A3102-04	Soil/Sediment	Soil/Sediment	01/29/2018 22:32:00	02/06/2018 09:46:00	02/26/2018 13:30:56	18B08018	PCBs	EPA8082	EPA 3545	PCB-1260	11096-82-5	FALSE	FALSE	38.3	1.42	4.30	ug/kg dry	TRUE	NA	1							CHL	58.3	13	
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_18_1	18A3102-04	Soil/Sediment	Soil/Sediment	01/29/2018 22:32:00	02/06/2018 09:46:00	02/26/2018 13:30:56	18B08018	PCBs	EPA8082	EPA 3545	2,4,5,6-Tetrachloro-m-xylene	877-09-8	TRUE	FALSE	6.06			ug/kg dry	TRUE	NA	1	101.3	59.8	125	40			CHL	58.3	19	
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_18_1	18A3102-04	Soil/Sediment	Soil/Sediment	01/29/2018 22:32:00	02/06/2018 09:46:00	02/26/2018 13:30:56	18B08018	PCBs	EPA8082	EPA 3545	Decachlorobiphenyl	2051-24-3	TRUE	FALSE	14.3			ug/kg dry	TRUE	NA	1	101.3	142	125	40			CHL	58.3	S-GC	
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_18_1	18A3102-04	Soil/Sediment	Soil/Sediment	01/29/2018 22:32:00	02/06/2018 09:46:00	02/26/2018 13:30:56	18B08018	PCBs	EPA8082	EPA 3545	PCB-1221	11104-28-2	FALSE	FALSE	ND	1.42	4.30	ug/kg dry	TRUE	NA	1							CHL	58.3	U	
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_18_1	18A3102-04	Soil/Sediment	Soil/Sediment	01/29/2018 22:32:00	02/06/2018 09:46:00	02/26/2018 13:30:56	18B08018	PCBs	EPA8082	EPA 3545	PCB-1232	11141-16-5	FALSE	FALSE	ND	1.42	4.30	ug/kg dry	TRUE	NA	1							CHL	58.3	U	
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_18_1	18A3102-04	Soil/Sediment	Soil/Sediment	01/29/2018 22:32:00	02/06/2018 09:46:00	02/26/2018 13:30:56	18B08018	PCBs	EPA8082	EPA 3545	PCB-1242	53469-21-9	FALSE	FALSE	ND	1.42	4.30	ug/kg dry	TRUE	NA	1							CHL	58.3	U	
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_18_1	18A3102-04	Soil/Sediment	Soil/Sediment	01/29/2018 22:32:00	02/06/2018 09:46:00	02/26/2018 13:30:56	18B08018	PCBs	EPA8082	EPA 3545	PCB-1248	12672-29-6	FALSE	FALSE	20.4	115.2	1.42	4.30	ug/kg dry	TRUE	NA	1							CHL	58.3	9
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_18_2	18A3102-05	Soil/Sediment	Soil/Sediment	01/29/2018 22:44:00	02/08/2018 08:24:00	02/08/2018 08:25:02	18B08018	Solids, Dry Weight	% Calculation	*** DEFAULT PREP * % Solids	NA	FALSE	FALSE	62.5	0.500	0.500	% Solids	FALSE	NA	1						DR	62.5	1			
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_18_2	18A3102-05	Soil/Sediment	Soil/Sediment	01/29/2018 22:44:00	02/06/2018 09:46:00	02/26/2018 10:56:14	18B08018	PAH SM2	EPA 8270C	EPA 3545	Naphthalene	91-20-3	FALSE	FALSE	374	18.9	61.5	ug/kg dry	TRUE	NA	10							CHL	62.5	1	
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_18_2	18A3102-05	Soil/Sediment	Soil/Sediment	01/29/2018 22:44:00	02/06/2018 09:46:00	02/26/2018 10:56:14	18B08018	PAH SM2	EPA 8270C	EPA 3545	Phenanthrene	85-01-8	FALSE	FALSE	9080	94.7	308	ug/kg dry	TRUE	NA	50							CHL	62.5	12	
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_18_2	18A3102-05	Soil/Sediment	Soil/Sediment	01/29/2018 22:44:00	02/06/2018 09:46:00	02/26/2018 10:56:14	18B08018	PAH SM2	EPA 8270C	EPA 3545	Anthracene	120-12-7	FALSE	FALSE	4400	94.7	308	ug/kg dry	TRUE	NA	50							CHL	62.5	13	
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_18_2	18A3102-05	Soil/Sediment	Soil/Sediment	01/29/2018 22:44:00	02/06/2018 09:46:00	02/26/2018 10:56:14	18B08018	PAH SM2	EPA 8270C	EPA 3545	Fluoranthene	206-44-0	FALSE	FALSE	13000	94.7	308	ug/kg dry	TRUE	NA	50							CHL	62.5	17	
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_18_2	18A3102-05	Soil/Sediment	Soil/Sediment	01/29/2018 22:44:00	02/06/2018 09:46:00	02/26/2018 10:56:14	18B08018	PAH SM2	EPA 8270C	EPA 3545	Pyrene	129-00-0	FALSE	FALSE	16000	94.7	308	ug/kg dry	TRUE	NA	50							CHL	62.5	18	
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_18_2	18A3102-05	Soil/Sediment	Soil/Sediment	01/29/2018 22:44:00	02/06/2018 09:46:00	02/26/2018 10:56:14	18B08018	PAH SM2	EPA 8270C	EPA 3545	2-Methylnaphthalene	91-20-3	FALSE	FALSE	121	18.9	61.5	ug/kg dry	TRUE	NA	10							CHL	62.5	2	
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_18_2	18A3102-05	Soil/Sediment	Soil/Sediment	01/29/2018 22:44:00	02/06/2018 09:46:00	02/26/2018 10:56:14	18B08018	PAH SM2	EPA 8270C	EPA 3545	Benzo (a) anthracene	56-55-3	FALSE	FALSE	3950	94.7	308	ug/kg dry	TRUE	NA	50							CHL	62.5	21	
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_18_2	18A3102-05	Soil/Sediment	Soil/Sediment	01/29/2018 22:44:00	02/06/2018 09:46:00	02/26/2018 10:56:14	18B08018	PAH SM2	EPA 8270C	EPA 3545	Chrysene	218-01-9	FALSE	FALSE	4760	18.9	61.5	ug/kg dry	TRUE	NA	10							CHL	62.5	22	
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_18_2	18A3102-05	Soil/Sediment	Soil/Sediment	01/29/2018 22:44:00	02/06/2018 09:46:00	02/26/2018 10:56:14	18B08018	PAH SM2	EPA 8270C	EPA 3545	Benzo (b) fluoranthene	205-99-2	FALSE	FALSE	1380	18.9	61.5	ug/kg dry	TRUE	NA	10							CHL	62.5	27	
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_18_2	18A3102-05	Soil/Sediment	Soil/Sediment	01/29/2018 22:44:00	02/06/2018 09:46:00	02/26/2018 10:56:14	18B08018	PAH SM2	EPA 8270C	EPA 3545	Benzo (k) fluoranthene	207-08-9	FALSE	FALSE	3490	18.9	61.5	ug/kg dry	TRUE	NA	10							CHL	62.5	28	
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_18_2	18A3102-05	Soil/Sediment	Soil/Sediment	01/29/2018 22:44:00	02/06/2018 09:46:00	02/26/2018 10:56:14	18B08018	PAH SM2	EPA 8270C	EPA 3545	Benzo (i) pyrene	50-32-8	FALSE	FALSE	4610	18.9	61.5	ug/kg dry	TRUE	NA	10							CHL	62.5	29	
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_18_2	18A3102-05	Soil/Sediment	Soil/Sediment	01/29/2018 22:44:00	02/06/2018 09:46:00	02/26/2018 10:56:14	18B08018	PAH SM2	EPA 8270C	EPA 3545	1-Methylnaphthalene	90-12-0	FALSE	FALSE	104	18.9	61.5	ug/kg dry	TRUE	NA	10							CHL	62.5	3	
Seattle District	ESTCP	[none]	ERDC-EL-EP-C	LDW_18_2	18A3102-05	Soil/Sediment	Soil/Sediment																												



USACE ERDC-EP-C
3909 Halls Ferry Road
Vicksburg, MS 39180-6199

28 February 2018

Mandy Michealson
Seattle District

-

Seattle, WA -

RE: ESTCP

Enclosed are the results of analyses for samples received by the laboratory on 31-Jan-2018. The samples associated with this report will be held for 90 days from the date of this report. The raw data associated with this report will be held for 5 years from the date of this report. If you need us to hold onto the samples or the data longer than these specified times, you will need to notify us in writing at least 30 days before the expiration dates. If you have any questions concerning this report, please feel free to contact me.

Sincerely,

Jenifer Milam
Database Manager



USACE ERDC-EP-C
3909 Halls Ferry Road
Vicksburg, MS 39180-6199

Seattle District

Project: ESTCP

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Reported:

Seattle WA, -

Project Manager: Mandy Michealson

28-Feb-2018

WORK ORDER SUMMARY

Sample ID	Laboratory ID	Matrix	Date Sampled	Date of Work Order
LDW_1_1	18A3102-01	Soil/Sediment	29-Jan-2018	31-Jan-2018
LDW_1_2	18A3102-02	Soil/Sediment	29-Jan-2018	31-Jan-2018
LDW_1_3	18A3102-03	Soil/Sediment	29-Jan-2018	31-Jan-2018
LDW_1B_1	18A3102-04	Soil/Sediment	29-Jan-2018	31-Jan-2018
LDW_1B_2	18A3102-05	Soil/Sediment	29-Jan-2018	31-Jan-2018
LDW_1B_3	18A3102-06	Soil/Sediment	29-Jan-2018	31-Jan-2018



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Reported:
28-Feb-2018

Case Narrative

No issues were experienced during the analysis of Work Order 18A3102 unless specified below.

Dilutions were required for all samples to fall within the standard concentration calibration curve. The required dilutions varied by sample with 1/10 and 1/50 for samples: 18A3102-01,-04,-05,-06, and the Batch duplicate (B18B018-DUP1). For samples 18A3102-02 and 18A3102-03, dilutions of $\frac{1}{4}$ and $\frac{1}{2}$, respectively, were utilized.

Quality control:

Sample, 18A3102-01, was used as the QC batch duplicate. The RPD for PAH analytes between sample and duplicate were above the accepted QC criteria due to heterogeneous nature of samples which occurs when vast dilution is required.

Matrix Spike and Matrix Spike Duplicate

The recoveries of matrix spike and matrix spike duplicate were drastically higher than the spiked concentration due to high sample concentration of PAH analytes.



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28-Feb-2018

Notes and Definitions

Z-03	See case narrative.
U	Analyte included in the analysis, but not detected
S-GC	Surrogate recovery outside of control limits. The data was accepted based on valid recovery of the remaining surrogate/s.
RPD-06	RPD exceeds acceptance limit.
RPD-03	The RPD value for the sample duplicate or MS/MSD was outside of QC acceptance limits due to matrix interference. QC batch accepted based on LCS and/or LCSD recovery and/or RPD values.
QM-11	The spike recovery was outside of QC acceptance limits for the MS and/or MSD due to inherent analyte concentration greater than the spike concentration. The QC batch was accepted based on LCS and/or LCSD recoveries within the acceptance limits.
Q	Value is outside of acceptance limits.
J	Detected but below the Reporting Limit (Limit of Quantitation); therefore, result is an estimated concentration.
DET	Analyte DETECTED
ND	Analyte NOT DETECTED at or above the reporting limit
NR	Not Reported
dry	Sample results reported on a dry weight basis
RPD	Relative Percent Difference



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28-Feb-2018

LDW_1_1

18A3102-01 (Soil/Sediment)

Analyte	Result	Detection Limit	Reporting Limit	Units	Prepared	Analyzed	Method	Notes

ERDC-EL-EP-C

Semivolatile Organics by GC/MS Selective Ion Monitoring

1-Methylnaphthalene	558	18.6	60.5	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	Z-03
2-Methylnaphthalene	579	18.6	60.5	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	Z-03
Acenaphthene	1280	18.6	60.5	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	Z-03
Acenaphthylene	679	18.6	60.5	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	Z-03
Anthracene	5030	93.1	303	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	Z-03
Benzo (a) anthracene	4110	93.1	303	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	Z-03
Benzo (a) pyrene	5160	18.6	60.5	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	Z-03
Benzo (b) fluoranthene	1280	18.6	60.5	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	Z-03
Benzo (g,h,i) perylene	1380	18.6	60.5	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	Z-03
Benzo (k) fluoranthene	3930	18.6	60.5	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	Z-03
Chrysene	4780	93.1	303	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	Z-03
Dibenz (a,h) anthracene	447	18.6	60.5	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	Z-03
Fluoranthene	13900	93.1	303	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	Z-03
Fluorene	1190	18.6	60.5	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	Z-03
Indeno (1,2,3-cd) pyrene	1610	18.6	60.5	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	Z-03
Naphthalene	753	18.6	60.5	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	Z-03
Phenanthrene	12600	93.1	303	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	Z-03
Pyrene	14600	93.1	303	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	Z-03
Surrogate: 2-Fluorobiphenyl	40		42.7 %	40-105	06-Feb-2018	26-Feb-2018	EPA 8270C	
Surrogate: Terphenyl-d14	78		83.8 %	30-125	06-Feb-2018	26-Feb-2018	EPA 8270C	

Classical Chemistry Parameters

% Solids	63.3	0.500	0.500	% Solids	08-Feb-2018	08-Feb-2018	% Calculation	

Polychlorinated Biphenyls by EPA Method 8082

PCB-1016	ND	1.30	3.96	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA8082	U
PCB-1221	ND	1.30	3.96	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA8082	U
PCB-1232	ND	1.30	3.96	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA8082	U
PCB-1242	ND	1.30	3.96	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA8082	U
PCB-1248	15.6	1.30	3.96	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA8082	
PCB-1254	30.9	1.30	3.96	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA8082	
PCB-1260	26.7	1.30	3.96	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA8082	
Surrogate: 2,4,5,6 Tetrachloro-m-xylene	5.90		63.3 %	40-125	06-Feb-2018	26-Feb-2018	EPA8082	
Surrogate: Decachlorobiphenyl	8.47		90.9 %	40-125	06-Feb-2018	26-Feb-2018	EPA8082	

The results in this report apply to the samples analyzed in accordance with the chain of custody document. This analytical report must be reproduced in its entirety.



USACE ERDC-EP-C
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Seattle District

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Seattle WA, -

Project Manager: Mandy Michealson

28-Feb-2018

LDW_1_2

18A3102-02 (Soil/Sediment)

Analyte	Result	Detection Limit	Reporting Limit	Units	Prepared	Analyzed	Method	Notes

ERDC-EL-EP-C

Semivolatile Organics by GC/MS Selective Ion Monitoring

1-Methylnaphthalene	24.3	7.54	24.5	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	J
2-Methylnaphthalene	42.3	7.54	24.5	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Acenaphthene	35.2	7.54	24.5	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Acenaphthylene	41.7	7.54	24.5	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Anthracene	162	7.54	24.5	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Benzo (a) anthracene	582	7.54	24.5	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Benzo (a) pyrene	486	7.54	24.5	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Benzo (b) fluoranthene	208	7.54	24.5	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Benzo (g,h,i) perylene	168	7.54	24.5	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Benzo (k) fluoranthene	403	7.54	24.5	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Chrysene	366	7.54	24.5	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Dibenz (a,h) anthracene	39.8	7.54	24.5	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Fluoranthene	1310	7.54	24.5	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Fluorene	96.8	7.54	24.5	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Indeno (1,2,3-cd) pyrene	237	7.54	24.5	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Naphthalene	139	7.54	24.5	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Phenanthrene	378	7.54	24.5	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Pyrene	1550	7.54	24.5	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Surrogate: 2-Fluorobiphenyl	59		62.3 %	40-105	06-Feb-2018	26-Feb-2018	EPA 8270C	
Surrogate: Terphenyl-d14	71		75.6 %	30-125	06-Feb-2018	26-Feb-2018	EPA 8270C	

Classical Chemistry Parameters

% Solids	63.1	0.500	0.500	% Solids	08-Feb-2018	08-Feb-2018	% Calculation	

Polychlorinated Biphenyls by EPA Method 8082

PCB-1016	ND	1.32	4.00	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA8082	U
PCB-1221	ND	1.32	4.00	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA8082	U
PCB-1232	ND	1.32	4.00	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA8082	U
PCB-1242	ND	1.32	4.00	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA8082	U
PCB-1248	3160	1.32	4.00	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA8082	
PCB-1254	4740	1.32	4.00	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA8082	
PCB-1260	1790	1.32	4.00	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA8082	
Surrogate: 2,4,5,6 Tetrachloro-m-xylene	6.91		73.3 %	40-125	06-Feb-2018	26-Feb-2018	EPA8082	
Surrogate: Decachlorobiphenyl	9.71		103 %	40-125	06-Feb-2018	26-Feb-2018	EPA8082	

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USACE ERDC-EP-C
3909 Halls Ferry Road
Vicksburg, MS 39180-6199

Seattle District

Project: ESTCP

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Reported:

Seattle WA, -

Project Manager: Mandy Michealson

28-Feb-2018

LDW_1_3

18A3102-03 (Soil/Sediment)

Analyte	Result	Detection Limit	Reporting Limit	Units	Prepared	Analyzed	Method	Notes

ERDC-EL-EP-C

Semivolatile Organics by GC/MS Selective Ion Monitoring

1-Methylnaphthalene	5.49	3.36	10.9	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	J
2-Methylnaphthalene	5.89	3.36	10.9	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	J
Acenaphthene	7.13	3.36	10.9	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	J
Acenaphthylene	9.17	3.36	10.9	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	J
Anthracene	68.0	3.36	10.9	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Benzo (a) anthracene	203	3.36	10.9	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Benzo (a) pyrene	172	3.36	10.9	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Benzo (b) fluoranthene	148	3.36	10.9	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Benzo (g,h,i) perylene	71.8	3.36	10.9	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Benzo (k) fluoranthene	152	3.36	10.9	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Chrysene	167	3.36	10.9	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Dibenz (a,h) anthracene	19.0	3.36	10.9	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Fluoranthene	607	3.36	10.9	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Fluorene	19.0	3.36	10.9	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Indeno (1,2,3-cd) pyrene	103	3.36	10.9	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Naphthalene	18.9	3.36	10.9	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Phenanthrene	152	3.36	10.9	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Pyrene	549	3.36	10.9	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Surrogate: 2-Fluorobiphenyl	26		30.8 %	40-105	06-Feb-2018	26-Feb-2018	EPA 8270C	RPD-06
Surrogate: Terphenyl-d14	69		82.2 %	30-125	06-Feb-2018	26-Feb-2018	EPA 8270C	

Classical Chemistry Parameters

% Solids	70.7	0.500	0.500	% Solids	08-Feb-2018	08-Feb-2018	% Calculation	

Polychlorinated Biphenyls by EPA Method 8082

PCB-1016	ND	1.18	3.57	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA8082	U
PCB-1221	ND	1.18	3.57	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA8082	U
PCB-1232	ND	1.18	3.57	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA8082	U
PCB-1242	ND	1.18	3.57	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA8082	U
PCB-1248	11.0	1.18	3.57	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA8082	
PCB-1254	27.8	1.18	3.57	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA8082	
PCB-1260	30.3	1.18	3.57	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA8082	
Surrogate: 2,4,5,6 Tetrachloro-m-xylene	5.09		60.6 %	40-125	06-Feb-2018	26-Feb-2018	EPA8082	
Surrogate: Decachlorobiphenyl	8.19		97.4 %	40-125	06-Feb-2018	26-Feb-2018	EPA8082	

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USACE ERDC-EP-C
3909 Halls Ferry Road
Vicksburg, MS 39180-6199

Seattle District
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 Seattle WA, -

Project: ESTCP

Project Manager: Mandy Michealson

Reported:
 28-Feb-2018

LDW_1B_1
18A3102-04 (Soil/Sediment)

Analyte	Result	Detection Limit	Reporting Limit	Units	Prepared	Analyzed	Method	Notes

ERDC-EL-EP-C

Semivolatile Organics by GC/MS Selective Ion Monitoring

1-Methylnaphthalene	104	20.3	65.8	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
2-Methylnaphthalene	138	20.3	65.8	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Acenaphthene	286	20.3	65.8	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Acenaphthylene	154	20.3	65.8	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Anthracene	3870	101	329	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Benzo (a) anthracene	2300	20.3	65.8	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Benzo (a) pyrene	1720	20.3	65.8	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Benzo (b) fluoranthene	1450	20.3	65.8	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Benzo (g,h,i) perylene	662	20.3	65.8	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Benzo (k) fluoranthene	1520	20.3	65.8	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Chrysene	1760	20.3	65.8	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Dibenz (a,h) anthracene	154	20.3	65.8	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Fluoranthene	4650	101	329	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Fluorene	463	20.3	65.8	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Indeno (1,2,3-cd) pyrene	968	20.3	65.8	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Naphthalene	429	20.3	65.8	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Phenanthrene	11200	101	329	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Pyrene	4980	101	329	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Surrogate: 2-Fluorobiphenyl	51		50.0 %	40-105	06-Feb-2018	26-Feb-2018	EPA 8270C	
Surrogate: Terphenyl-d14	100		99.1 %	30-125	06-Feb-2018	26-Feb-2018	EPA 8270C	

Classical Chemistry Parameters

% Solids	58.3	0.500	0.500	% Solids	08-Feb-2018	08-Feb-2018	% Calculation	

Polychlorinated Biphenyls by EPA Method 8082

PCB-1016	ND	1.42	4.30	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA8082	U
PCB-1221	ND	1.42	4.30	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA8082	U
PCB-1232	ND	1.42	4.30	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA8082	U
PCB-1242	ND	1.42	4.30	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA8082	U
PCB-1248	20.4	1.42	4.30	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA8082	
PCB-1254	36.1	1.42	4.30	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA8082	
PCB-1260	38.3	1.42	4.30	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA8082	
Surrogate: 2,4,5,6 Tetrachloro-m-xylene	6.06		59.8 %	40-125	06-Feb-2018	26-Feb-2018	EPA8082	
Surrogate: Decachlorobiphenyl	14.3		142 %	40-125	06-Feb-2018	26-Feb-2018	EPA8082	S-GC

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USACE ERDC-EP-C
3909 Halls Ferry Road
Vicksburg, MS 39180-6199

Seattle District

Project: ESTCP

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Reported:

Seattle WA, -

Project Manager: Mandy Michealson

28-Feb-2018

LDW_1B_2

18A3102-05 (Soil/Sediment)

Analyte	Result	Detection Limit	Reporting Limit	Units	Prepared	Analyzed	Method	Notes

ERDC-EL-EP-C

Semivolatile Organics by GC/MS Selective Ion Monitoring

1-Methylnaphthalene	104	18.9	61.5	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
2-Methylnaphthalene	112	18.9	61.5	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Acenaphthene	535	18.9	61.5	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Acenaphthylene	217	18.9	61.5	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Anthracene	4400	94.7	308	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Benzo (a) anthracene	3950	94.7	308	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Benzo (a) pyrene	4610	18.9	61.5	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Benzo (b) fluoranthene	1380	18.9	61.5	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Benzo (g,h,i) perylene	1250	18.9	61.5	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Benzo (k) fluoranthene	3490	18.9	61.5	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Chrysene	4760	18.9	61.5	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Dibenz (a,h) anthracene	339	18.9	61.5	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Fluoranthene	13000	94.7	308	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Fluorene	2370	18.9	61.5	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Indeno (1,2,3-cd) pyrene	1920	18.9	61.5	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Naphthalene	374	18.9	61.5	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Phenanthrene	9080	94.7	308	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Pyrene	16300	94.7	308	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Surrogate: 2-Fluorobiphenyl	40		42.1 %	40-105	06-Feb-2018	26-Feb-2018	EPA 8270C	
Surrogate: Terphenyl-d14	86		90.7 %	30-125	06-Feb-2018	26-Feb-2018	EPA 8270C	

Classical Chemistry Parameters

% Solids	62.5	0.500	0.500	% Solids	08-Feb-2018	08-Feb-2018	% Calculation	

Polychlorinated Biphenyls by EPA Method 8082

PCB-1016	ND	1.33	4.02	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA8082	U
PCB-1221	ND	1.33	4.02	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA8082	U
PCB-1232	ND	1.33	4.02	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA8082	U
PCB-1242	ND	1.33	4.02	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA8082	U
PCB-1248	26.6	1.33	4.02	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA8082	
PCB-1254	31.4	1.33	4.02	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA8082	
PCB-1260	14.7	1.33	4.02	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA8082	
Surrogate: 2,4,5,6 Tetrachloro-m-xylene	6.18		65.3 %	40-125	06-Feb-2018	26-Feb-2018	EPA8082	
Surrogate: Decachlorobiphenyl	7.78		82.2 %	40-125	06-Feb-2018	26-Feb-2018	EPA8082	

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USACE ERDC-EP-C
3909 Halls Ferry Road
Vicksburg, MS 39180-6199

Seattle District
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 Seattle WA, -

Project: ESTCP

Project Manager: Mandy Michealson

Reported:
 28-Feb-2018

LDW_1B_3
18A3102-06 (Soil/Sediment)

Analyte	Result	Detection Limit	Reporting Limit	Units	Prepared	Analyzed	Method	Notes

ERDC-EL-EP-C

Semivolatile Organics by GC/MS Selective Ion Monitoring

1-Methylnaphthalene	45.3	18.9	61.5	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	J
2-Methylnaphthalene	67.7	18.9	61.5	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Acenaphthene	125	18.9	61.5	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Acenaphthylene	91.6	18.9	61.5	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Anthracene	1270	18.9	61.5	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Benzo (a) anthracene	5660	18.9	61.5	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Benzo (a) pyrene	3420	18.9	61.5	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Benzo (b) fluoranthene	2430	18.9	61.5	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Benzo (g,h,i) perylene	1020	18.9	61.5	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Benzo (k) fluoranthene	2390	18.9	61.5	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Chrysene	3740	18.9	61.5	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Dibenz (a,h) anthracene	231	18.9	61.5	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Fluoranthene	10700	94.6	307	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Fluorene	355	18.9	61.5	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Indeno (1,2,3-cd) pyrene	1530	18.9	61.5	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Naphthalene	260	18.9	61.5	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Phenanthrene	1890	18.9	61.5	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Pyrene	9240	94.6	307	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA 8270C	
Surrogate: 2-Fluorobiphenyl	40		42.2 %	40-105	06-Feb-2018	26-Feb-2018	EPA 8270C	
Surrogate: Terphenyl-d14	73		77.2 %	30-125	06-Feb-2018	26-Feb-2018	EPA 8270C	

Classical Chemistry Parameters

% Solids	62.4	0.500	0.500	% Solids	08-Feb-2018	08-Feb-2018	% Calculation	

Polychlorinated Biphenyls by EPA Method 8082

PCB-1016	ND	1.32	4.02	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA8082	U
PCB-1221	ND	1.32	4.02	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA8082	U
PCB-1232	ND	1.32	4.02	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA8082	U
PCB-1242	ND	1.32	4.02	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA8082	U
PCB-1248	34.5	1.32	4.02	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA8082	
PCB-1254	62.5	1.32	4.02	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA8082	
PCB-1260	20.9	1.32	4.02	ug/kg dry	06-Feb-2018	26-Feb-2018	EPA8082	
Surrogate: 2,4,5,6 Tetrachloro-m-xylene	6.80		71.9 %	40-125	06-Feb-2018	26-Feb-2018	EPA8082	
Surrogate: Decachlorobiphenyl	8.94		94.6 %	40-125	06-Feb-2018	26-Feb-2018	EPA8082	

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USACE ERDC-EP-C
3909 Halls Ferry Road
Vicksburg, MS 39180-6199

Seattle District

Project: ESTCP

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Reported:

Seattle WA, -

Project Manager: Mandy Michealson

28-Feb-2018

Semivolatile Organics by GC/MS Selective Ion Monitoring - Quality Control

ERDC-EL-EP-C

Analyte	Result	Detection Limit	Reporting Limit	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Notes

Batch B18B018 - EPA 3545

Blank (B18B018-BLK1)

Prepared: 06-Feb-2018 Analyzed: 26-Feb-2018

1-Methylnaphthalene	ND	1.20	3.90 ug/kg wet								U
2-Methylnaphthalene	ND	1.20	3.90 ug/kg wet								U
Acenaphthene	ND	1.20	3.90 ug/kg wet								U
Acenaphthylene	ND	1.20	3.90 ug/kg wet								U
Anthracene	ND	1.20	3.90 ug/kg wet								U
Benzo (a) anthracene	ND	1.20	3.90 ug/kg wet								U
Benzo (a) pyrene	ND	1.20	3.90 ug/kg wet								U
Benzo (b) fluoranthene	ND	1.20	3.90 ug/kg wet								U
Benzo (g,h,i) perylene	ND	1.20	3.90 ug/kg wet								U
Benzo (k) fluoranthene	ND	1.20	3.90 ug/kg wet								U
Chrysene	ND	1.20	3.90 ug/kg wet								U
Dibenz (a,h) anthracene	ND	1.20	3.90 ug/kg wet								U
Fluoranthene	ND	1.20	3.90 ug/kg wet								U
Fluorene	ND	1.20	3.90 ug/kg wet								U
Indeno (1,2,3-cd) pyrene	ND	1.20	3.90 ug/kg wet								U
Naphthalene	ND	1.20	3.90 ug/kg wet								U
Phenanthrene	ND	1.20	3.90 ug/kg wet								U
Pyrene	ND	1.20	3.90 ug/kg wet								U
Surrogate: 2-Fluorobiphenyl	40		ug/kg wet		60.00		66.9	40-105			
Surrogate: Terphenyl-d14	42		ug/kg wet		60.00		70.8	30-125			

The results in this report apply to the samples analyzed in accordance with the chain of custody document. This analytical report must be reproduced in its entirety.



USACE ERDC-EP-C
3909 Halls Ferry Road
Vicksburg, MS 39180-6199

Seattle District

Project: ESTCP

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Reported:

Seattle WA, -

Project Manager: Mandy Michealson

28-Feb-2018

Semivolatile Organics by GC/MS Selective Ion Monitoring - Quality Control

ERDC-EL-EP-C

Analyte	Result	Detection Limit	Reporting Limit	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Notes

Batch B18B018 - EPA 3545

LCS (B18B018-BS1)

Prepared: 06-Feb-2018 Analyzed: 26-Feb-2018

1-Methylnaphthalene	33.9	1.20	3.90 ug/kg wet	60.00			56.5	40-105			
2-Methylnaphthalene	39.4	1.20	3.90 ug/kg wet	60.00			65.7	40-105			
Acenaphthene	31.6	1.20	3.90 ug/kg wet	60.00			52.7	45-110			
Acenaphthylene	34.7	1.20	3.90 ug/kg wet	60.00			57.8	45-110			
Anthracene	38.1	1.20	3.90 ug/kg wet	60.00			63.4	50-115			
Benzo (a) anthracene	46.9	1.20	3.90 ug/kg wet	60.00			78.1	50-125			
Benzo (a) pyrene	42.6	1.20	3.90 ug/kg wet	60.00			70.9	50-130			
Benzo (b) fluoranthene	47.4	1.20	3.90 ug/kg wet	60.00			79.1	45-130			
Benzo (g,h,i) perylene	52.8	1.20	3.90 ug/kg wet	60.00			87.9	40-125			
Benzo (k) fluoranthene	41.7	1.20	3.90 ug/kg wet	60.00			69.5	45-130			
Chrysene	43.0	1.20	3.90 ug/kg wet	60.00			71.6	50-125			
Dibenz (a,h) anthracene	55.1	1.20	3.90 ug/kg wet	60.00			91.8	40-125			
Fluoranthene	43.9	1.20	3.90 ug/kg wet	60.00			73.2	50-120			
Fluorene	46.4	1.20	3.90 ug/kg wet	60.00			77.3	50-110			
Indeno (1,2,3-cd) pyrene	52.3	1.20	3.90 ug/kg wet	60.00			87.1	40-125			
Naphthalene	34.5	1.20	3.90 ug/kg wet	60.00			57.5	40-105			
Phenanthrene	39.6	1.20	3.90 ug/kg wet	60.00			66.0	50-130			
Pyrene	35.3	1.20	3.90 ug/kg wet	60.00			58.8	45-125			
Surrogate: 2-Fluorobiphenyl	37		ug/kg wet	60.00			61.4	40-105			
Surrogate: Terphenyl-d14	35		ug/kg wet	60.00			57.5	30-125			

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28-Feb-2018

Semivolatile Organics by GC/MS Selective Ion Monitoring - Quality Control

ERDC-EL-EP-C

Analyte	Result	Detection Limit	Reporting Limit	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Notes

Batch B18B018 - EPA 3545

LCS Dup (B18B018-BSD1)

Prepared: 06-Feb-2018 Analyzed: 26-Feb-2018

1-Methylnaphthalene	36.0	1.20	3.90 ug/kg wet	60.00			60.0	40-105	6.06	30	
2-Methylnaphthalene	39.7	1.20	3.90 ug/kg wet	60.00			66.1	40-105	0.647	30	
Acenaphthene	27.2	1.20	3.90 ug/kg wet	60.00			45.3	45-110	15.1	30	
Acenaphthylene	43.5	1.20	3.90 ug/kg wet	60.00			72.6	45-110	22.6	30	
Anthracene	37.8	1.20	3.90 ug/kg wet	60.00			63.0	50-115	0.749	30	
Benzo (a) anthracene	48.7	1.20	3.90 ug/kg wet	60.00			81.2	50-125	3.90	30	
Benzo (a) pyrene	43.2	1.20	3.90 ug/kg wet	60.00			71.9	50-130	1.40	30	
Benzo (b) fluoranthene	42.9	1.20	3.90 ug/kg wet	60.00			71.4	45-130	10.1	30	
Benzo (g,h,i) perylene	51.0	1.20	3.90 ug/kg wet	60.00			85.0	40-125	3.44	30	
Benzo (k) fluoranthene	43.0	1.20	3.90 ug/kg wet	60.00			71.7	45-130	3.16	30	
Chrysene	44.5	1.20	3.90 ug/kg wet	60.00			74.1	50-125	3.48	30	
Dibenz (a,h) anthracene	49.3	1.20	3.90 ug/kg wet	60.00			82.2	40-125	11.1	30	
Fluoranthene	56.5	1.20	3.90 ug/kg wet	60.00			94.2	50-120	25.0	30	
Fluorene	28.2	1.20	3.90 ug/kg wet	60.00			47.1	50-110	48.6	30	Q, RPD-06
Indeno (1,2,3-cd) pyrene	51.7	1.20	3.90 ug/kg wet	60.00			86.2	40-125	1.07	30	
Naphthalene	37.2	1.20	3.90 ug/kg wet	60.00			62.0	40-105	7.53	30	
Phenanthrene	54.2	1.20	3.90 ug/kg wet	60.00			90.2	50-130	31.1	30	RPD-06
Pyrene	36.9	1.20	3.90 ug/kg wet	60.00			61.5	45-125	4.39	30	
Surrogate: 2-Fluorobiphenyl	40		ug/kg wet	60.00			66.5	40-105			
Surrogate: Terphenyl-d14	37		ug/kg wet	60.00			61.0	30-125			

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Semivolatile Organics by GC/MS Selective Ion Monitoring - Quality Control

ERDC-EL-EP-C

Analyte	Result	Detection Limit	Reporting Limit	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Notes

Batch B18B018 - EPA 3545

Duplicate (B18B018-DUP1)	Source: 18A3102-01			Prepared: 06-Feb-2018 Analyzed: 26-Feb-2018							
1-Methylnaphthalene	315	18.8	61.1 ug/kg dry		558				55.6	30	RPD-03, Z-03
2-Methylnaphthalene	336	18.8	61.1 ug/kg dry		579				53.0	30	RPD-03, Z-03
Acenaphthene	583	18.8	61.1 ug/kg dry		1280				74.7	30	RPD-03, Z-03
Acenaphthylene	274	18.8	61.1 ug/kg dry		679				84.8	30	RPD-03, Z-03
Anthracene	304	18.8	61.1 ug/kg dry		5030				177	30	RPD-03, Z-03
Benzo (a) anthracene	3890	18.8	61.1 ug/kg dry		4110				5.47	30	Z-03
Benzo (a) pyrene	2510	18.8	61.1 ug/kg dry		5160				69.0	30	RPD-03, Z-03
Benzo (b) fluoranthene	1560	18.8	61.1 ug/kg dry		1280				19.6	30	Z-03
Benzo (g,h,i) perylene	776	18.8	61.1 ug/kg dry		1380				55.7	30	RPD-03, Z-03
Benzo (k) fluoranthene	1870	18.8	61.1 ug/kg dry		3930				70.8	30	RPD-03, Z-03
Chrysene	3030	18.8	61.1 ug/kg dry		4780				44.6	30	RPD-03, Z-03
Dibenz (a,h) anthracene	253	18.8	61.1 ug/kg dry		447				55.4	30	RPD-03, Z-03
Fluoranthene	4970	94.0	306 ug/kg dry		13900				94.8	30	RPD-03, Z-03
Fluorene	585	18.8	61.1 ug/kg dry		1190				68.2	30	RPD-03, Z-03
Indeno (1,2,3-cd) pyrene	1110	18.8	61.1 ug/kg dry		1610				37.2	30	RPD-03, Z-03
Naphthalene	505	18.8	61.1 ug/kg dry		753				39.4	30	RPD-03, Z-03
Phenanthrene	5980	94.0	306 ug/kg dry		12600				71.0	30	RPD-03, Z-03
Pyrene	5920	94.0	306 ug/kg dry		14600				84.4	30	RPD-03, Z-03
Surrogate: 2-Fluorobiphenyl	33		ug/kg dry		94.05		35.6	40-105			S-GC
Surrogate: Terphenyl-d14	72		ug/kg dry		94.05		77.0	30-125			

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28-Feb-2018

Semivolatile Organics by GC/MS Selective Ion Monitoring - Quality Control

ERDC-EL-EP-C

Analyte	Result	Detection Limit	Reporting Limit	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Notes

Batch B18B018 - EPA 3545

Matrix Spike (B18B018-MS1)

Source: 18A3102-04

Prepared: 06-Feb-2018 Analyzed: 26-Feb-2018

1-Methylnaphthalene	189	2.05	6.68 ug/kg dry	102.7	104	82.5	40-105				Z-03
2-Methylnaphthalene	225	2.05	6.68 ug/kg dry	102.7	138	84.8	40-105				Z-03
Acenaphthene	259	2.05	6.68 ug/kg dry	102.7	286	NR	45-110				QM-11, Z-03
Acenaphthylene	283	2.05	6.68 ug/kg dry	102.7	154	125	45-110				QM-11, Z-03
Anthracene	2030	2.05	6.68 ug/kg dry	102.7	3870	NR	50-115				QM-11, Z-03
Benzo (a) anthracene	7350	2.05	6.68 ug/kg dry	102.7	2300	NR	50-125				QM-11, Z-03
Benzo (a) pyrene	4470	2.05	6.68 ug/kg dry	102.7	1720	NR	50-130				QM-11, Z-03
Benzo (b) fluoranthene	2760	2.05	6.68 ug/kg dry	102.7	1450	NR	45-130				QM-11, Z-03
Benzo (g,h,i) perylene	1580	2.05	6.68 ug/kg dry	102.7	662	893	40-125				QM-11, Z-03
Benzo (k) fluoranthene	2640	2.05	6.68 ug/kg dry	102.7	1520	NR	45-130				QM-11, Z-03
Chrysene	3660	2.05	6.68 ug/kg dry	102.7	1760	NR	50-125				QM-11, Z-03
Dibenz (a,h) anthracene	507	2.05	6.68 ug/kg dry	102.7	154	344	40-125				QM-11, Z-03
Fluoranthene	18600	2.05	6.68 ug/kg dry	102.7	4650	NR	50-120				QM-11, Z-03
Fluorene	360	2.05	6.68 ug/kg dry	102.7	463	NR	50-110				QM-11, Z-03
Indeno (1,2,3-cd) pyrene	2400	2.05	6.68 ug/kg dry	102.7	968	NR	40-125				QM-11, Z-03
Naphthalene	533	2.05	6.68 ug/kg dry	102.7	429	102	40-105				Z-03
Phenanthrene	2680	2.05	6.68 ug/kg dry	102.7	11200	NR	50-130				QM-11, Z-03
Pyrene	7850	2.05	6.68 ug/kg dry	102.7	4980	NR	45-125				QM-11, Z-03
Surrogate: 2-Fluorobiphenyl	61		ug/kg dry	102.7		59.1	40-105				
Surrogate: Terphenyl-d14	79		ug/kg dry	102.7		77.2	30-125				

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Semivolatile Organics by GC/MS Selective Ion Monitoring - Quality Control

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Analyte	Result	Detection Limit	Reporting Limit	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Notes

Batch B18B018 - EPA 3545

Matrix Spike Dup (B18B018-MSD1)

Source: 18A3102-04

Prepared: 06-Feb-2018 Analyzed: 26-Feb-2018

1-Methylnaphthalene	277	2.04	6.64 ug/kg dry	102.2	104	169	40-105	37.8	30	QM-11, RPD-03,
2-Methylnaphthalene	333	2.04	6.64 ug/kg dry	102.2	138	191	40-105	38.8	30	QM-11, RPD-03,
Acenaphthene	526	2.04	6.64 ug/kg dry	102.2	286	235	45-110	68.2	30	QM-11, RPD-03,
Acenaphthylene	284	2.04	6.64 ug/kg dry	102.2	154	127	45-110	0.326	30	QM-11, Z-03
Anthracene	1910	2.04	6.64 ug/kg dry	102.2	3870	NR	50-115	5.77	30	QM-11, Z-03
Benzo (a) anthracene	6530	2.04	6.64 ug/kg dry	102.2	2300	NR	50-125	11.8	30	QM-11, Z-03
Benzo (a) pyrene	4440	2.04	6.64 ug/kg dry	102.2	1720	NR	50-130	0.792	30	QM-11, Z-03
Benzo (b) fluoranthene	2990	2.04	6.64 ug/kg dry	102.2	1450	NR	45-130	8.11	30	QM-11, Z-03
Benzo (g,h,i) perylene	1820	2.04	6.64 ug/kg dry	102.2	662	NR	40-125	14.1	30	QM-11, Z-03
Benzo (k) fluoranthene	2360	2.04	6.64 ug/kg dry	102.2	1520	822	45-130	11.2	30	QM-11, Z-03
Chrysene	3390	2.04	6.64 ug/kg dry	102.2	1760	NR	50-125	7.55	30	QM-11, Z-03
Dibenz (a,h) anthracene	597	2.04	6.64 ug/kg dry	102.2	154	434	40-125	16.4	30	QM-11, Z-03
Fluoranthene	18300	2.04	6.64 ug/kg dry	102.2	4650	NR	50-120	1.40	30	QM-11, Z-03
Fluorene	1230	2.04	6.64 ug/kg dry	102.2	463	750	50-110	110	30	QM-11, RPD-03,
Indeno (1,2,3-cd) pyrene	3080	2.04	6.64 ug/kg dry	102.2	968	NR	40-125	25.1	30	QM-11, Z-03
Naphthalene	613	2.04	6.64 ug/kg dry	102.2	429	180	40-105	13.9	30	QM-11, Z-03
Phenanthrene	5280	2.04	6.64 ug/kg dry	102.2	11200	NR	50-130	65.4	30	QM-11, RPD-03,
Pyrene	9620	2.04	6.64 ug/kg dry	102.2	4980	NR	45-125	20.3	30	QM-11, Z-03
Surrogate: 2-Fluorobiphenyl	62		ug/kg dry	102.2		61.1	40-105			
Surrogate: Terphenyl-d14	86		ug/kg dry	102.2		84.4	30-125			

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Semivolatile Organics by GC/MS Selective Ion Monitoring - Quality Control

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Analyte	Result	Detection Limit	Reporting Limit	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Notes

Polychlorinated Biphenyls by EPA Method 8082 - Quality Control

ERDC-EL-EP-C

Analyte	Result	Detection Limit	Reporting Limit	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Notes

Batch B18B018 - EPA 3545

Blank (B18B018-BLK1)

Prepared: 06-Feb-2018 Analyzed: 26-Feb-2018

PCB-1016	ND	0.84	2.55 ug/kg wet								U
PCB-1221	ND	0.84	2.55 ug/kg wet								U
PCB-1232	ND	0.84	2.55 ug/kg wet								U
PCB-1242	ND	0.84	2.55 ug/kg wet								U
PCB-1248	ND	0.84	2.55 ug/kg wet								U
PCB-1254	ND	0.84	2.55 ug/kg wet								U
PCB-1260	ND	0.84	2.55 ug/kg wet								U
Surrogate: 2,4,5,6 Tetrachloro-m-xylene	3.25		ug/kg wet	6.000		54.2	40-125				
Surrogate: Decachlorobiphenyl	4.40		ug/kg wet	6.000		73.3	40-125				

LCS (B18B018-BS1)

Prepared: 06-Feb-2018 Analyzed: 26-Feb-2018

PCB-1016	40.5	0.84	2.55 ug/kg wet	50.00		81.0	50-140				
PCB-1260	44.7	0.84	2.55 ug/kg wet	50.00		89.4	50-140				
Surrogate: 2,4,5,6 Tetrachloro-m-xylene	4.25		ug/kg wet	6.000		70.8	50-140				
Surrogate: Decachlorobiphenyl	5.44		ug/kg wet	6.000		90.7	50-140				

LCS Dup (B18B018-BSD1)

Prepared: 06-Feb-2018 Analyzed: 26-Feb-2018

PCB-1016	39.0	0.84	2.55 ug/kg wet	50.00		78.0	50-140	3.84	30		
PCB-1260	36.8	0.84	2.55 ug/kg wet	50.00		73.5	50-140	19.4	30		
Surrogate: 2,4,5,6 Tetrachloro-m-xylene	4.10		ug/kg wet	6.000		68.3	50-140				
Surrogate: Decachlorobiphenyl	1.27		ug/kg wet	6.000		21.2	50-140				S-GC

Duplicate (B18B018-DUP1)

Source: 18A3102-01

Prepared: 06-Feb-2018 Analyzed: 26-Feb-2018

PCB-1016	ND	1.32	4.00 ug/kg dry		ND				30		U
PCB-1221	ND	1.32	4.00 ug/kg dry		ND				30		U
PCB-1232	ND	1.32	4.00 ug/kg dry		ND				30		U
PCB-1242	ND	1.32	4.00 ug/kg dry		ND				30		U
PCB-1248	17.8	1.32	4.00 ug/kg dry		15.6				13.0	30	
PCB-1254	46.4	1.32	4.00 ug/kg dry		30.9				40.0	30	RPD-06
PCB-1260	36.4	1.32	4.00 ug/kg dry		26.7				30.6	30	RPD-06
Surrogate: 2,4,5,6 Tetrachloro-m-xylene	7.21		ug/kg dry	9.405		76.6	40-125				
Surrogate: Decachlorobiphenyl	10.9		ug/kg dry	9.405		116	40-125				

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Polychlorinated Biphenyls by EPA Method 8082 - Quality Control

ERDC-EL-EP-C

Analyte	Detection Result	Detection Limit	Reporting Limit	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Notes

Batch B18B018 - EPA 3545

Matrix Spike (B18B018-MS1)		Source: 18A3102-04			Prepared: 06-Feb-2018 Analyzed: 26-Feb-2018						
PCB-1016	81.3	1.44	4.36 ug/kg dry	85.58	ND	95.0	40-140				
PCB-1260	107	1.44	4.36 ug/kg dry	85.58	38.3	80.8	40-140				
Surrogate: 2,4,5,6 Tetrachloro-m-xylene	7.09		ug/kg dry	10.27		69.1	40-140				
Surrogate: Decachlorobiphenyl	14.0		ug/kg dry	10.27		136	40-140				
Matrix Spike Dup (B18B018-MSD1)		Source: 18A3102-04			Prepared: 06-Feb-2018 Analyzed: 26-Feb-2018						
PCB-1016	63.3	1.43	4.34 ug/kg dry	85.18	ND	74.4	40-140	24.8	30		
PCB-1260	114	1.43	4.34 ug/kg dry	85.18	38.3	89.3	40-140	6.25	30		
Surrogate: 2,4,5,6 Tetrachloro-m-xylene	6.96		ug/kg dry	10.22		68.1	40-140				
Surrogate: Decachlorobiphenyl	15.5		ug/kg dry	10.22		152	40-140				S-GC



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Items for Project Manager Review

LabNumber	Analysis	Analyte	Exception

APPENDIX B

Standardized polymeric sampler methods

PDMS TASK 3 INSTRUCTIONS

Task 3: Loading of Performance Reference Compounds (PRCs) (C13-PCBs or C13-PAHs) and Ex-situ study.

Note: Please refer to the standard operating procedure (SOP) for details on preparation and extraction of polydimethylsiloxane fibers. Information provided below should be used in conjunction with the SOP.

Part A: PRC loading on PDMS

Step 1: For this task, the desired concentration of PRCs in extract after analysis is 30 ng per mL of extract (high resolution) and 100 ng/mL (low resolution) for C13 PCBs/PAHs.

Step 2: The length of PDMS per sample (extract) is 10 cm for C13 PCBs and 2 cm for C13-PAHs. Minimum of six replicates is required for initial PRC concentration and six replicates (*triplicates active* and *triplicates passive*) for ex-situ contaminants analysis and an assumption of three replicates for quality control. Therefore,

- For PCBs, the total amount of PDMS needed for the loading and sampling exercise is **30** pieces of **5** cm segments resulting in a total fiber length of **150** cm. Choose a vessel to accommodate the PDMS and water-methanol (80:20) inside without much headspace (here 120 mL amber glass bottle is used). For the PDMS length (**10** cm) and extract volume (**100** μ L for high sensitivity and **50** μ L for low resolution), calculate the concentration in PDMS. Here, the calculated concentration for each PRC in PDMS is **474** ng/mL for High sensitivity and is **790** ng/mL for Low resolution. Use the PDMS-water partition coefficients (Ghosh et al., 2014) to calculate the concentration in water (only) at equilibrium ($C_{w,eq}$).
- For PAHs, 15 pieces of 5 cm segment (resulting in 75 cm length of fiber) is provided. 120 mL volume of amber vessel is likewise used to accommodate the fiber and water-methanol (80:20) solution. Although 5 cm length PDMS fiber will be required for loading, only 2 cm length will be used for extraction. Here, the 2 cm length fiber per extract volume (**500** μ L for high sensitivity and **200** μ L for low resolution) is required. Therefore, the concentration for each PRC in PDMS is **11844** ng/mL for High sensitivity and is **15792** ng/mL for Low resolution. The additional 3 cm can be used as contingency samplers or as additional replication, if needed.

Step 3. Solve for initial solution concentration of PRCs ($C_{initial\ solution}$, ng/mL) that result in the PRC loadings in the PDMS:

$$C_{initial\ solution} = \frac{C_{PDMS} \times L_{fiber} \times V_{PDMS} + C_{w,eq} \times V_W}{V_W} \quad (1)$$

where, C_{PDMS} is the concentration of PRC in PDMS (e.g 474 ng/mL for high sensitivity instruments), L_{fiber} is the fiber length, V_{PDMS} is the volume of PDMS coating (0.633 μ L/cm for the

fibers provided). $C_{w,eq}$ [is the concentration of PRCs in water at equilibrium and V_W is the volume of water:MeOH (100 mL).

Step 4. The working solution (2500 ng/ml) is prepared by diluting the stock solution (concentration of 40000 ng/ml for PCBs and 100000 ng/mL for PAHs in nonane) in acetone. Here we used 125 μ L of stock solution for PCBs and 50 μ L for PAHs and diluted with acetone to a final volume of 2000 μ L. Nonane is miscible in acetone. The fraction of nonane in the prepared working standard is 0.06. **Caution should be taken in preparing working standards because of the potential for solvent incompatibility. The solvent ratios employed here lead to homogeneous solutions. Use of different solvents or different solvent amounts may lead to phase separation in the preparation of the working standard or the loading solution which can lead to an inability to achieve targeted PRC concentrations.**

The tables below summarize the number of fibers and the volume of working solution to be added to the PRC solution.

PCBs – High Sensitivity Instruments

			fiber		
Water:MeOH (80:20) volume:	100	ml		5	cm
extract solvent (μ l):	100	μ l		30	No of 5 cm segments
Total fiber spiked:	150	cm		150	total fiber spiked cm
PDMS volume (μ L/cm):	0.633	μ L/cm	Based upon geometry of fibers used		
Fiber length per sample extract:	10	cm			
Working standard needed		18 μ L	(Calculated in worksheet)		

PCBs – Low Sensitivity Instruments

			fiber		
Water:MeOH (80:20) volume:	100	ml		5	Cm
extract solvent (μ l):	50	μ l		30	No of 5 cm segments
Total fiber spiked:	150	cm		150	total fiber spiked cm
PDMS volume (μ L/cm):	0.633	μ L/cm	Based upon geometry of fibers used		
Fiber length per sample extract:	10	cm			
Working standard needed		30 μ L	(Calculated in worksheet)		

PAHs – High Sensitivity Instruments

			fiber		
Water:MeOH (80:20) volume:	100	ml		5	Cm
extract solvent (μ l):	500	μ l		15	No of 5 cm segments
Total fiber spiked:	75	cm		75	total fiber spiked cm
PDMS volume (μ L/cm):	0.633	μ L/cm	Based upon geometry of fibers used		

Fiber length per sample extract:	2	cm	
Working standard needed	247	μL	(Calculated in worksheet)

PAHs – Low Sensitivity Instruments

			fiber	
Water:MeOH (80:20) volume:	100	ml	5	Cm
extract solvent (μl):	200	μl	15	No of 5 cm segments
Total fiber spiked:	75	cm	75	total fiber spiked cm
PDMS volume (μL/cm):	0.633	μL/cm	Based upon geometry of fibers used	
Fiber length per sample extract:	2	cm		
Working standard needed	330	μL		(Calculated in worksheet)

Part B: Confirm PRC loaded concentrations (Co) in PDMS fiber segments *before* proceeding with sediment exposure.

The PRC loading is assumed completed after a minimum of 28 days. The initial PRCs loaded on PDMS must be determined before exposure of the polymer with test sediment.

1. Initial PRC determination, Co (s): Minimum of Six replicates are analyzed for initial PRC concentrations {Co (s)}. For PCBs, 10 cm length per extract (100 μL/HR or 50 μL/LR) is required per sample. And PAHs, 2 cm length of fiber per extract (500 μL/HR or 200 μL/LR) is required for sample (that is, 2 cm is sectioned out of the 5 cm length PDMS length and analyzed).

Extract/analyze PRC-loaded PDMS segments per SOPs and report results to USACE.
Accuracy/precision of Co results must be assessed *before* proceeding with sediment measurement.

Part C: Ex-situ Study- pore water measurement.

1. After confirmation of Co (s), porewater concentration is assessed using the pre-loaded PDMS fibers. The PDMS fiber must be enclosed in a mesh bag before insertion into the sediment. A prototype of the mesh bag is provided and each lab is expected to fabricate their mesh bags from the stainless mesh sheet provided. The mesh bag with PDMS is exposed for 28 days. After exposure to the sediment for 28 days is completed, retrieve the fiber from the sediment and mesh bag. Then, wipe the PDMS fiber with deionized water (DI) wetted kimwipes till it is clean. Dry away the moisture using kimwipes. **Note: DI**

wetted wipes are recommended for cleaning the fiber. The use of solvent such as dichloromethane introduces the risk of analyte loss from PDMS fiber. It is also advised to work as quickly as possible to prevent loss of volatile analytes during PDMS fiber processing.

- For PCBs, **10 cm length of PDMS fiber** is required per sediment jar and prepared per extract volume to assess target PCB congeners.
 - For PAHs, **5 cm length of PDMS** is inserted in sediment jar. However, **only 2 cm length** of this PDMS is sectioned and prepared per extract volume for PAHs analysis.
2. Section the PDMS fiber into smaller lengths (e.g 1 cm) and transfer into inserts.
 3. Add the extract solvent (inclusive of the internal standard, IS). For instance; for **HR C13-PCB, 100 µL of final extract solvent (Hexane + IS)** is advised for extraction and **50 µL of final extract solvent (Hexane + IS)** for **LR C13-PCBs**. For **HR C13-PAHs, 500 µL** is required for extraction of **2 cm length PDMS** and for **LR C13-PAHs, 200 µL** is required for the **2 cm length PDMS fiber processed**. Note that the sediments to be analyzed are expected to have relatively high levels of PAHs and different volumes may be needed to ensure detection in the calibration range of your instruments. The extra length of PAHs may be useful if your analysis must be repeated.
 4. After adding the solvent, vortex for 2 minutes and store at -17°C until analysis. Analyze after a minimum of 24 hours.
 5. After analysis of ex-situ samples, convert equipment concentration to concentration on PDMS and then to porewater concentration. The porewater concentration of PAHs or PCBs can be calculated using;

$$C_{pw,target} = \frac{C_{PDMS}}{K_{PDMS-W}}$$

where, C_{pw} is the porewater concentration, C_{PDMS} is the concentration on PDMS and K_{PDMS-W} is the correlation from Ghosh et.al, 2014.

Part D: Fraction steady state (fss).

Here the first step is to calculate the fraction of steady state (fss) of the PRC compounds. Secondly, a correlation of the fss and hydrophobicity (K_{ow}) of the compounds can be derived using the attached model. The fss of target compounds can then be estimated by extrapolating values from the FSS curve versus their K_{ow} .

1. After the ex-situ study, the concentration of PRCs after exposure in sediment is determined in addition to the target PCBs/PAHs. The rates of PRC release and target compound uptake are assumed to be the same, which implies that the loss of PRCs reflect the degree of approach to equilibrium of target compounds. Therefore, the fraction approach to steady state using the PRCs can be written as;

$$\text{FSS, PRC} = \frac{C_{\text{deployment}} - C_{\text{retrieval}}}{C_{\text{deployment}}}$$

$$\text{FSS, PRC} = 1 - \frac{C}{C_0}$$

where C_0 is the initial concentration of PRC before the ex-situ study (deployment in the sediment) and C is the final concentration of PRC after exposure in the sediment. The fss indicates the extent of equilibration for individual target PCBs/PAHs.

2. FSS for other congeners or compounds: The FSS for other congeners/compounds are estimated using the **model** (Shen and Reible, 2018). The model uses measured values of FSS for PRCs to develop a relationship for retardation factor as a function of K_{ow} and then calculates FSS for target PAHs and/or PCBs (see Appendix A for illustration). Generally, the model assumes that the FSS is controlled by external mass transfer resistances (typical for PDMS) and includes the parameters of retardation factor (R) and effective diffusivity (D) of compounds external to the PDMS fiber. In the attached file, there are 2 methods for calculating the FSS for target compounds namely, the cylindrical approach and the rectangular approach. The rectangular approach is simpler but potentially could lead to errors in estimation of FSS for compounds that are less hydrophobic or more hydrophobic than the PRCs. With the range of the PRCs, the models will give similar results. Only the more general cylindrical model will be utilized for this exercise.

3. Model Requirement.

This file was developed in macro-enabled Microsoft Excel and can be run by Excel of any version after 2003. Changes to the spreadsheet must be done with care and consistency to avoid conflicts in the plot. The remaining worksheets provide supporting information that should not be changed.

The file contains ten (10) worksheets. The worksheets ‘PRC model’, ‘cyl_fitted_plot’, ‘rec_fitted_plot’, and ‘kinetic_fitted_plot’ are designed for updating target compounds information (PAHs and/or PCBs with the K_{ow}). Items that can be modified for particular conditions are highlighted in **GREEN** on the first worksheet “PRC model” in the spreadsheet. The other worksheets **are not to be changed**. The last two sheets are lists of $\text{Log } K_{ow}$ (octanol-water partition coefficient) for polycyclic aromatic hydrocarbons (PAHs) (SPARC estimates) and polychlorinated biphenyls (PCBs) (Hawker and Connell, 1988). $\text{Log } K_f$ (PDMS-water partition coefficient) used here are calculated based on their relationships with $\text{Log } K_{ow}$ (Ghosh, et al 2014).

To apply the model for estimating fss and freely dissolved concentration, only the “**PRC model**”, “**cyl_fitted_plot**”, “**rec_fitted_plot**” and “**kinetic_fitted_plot**” worksheets. The highlighted cells in green in “PRC model” worksheet are variables that can be changed and peculiar to the PDMS fiber parameter and PRC compounds used. For this exercise, the fiber

parameters remain same for all the PRC compounds used. There are three (3) parts that require inputs;

Steps

- Input PDMS fiber parameter.
The dimensions of the PDMS fiber being used are input as well as the sampling time or period. The PDMS is assumed to be a cylindrical annulus with an outside and inside dimension along with the time period of the passive sampler deployment. In the section, the dimensions of PDMS fiber are supplied already as 0.025 cm for inner radius and 0.029 cm for outer radius.
- Input PRCs and its properties.
Here, the number of PRCs employed, the corresponding Log K_{ow}, Log K_{PDMS-W} (Ghosh et.al, 2014) and measured f_{ss} (PRC) are to be entered in the worksheet “PRC model”.
- The log value of K_{ow} and K_{PDMS-W} of targets compounds should be entered in worksheets titled “**cyl_fitted_plot**”, “**rec_fitted_plot**” and “**kinetic_fitted_plot**”. The partition coefficients correlations for PAHs and PCBs from Ghosh et.al, 2014 as shown below are to be supplied as well as the measured f_{ss} for the PRC compounds on PRC.

For PCBs,

$$\log K_f = 0.947 * \log K_{ow} - 0.017$$

For PAHs,

$$\log K_f = 0.725 * \log K_{ow} + 0.479$$

- Result
Assuming the section of “fitting parameters” are assumed not to change (N). That is, the a/alpha values do not change. Then, the f_{ss} data for the Targets are extrapolated from the PRC FSS by clicking the “**fit fss Data**” button. These are based on the parameters you input in part 2, part 3 (Part C) will provide you calculation results, including C_{pw}, f_{ss}, R, RD, Log R and logRD. RD is the product of the effective compound retardation factor and effective medium diffusivity which is used to characterize the mixing rates external to the fiber. This parameter is the single parameter (based on K_{ow}) needed to extrapolate the extent of equilibration for other compounds from the PRCs. **Please note that if you have more than 4 PAH PRCs or 7 PCB PRCs, you need to extend the sheets here as well.**
- Finally, the FSS for the target compounds are copied from worksheet “**cyl_fitted_plot**”. The f_{ss} are used to correct for equilibrium of the obtained porewater concentration using the relationship:

$$C_{pw,corrected} = \frac{C_{pw\ target}}{f_{ss}}$$

where

$$C_{pw,target} = \frac{C_{PDMS}}{K_{PDMS-W}}$$

Illustration of the use of the model is available in Appendix A.

Appendix A. Example fitting of FSS for Target PCB/PAHs.

For the purpose of illustration, The PRCs information for High sensitivity group were utilized in the attached model.

1. In the “PRC model” sheet

- the PDMS fiber parameter, that is the diameter of PDMS with and without coating are supplied. Here, 500 μm and 575 μm are entered, this automatically calculates the inner and outer radius of the PDMS fiber.
- Enter the sampling time, 30 days is used here.
- Input number of PRCs, 7 PRCs for High sensitivity is used here.
- Input PRC name; PCBs 28, 47, 70, 80, 111, 141 and 182 are supplied.
- Fitting R or RD parameters: here we want a changing α that is based on the properties of the PRC compounds employed. So, “N” for No is inputted.

2. Update the target compounds (and properties) of interest in worksheets “cyl_fitted_plot”, “rec_fitted_plot” and “kinetic_fitted_plot”. That is, the compounds, the log kow and partition coefficient relationship (log kPDMS-W). Here, 20 PCB congeners are inputted, the log Kow (Hawkers and Connell, 1988) and KPDMS-W for PCBs as “0.947*logKow-0.017”

3. Fit the fss data. Back to worksheet “PRC model” – click on the button “Fit fss data” to obtain the fss for the target compounds.

4. Copy the fss data from either “cyl_fitted_plot” or “rec_fitted_plot”. But for this exercise the fss for the cylindrical model will be used.

LDPE TASK 3 INSTRUCTIONS

Task 3: Using Polyethylene (PE) Samplers to Assess Porewater Concentrations of PAHs and PCBs in Indiana Harbor Sediment

In this project task, we will test our collective abilities to assess individual PAH and PCB concentrations in a contaminated sediment from Indiana Harbor. As a first step, colleagues at the Army Corp of Engineers have characterized this sediment finding it to have an f_{oc} of 7% and a water content near 65% (implying a porosity near 80%).

In order to prepare the polyethylene (PE) samplers, one would like to load the PE films with amounts of PRCs (C13-labeled PAHs and PCBs) that will ultimately be comparable to the loads of target PAHs and PCBs that accumulate in the samplers over the duration of the “deployments” (here taken to be 30 days). For the “ex situ active sampling” tests, one can assume the PE will reach equilibration with the sediment. If it is correct to assume the mass of each PAH or PCB accumulated in the PE is small compared to the mass of each PAH or PCB in the sediment used, then one can find the expected PE concentrations using:

$$C_{PE} \text{ (ug/kg PE)} = C_{\text{sediment}} \text{ (ug/kg dw sediment)} * K_{PEw} / K_d$$

Hence, an estimate of the sediment concentrations is needed. In the attached spreadsheet, we use sediment values reported of the US ACoE, as well as estimates of K_{PEw} and $K_d (= f_{oc}K_{oc})$ to find expected C_{PE} values at equilibrium. Further, one can use the PE sampler masses (e.g. a 25 um thick film of 2 cm width and 5 cm length) and the laboratory’s expected extract and injection volumes to anticipate the masses of PAHs and PCBs to be injected into the analytical systems. These calculations suggest individual PAHs and PCBs would be injected at about 10 ng/uL and 100 pg/uL, respectively. (The lower PCB amounts correspond to their much lower concentrations in the sediments; see spreadsheet). If such calculation results prove too low, one may increase the PE sampler mass accordingly.

The only difference for the “ex situ passive sampling” tests is that the target and PRC compounds are unlikely to achieve sediment-PE equilibration. One can use properties of the sediment of compounds of interest to estimate the fraction of equilibration (f_{eq}) likely to be achieved (e.g. Lampert et al., 2015; Apell et al., 2015). For the larger PAHs and PCBs, this consideration suggests they will only achieve about 10% equilibration after a month of sediment-PE contact (see figure from Apell et al. pasted on spreadsheet). Hence, expected injection masses will be decreased by about a factor of 10 for the larger PAHs and PCBs in these “passive” tests (i.e., no mixing or tumbling while PE is inserted).

With such preliminary calculations, one can choose “reasonable” PRC loading levels to enhance the chances that both target contaminants and PRCs will be present in extracts at similar levels, thereby facilitating the likelihood that extracts can be analyzed once without needing to rerun for widely disparate injection masses. In the case of Indiana Harbor PAHs, one might choose to load

the PRCs at about $10 \text{ ug}/0.025 \text{ g}_{\text{PE}} = 400 \text{ ug/g}_{\text{PE}}$, while the individual PCB PRCs might be loaded at about $100 \text{ ng}/0.025 \text{ g}_{\text{PE}} = 4 \text{ ug/g}_{\text{PE}}$.

Part A: PE film Preparations – PRC loading into LDPE films

Note: Please refer to the standard operating procedures (SOPs) for details on PE film preparation, PRC loadings, extractions, and analyses of polyethylene films.

Step 1: We will supply 1 mil (25 μm) PE sheet to everyone so that we are all working with the same material.

The PE sheet should be cut so as to yield 20 strips of 2 cm width and 5 cm length (each weighing about 25 mg).

Next the PE strips should be cleaned as described in SOP step 7.1.

After cleaning, the PE strips should be loaded with the C13-labelled PRCs as described in SOP step 7.3.4 at the levels deduced as described above.

Part B: Confirm PRC loaded concentrations (Co) in LDPE film segments *before* proceeding with sediment exposure.

Six PRC loaded films should be set aside (i.e., no sediment exposures) for analysis of the $t = 0$ concentrations of loaded PRCs and to ensure no background analytes are present that would interfere with eventual target PAH and PCB analyses.

Extract/analyze PRC-loaded PE film segments per SOPs and report results to USACE. **Accuracy/precision of Co results must assessed *before* proceeding with sediment measurement.**

Part C: Ex-situ Study - pore water measurements.

Active sampling. Individual PE sheets should then be added to individual sediment-filled jars for the ex situ active sampling. These jars will be mixed (e.g. by placing on a roller table) so as to enhance the rates of PAH and PCB exchanges between the PE films and the sediment.

After one month, the PE films should be removed from these jars and analyzed for PAHs and PCBs.

Static sampling. Individual PE sheets should then be inserted using stainless steel forceps into individual sediment-filled jars for the ex situ passive sampling. These jars will be kept “static” (i.e., with no mixing) so as to mimic the rates of PAH and PCB exchanges between the PE films and an unmixed sediment bed.

After one month, the PE films should be removed from these jars and analyzed for PAHs and PCBs.

Part D: Fraction steady state (f_{eq}).

1. After the active and passive ex-situ studies, the concentration of PRCs after exposure in sediment are determined in addition to the target PCBs/PAHs. The rates of PRC release and target compound uptake are assumed to be the same, which implies that the loss of PRCs reflect the degree of approach to equilibrium of target compounds. Therefore, the fraction approach to steady state using the PRCs can be written as;

$$f_{eq} = 1 - \frac{C(t = 0) - C(t = 30)}{C(t = 0)}$$

where $C(t=0)$ is the initial concentration of PRC before deployment in the sediment and $C(t=30)$ is the final concentration of PRC after exposure in the sediment. The f_{eq} indicates the extent of equilibration for individual target PCBs/PAHs. *Note that PDMS instructions features variable name F_{ss} (fraction steady state) instead of f_{eq} used here.*

2. These f_{eq} results will then be used:

- a. in the “active” sampling cases to ascertain whether individual PAHs and PCBs were equilibrated between the sediment and the PE films.
- b. in the “passive” sampling cases to adjust the measured concentration of PAHs and PCBs upward to obtain estimates of their concentrations in the PE samplers had deployment times been sufficient to achieve sediment-PE equilibration.

3. Finally, the K_{PEW} values of each target PAH and PCB will be used to calculate the porewater concentrations of each target contaminant:

$$C_{\text{porewater}} (\text{ng/L}) = C_{\text{PE at equilibrium}} (\text{ng/kg PE}) / K_{PEW}$$

ATTACHMENT 1 – POLYMERIC SAMPLER STANDARD OPERATING PROCEDURES



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

1. SCOPE AND APPLICATION

- 1.1. This method is an operating procedure for handling and loading solid phase micro-extraction polydimethylsiloxane (SPME-PDMS) fibers with performance reference compounds (PRCs) for measuring environmental contaminant concentrations in sediment pore water and overlying water.
- 1.2. The method is applicable to hydrophobic organic contaminants (HOCs) and the focus herein is on polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs).
- 1.3. This procedure generates extracts suitable for High Performance Liquid Chromatography (HPLC) and gas chromatography with mass spectroscopy detection GC-MS analysis for priority and alkyl PAHs (PAH-38); and GC-MS/MS and gas chromatography with electron capture detection (GC-ECD) for PCBs.
- 1.4. 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. SUMMARY OF METHOD

- 2.1. A specific length of PDMS-coated fiber is cleaned by consecutive extraction with dichloromethane, hexane, methanol and ultrapure water.
- 2.2. Performance reference compounds are loaded onto cleaned PDMS fiber in water-methanol (80:20%) solution.
- 2.3. A shaker table is required to facilitate well-mixing of the PRC spiking solution and contact with the PDMS fibers.
- 2.4. The PDMS fibers are kept in the PRC solution until preparation for deployment.
- 2.5. 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 into the water column.
- 2.6. 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 atmospheric and surficial sources, 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 MilliQ 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 non-aqueous 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 phase 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.
- 4.2. Solid phase micro-extraction polydimethylsiloxane fibers – commercially available through suppliers like Polymicro Technologies™ (Molex, Phoenix, AZ, USA) and Fiberguide (Stirling, NJ, USA).
- 4.3. Extraction vessels – 2 mL amber (for PAHs) or clear glass (for PCBs) autosampler vials.
- 4.4. 300 µL glass inserts with springs for ultra-low solvent volumes.
- 4.5. PTFE/Silicone/PTFE screw caps and PTFE lined solid tops for long-term storage.
- 4.6. Kimwipes®
- 4.7. Food-grade aluminum foil
- 4.8. Tweezers
- 4.9. Ceramic Cutter or nippers
- 4.10. Shaker table or overhead tumbler

5. REAGENTS

- 5.1. Dichloromethane (i.e., methylene chloride, CH₂Cl₂)
- 5.2. Hexane
- 5.3. Acetonitrile
- 5.4. Methanol
- 5.5. MilliQ Water (Barnstead, GenPure Pro) or equivalent
- 5.6. Research grade deuterated or ¹³C labeled compounds as performance reference compounds (PRCs) from Ultra Scientific and Cambridge Isotope Laboratories (**Appendix 1**).
- 5.7. Research grade deuterated or ¹³C labeled compounds as surrogates (**Appendix 1**) or internal standards for GC-MS or GC-MS/MS analysis: d-acenaphthene, d-phenanthrene and d-perylene for PAHs (working standard concentration of 1000 ng/mL in hexane),

and ^{13}C mix containing PCBs 9/118/188 (working standard concentration of 1000 ng/mL in hexane).

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/column cutter or nippers 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 thicknesses 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 2.
- 7.2. PDMS washing procedure
 - 7.2.1. The cut PDMS fibers are placed in the 120 ml glass vessel and cleaned by washing consecutively by soaking in three solvents (i.e., dichloromethane (2x), hexane (2x) and methanol (2x)) for 30 minutes each on a shaker table. Larger vessels and volumes are recommended for large sampling efforts. Care should be taken to avoid PDMS breakage during washing with solvents especially if the vessel is filled with solvent half way. 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 MilliQ water 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 cleaned PDMS fibers should be stored closed in the glass vessel 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. 100 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

(**Appendix 1**) at working concentration of 2500 ng/ml in acetone or methanol are added to the water-20% methanol solution.

Note: Acetone must be used for preparation of diluted working standards to ensure miscibility with stock solutions purchased in nonane. When stock solutions are purchased in methanol, working standards should be prepared in methanol. Deviations could lead to phase separation in the working standard causing potential loss of control of PRC loading concentrations. If unsure, preliminary testing should be conducted to make sure that the standard solvent and working solution solvents are miscible. Example calculations for preparation of working standards and the fraction of nonane is provided as **Appendix 1**. The levels of PRCs on PDMS should be similar to the target analytes after uptake from the environment and can be predetermined by using PDMS-water partition coefficients (see PRC spiking calculation in **Appendix 2**). 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. PRCs should be loaded onto fibers targeting a final extract concentration at least 10 times practical quantification limits to ensure detection after losses during exposure.

7.3.3. The spiking solution with PDMS is agitated (approximately 120-130 strokes per minute) using a shaker table for a minimum of 7 days with deuterated PAHs and a minimum of three weeks with C¹³ labeled PCBs before using the PRC loaded PDMS. Longer equilibration times may be required for thicker samplers. Note, with minimal headspace the movement of PDMS during 1D agitation at 130 strokes per minute is not vigorous even at high mixing rates. If fewer than 130 strokes is used, longer PDMS exposure to PRC solution is required. For example, 130 strokes agitation achieves acceptable loading of PCBs in 3 weeks but 60 strokes agitation may require 5 weeks. Alternatively, effective loading of PRCs onto PDMS within 3 weeks can be achieved using a roller mixer with ca. 45-50 rpm. A horizontal placement of the loading vessel in a tumbler and mixing at 45 rpm may also be used but in this case the vessel should allow unobstructed movement of the PDMS to avoid breakage. Overhead tumbling of the vessel is not recommended as PDMS at both ends may break.

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 via the methods in Section 7.7. At least 6 PRC loaded PDMS fibers should be analyzed for initial PRC concentrations.

7.4. Deployment of PDMS in sediment samples

7.4.1. The loaded PDMS fiber (5 cm) is withdrawn from the PRC solution using clean tweezers, rinsed with MilliQ water and liquids blotted on Kimwipes® and allowed to evaporate

- 7.4.2. The 5 cm loaded PDMS fiber is deployed in sediment and the sediment placed on a shaker table if desired. A shaker tool can speed equilibration if the sediment contains sufficient moisture (e.g. above the liquid limit)
- 7.5. Retrieval
- 7.5.1. All surfaces that the PDMS fiber will come into contact with must be covered with clean food grade aluminum foil.
- 7.5.2. 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.
- 7.5.3. All laboratory and field personnel must wear nitrile or powder-free gloves when handling the PDMS fiber.
- 7.5.4. After 21-28 d the vials are removed from the shaker table and the 5 cm PDMS fiber is carefully withdrawn from the sediment. Any adhering sediment, particles, biofilm, or residue is removed from the PDMS fiber using a MilliQ water wetted Kimwipe®. After cleaning, the fiber should be blotted dry prior to segmentation and extraction.
- 7.5.5. Segmentation of the 5 cm PDMS fiber should be performed as quickly as possible to minimize volatilization of more volatile analytes of concern.
- 7.5.6. The 5 cm PDMS fibers are segmented using a ceramic column cutter into 2+2+1 cm lengths.
- 7.6. 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 sufficient for the complete immersion of the PDMS fiber segments. 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.
- 7.6.1. 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
- 7.6.2. The PDMS fiber segments are left in the solvent overnight and stored at -17°C to avoid any losses if employing a volatile solvent (e.g. hexane).
- 7.6.3. Following overnight extraction, vials with inserts containing SPME segments and solvent are sonicated for 1 min to ensure homogenization.
- 7.6.4. 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. Extracts in GC vials without inserts can be vortexed before transfer and IS addition.
- 7.6.5. Priority pollutant PAHs can be analyzed without cleanup steps by EPA Method 8310 or 8270 and PCB congeners by EPA Method 8082/8270 or modified Method 1668. Cleanup steps can be optional when complex matrices are analyzed.

8. QUALITY CONTROL & METHOD PERFORMANCE

- 8.1. PRC loading before deployment: at $t=0$ i.e. after withdrawing PDMS from PRC solution: 6 samples of loaded PDMS (5 cm segments) must be collected from different parts of the PDMS fiber, extracted, and analyzed prior to deployment (see section 7.3.5).
- 8.2. Blanks
 - 8.2.1. Solvent Blanks: Solvent blanks will be analyzed at the time of filling the inserts with designated solvent. If these contain significant levels of contamination, new vials with inserts will be filled with a separate source and the process will be repeated.

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Appendix 1. Suggested Performance Reference Compounds (PRCs) and Surrogate Compounds for ESTCP ER-201735 project.

Candidate PRCs and surrogate compounds suitable for polycyclic aromatic hydrocarbon (PAH) and polychlorinated biphenyl (PCB) determinations when GCMS or GC-MS/MS is the method of detection.

Table 1. PRCs used for loading PDMS in ESTCP ER-201735.

Method 8270		Method 1668
PRCs		PRCs
PCBs #	PAHs	PCBs #
Low Sensitivity	Low Sensitivity	High Sensitivity
C13-37	C13-PHENANTHRENE	C13-28
C13-47	C13-FLUORANTHENE	C13-47
C13-54	C13-CHRYSENE	C13-70
C13-111	C13-INDENO(123-cd)PYRENE	C13-80
C13-138		C13-111
C13-178		C13-141
		C13-182
Example surrogates		Example surrogates
	d10-anthracene	C13-52
	d10-fluoranthene	C13-101
	d12-benz(a)anthracene	C13-138
		C13-153
		C13-180
		C13-209

Appendix 2. 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 30 ng per mL of extract (high resolution) and 150 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 30 ng/mL and approximately 80% of the compound is lost from the PDMS within the exposure timeframe (28 days), the expected concentration in the extract will be 6 ng/mL after 28 d.

Step 2: Indicate the length of PDMS per sample (extract). Here, we have chosen **10 cm** per sample extract and six replications. Therefore, the total amount of PDMS needed for the loading and sampling exercise is **12** pieces of **5 cm** segments resulting in a total fiber length of **60 cm**. Choose a vessel to accommodate the PDMS and water-methanol (80:20) inside without much headspace (here 120 mL amber glass bottle is used). For the PDMS length (**10 cm**) and extract volume (**250 μ L**), calculate the concentration in PDMS. Here, the calculated concentration in PDMS is **1184 ng/mL**. Use the PDMS-water partition coefficients (Ghosh et al., 2014) to calculate the concentration in water (only) at equilibrium ($C_{w,eq}$).

Step 3. Solve for initial solution concentration of PRCs ($C_{initial\ solution}$, ng/mL) that result in the PRC loadings in the PDMS:

$$C_{initial\ solution} = \frac{C_{PDMS} \times L_{fiber} \times V_{PDMS} + C_{w,eq} \times V_W}{V_W} \quad (1)$$

where, C_{PDMS} is the concentration of PRC in PDMS (1184 ng/mL), L_{fiber} is the fiber length (60 cm), V_{PDMS} is the volume of PDMS coating (0.633 μ L/cm). $C_{w,eq}$ [0.00526 ng/mL (C13-28)] is the concentration of PRCs in water at equilibrium and V_W is the volume of water:MeOH (100 mL).

Step 4. Solve for volume of working standard ($V_{working\ stand}$, μ L), that must be added to the water:methanol solution (W:M) (100 ml) for PRC loading on PDMS.

$$V_{working\ stand.} = \frac{C_{initial\ solution} \times V_{W:M}}{C_{Working\ stand.}} \quad (2)$$

The calculated volume of working standard is **18 μ L**. The $C_{initial\ solution}$ concentration of PRCs is 0.455 ng/mL and $C_{working\ stand.}$ is the concentration of PRCs in working standard (2500 ng/ml) in **acetone**. The working standard (2500 ng/ml) is prepared by diluting the stock solution (40000 ng/ml). Here we used 125 μ L of stock solution and diluted with acetone to a final volume of 2000 μ L. Nonane is miscible in acetone. The fraction of nonane in the prepared working standard is 0.06. **Caution should be taken in preparing working standards because of the potential for solvent incompatibility. The solvent ratios employed here lead to homogeneous solutions. Use of different solvents or different solvent amounts may lead to phase separation in the preparation of the working standard or the loading solution which can lead to an inability to achieve targeted PRC concentrations.**

Fiber Parameters															
575	core diameter with PDMS coating (μm)									fiber					
500	core diameter without PDMS coating (μm)									5	cm				
0.001806416	area (m2)									12	No of 5 cm segments				
6.33227E-08	volume (m3)									60	total fiber spiked cm				
3.50543E-05	length (m) i.e. coating thickness														
35.05	length (μm) i.e. coating thickness														

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)

Color Legends

Volume of solvent for extract

Fiber length per sample

log K_{ow} - Hawker and Connell, 1988 (PCB) and log Kow (SPARC estimates) PAH

	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 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	stock solution in nonane ng/mL	volume of stock solution ml	volume of stock solution μl
High Res PCBs														
C13-28	5.67	5.35	30	0.0075	1184	0.00526	0.9884	0.455	0.02	18.2	2500	40000	0.125	125
C13-47	5.85	5.52	30	0.0075	1184	0.00355	0.9922	0.454	0.02	18.1	2500	40000	0.125	125
C13-70	6.2	5.85	30	0.0075	1184	0.00166	0.9963	0.452	0.02	18.1	2500	40000	0.125	125
C13-80	6.48	6.12	30	0.0075	1184	0.00090	0.9980	0.451	0.02	18.0	2500	40000	0.125	125
C13-111	6.76	6.38	30	0.0075	1184	0.00049	0.9989	0.450	0.02	18.0	2500	40000	0.125	125
C13-141	6.82	6.44	30	0.0075	1184	0.00043	0.9990	0.450	0.02	18.0	2500	40000	0.125	125
C13-182	7.2	6.80	30	0.0075	1184	0.00019	0.9996	0.450	0.02	18.0	2500	40000	0.125	125

Standard Operating Procedure for the Preparation of Polyethylene (PE) Used for Passive Sampling

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Standard Operating Procedure for the Preparation of Polyethylene (PE)

Used for Passive and Active Sampling of HOCs

SCOPE AND APPLICATION

- 1.1 This method describes a procedure for preparing and handling polyethylene (PE) films that will be cut into strips and deployed to sample hydrophobic organic compounds (HOCs) in environmental media.
- 1.2 This method generates PE that can be deployed for passive or active (i.e., using mixing) sampling of HOCs in atmospheric, aqueous, or sediment-porewater systems.
- 1.3 PE that is prepared by this method is suitable for *ex situ* laboratory or *in situ* field deployment.

SUMMARY OF METHOD

- 2.1 A known mass of low density polyethylene (LDPE) sheet, usually gram quantities, is cleaned by sequentially extracting with methylene chloride, methanol, and ultrapure water in a closed glass vessel.
- 2.2 Clean PE is equilibrated with performance reference compounds (PRCs) dissolved in water or methanol-water (see Appendix 1 for possible PRCs).
- 2.3 PRC-impregnated PE is stored in water or aqueous PRC loading solution in glass vessels until use.
- 2.4 Shortly before deployment, the PE is cut into suitably sized strips and prepared for deployment.
- 2.5 During deployment, the PE is exposed to the environmental medium of concern. HOCs in the medium diffuse into the PE, while PRCs diffuse out.

INTERFERENCES

- 3.1 PE is susceptible to contamination from atmospheric vapors and contact with surfaces (e.g., worker hands), so it must remain in clean sealed vessels until deployment.

APPARATUS AND MATERIALS

- 4.1 Extraction vessels: 1-L glass bottles or screw capped jars (foil-lined lids).
- 4.2 Storage vessels: bottles with glass stoppers or amber jars (foil-lined lids).
- 4.3 Bottle/jar tumbler, shaker table, bottle roller, or equivalent.
- 4.4 Low density polyethylene (LDPE): commercial grade, large sheet at 25 μ m (1 mil) or 51 μ m (2 mil) thickness. The thickness is chosen to be strong enough to withstand stresses during deployment (e.g., insertion into sediment), but thin enough to exchange a significant fraction (e.g., >20%) of its PRCs during the deployment time to be used.
- 4.5 Food grade aluminum foil (solvent cleaned and/or combusted to remove any organic residue from foil production)

- 4.6 Stainless steel forceps
- 4.7 Teflon (or similar non-contaminating material) cutting board

REAGENTS

- 5.1 Methylene chloride, CH_2Cl_2 , pesticide grade or equivalent
- 5.2 Methanol, CH_3OH , pesticide grade or equivalent
- 5.3 Organic-free reagent water (as defined in SW-846 Chapter 1)
- 5.4 Research grade PRCs certified >98+% pure.

Note: Specific standard materials, concentrations, solvents, and solvent purity requirements must be determined based upon the target HOCs of concern and their likely concentrations in any particular application.

PRESERVATION AND HANDLING

- 6.1 Clean PE should be stored in clean, sealed, glass vessels.
- 6.2 PE loaded with PRCs should be stored in sealed glass containers that contain either:
 - (a) a few mL of organic-free reagent water added to maintain 100% relative humidity within the storage vessels (minimizing sorptive losses of PRCs to glass vessel walls),
 - (b) completely filled with organic-free reagent water (common after loading from aqueous methanol solutions), or
 - (c) still filled with the aqueous PRC-loading solution (preferred, but may lead to shipping concerns).
- 6.3 Laboratory and field personnel should wear nitrile or latex gloves whenever handling clean PE.
- 6.4 Methylene chloride-rinsed, stainless steel forceps and scissors are used when manipulation of clean PE is required.
- 6.5 Methylene chloride-rinsed, aluminum foil is used to cover any surface that clean PE may encounter.

PROCEDURE

- 7.1 Polyethylene Cleaning Procedure: LDPE is purchased from hardware/painting stores in large sheets ('dropcloth or plastic tarp' material) with thickness of 25 μm (1 mil) or 51 μm (2 mil), depending on the user's need for strength (choose thicker) and desire to use short deployment times (use thinner). The sheet is cut into strips sized for the environment and deployment apparatus to be used. An organic solvent cleaning sequence is then used to prepare the PE. This process ensures that extractable oligomers, plasticizers, and contaminating organic chemicals are removed from the PE prior to use. All extractions are performed sequentially in the same container.
 - 7.1.1 Methylene chloride is placed into the extraction vessel, and the PE strips are immersed in the container for 24 hours to enable time for diffusive transfers

out of the PE. The initial methylene chloride extract is discarded and a second methylene chloride extraction is performed for 24 hours. The second methylene chloride extract is discarded and replaced by methanol to remove methylene chloride from the PE. Methanol immersion is also done for 24 hours. The initial methanol extract is discarded and followed by a second methanol soak for 24 hours. Finally, the second methanol extract is discarded and the PE undergoes three 24-hour soaks with organic-free reagent water (within the same extraction vessel) to remove residual methanol from the PE.

7.1.2 The cleaned PE is stored in organic-free reagent water in the extraction vessel until further processing.

7.2 Polyethylene Preparation with Performance Recovery Compounds (PRCs): PRCs are loaded into the clean PE, prior to its field deployment, by utilizing either aqueous (Fernandez et al. 2009) or 80:20 methanol:water equilibrations (Booij et al., 2002). Depending on the hydrophobic organic compounds of interest, PRCs should be chosen to mimic mass transfer phenomena governing exchanges during field deployments. It is important to avoid adding PRCs that the analytical laboratory already uses as surrogate recovery, cleanup, or injection standards. PRC loading is performed by placing the PE in pre-cleaned glass vessels containing known PRC solutions made up in organic-free reagent water with or without pesticide-grade methanol. (The methanol swells the PE, enabling faster PRC uptake; but use of methanol also requires post PRC-impregnation removal of the methanol from the PE by soaking in water.) The PE user should load the PE with levels of PRCs that are a little greater than the concentrations of target HOCs that are expected to be accumulated from the environment, thereby facilitating the eventual chemical analyses. The PRC concentrations loaded in the PE can be found using each PRC's PE-water partition coefficient (e.g., Burgess et al. 2017) and the ratio of the PE mass to the aqueous solution volume of the loading solution. For example, one may set out to load 1 g of PE using an aqueous solution containing 10 ug of a PRC in a liter of water, so the ratio of PE to water, r_{PEw} , is 1/1000. If that PRC's K_{PEw} is 10^5 (ug/g_{PE})/(ug/mL_w), then one finds the fraction of that PRC that ends up in the 1 g of PE as:

$$\begin{aligned} f_{PE} &= (r_{PEw})(K_{PEw}) / (1 + r_{PEw}K_{PEw}) \\ &= (1 \text{ g}_{PE} / 1000 \text{ mL}_w)(10^5 \text{ mL}_w / \text{g}_{PE}) / [1 + (1 \text{ g}_{PE} / 1000 \text{ mL}_w)(10^5 \text{ mL}_w / \text{g}_{PE})] \\ &= 0.99 \end{aligned}$$

or 9.9 ug of the PRC is in the PE at equilibrium (i.e., 9.9 ug_{PRC}/g_{PE})

and the water concentration has dropped to 0.1 ug_{PRC} / L_w.

7.3 Sufficient PRC equilibration time during this PE preparation step is necessary to

ensure uniform PE loading across the entire PE thickness; hence thicker PE sheet is more robust for field use, but takes longer to load with PRCs. If previously untested PRCs are used, a time course study should be used to performed to confirm PE-solution equilibration of the PRCs (e.g., Booij et al. 2002).

7.3.1 Isotopically labeled compounds are useful PRCs, surrogate recovery standards, and injection standards when Gas Chromatography-Mass Spectrometry (GCMS) is the method of separation and detection. For example, deuterated and C13-labeled polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) are effective methodological standards for PE passive sampling. If PAHs are the target contaminants, one subset of compounds, distributed across the range of PAHs to be assessed (e.g., d10-phenanthrene, d10-pyrene, and d12-chrysene), should be used as PRCs, while another set (e.g., d10-anthracene, d10-fluoranthene, and d12-benz(a)anthracene) is used as surrogate (recovery) compounds during later analysis of laboratory or field-deployed PE. Finally, still another set of compounds (e.g., d10-acenaphthene, d14-*m*-terphenyl, and d12-perylene) should be used as injection standards. Similar sets of labeled compounds should be used for other compound classes (see Appendix 1). Note: if PE samples are eventually to be analyzed at a contract laboratory, PRC choices must be made so as not to conflict with recovery and injection standards used by that laboratory.

7.3.2 As subsequent analysis (e.g., GCMS) is best achieved with both PRCs and target HOCs present at like concentrations in the PE extracts, the optimal concentration level of the PRC loaded into the PE is dependent on the environment in which the PE is to be deployed. For example, if a target HOC is expected to occur in the water or pore water near 1 ng/L levels, one can use that compound's LDPE-water partition coefficient (e.g., Fernandez et al., 2009; Lohmann, 2012; Burgess et al. 2017) to estimate the expected levels in the PE after deployment:

$$\text{Concentration in PE (ng/kg)} \sim K_{PE-water} * \text{concentration in (pore)water (ng/L)}$$

For example, if the $K_{PE-water}$ for the target HOC of interest is 10^5 (L/kg), then the concentration of the target HOC in the PE will approach 100 ug/kg as it equilibrates with water at 1 ng/L. Based on this estimate, the PRCs are loaded into the PE at slightly higher (e.g., factor of 2) concentrations since some fraction of these will be lost from the PE during deployment. Appendix 2 shows a typical calculation used to design a PRC-containing MeOH:H₂O solution of PCBs suited to loading an 0.82 g mass of PE (i.e., one or more PE pieces summing to 0.82 g) to achieve about 100 ug of each PRC per kg of PE.

7.3.3 Aqueous PRC Loading: A solvent-cleaned and dried glass container is filled with ultrapure water that has been spiked with known concentrations of PRCs (e.g., based on calculations like those shown in Appendix 2). A known mass of pre-cleaned PE is then added and weighted to insure complete PE submersion

and full exposure of PE surfaces to the solution. The vessel is agitated to remove any air pockets/bubbles adhering to the submerged PE. Equilibration times vary for different PRC/PE thickness combinations and the PE-water phase ratio. For PAHs and PCBs, one should use at least 30 days to insure homogeneous distributions of the PRCs throughout the entire thickness of the PE film unless faster equilibration has been confirmed with PRC/PE specific time-course testing of PRC concentrations in the PE or by showing that concentrations of PRCs are the same for films of different thicknesses, but the same masses. Generally, PE is stored in the aqueous PRC solution until that PE is to be deployed.

- 7.3.4 **Methanol-Aided PRC Loading:** A solvent-cleaned and dried glass container is filled with an 80:20 mixture of pesticide grade methanol and ultrapure water (e.g., Booij et al. 2002). This solvent mixture is then spiked with known concentrations of PRCs (e.g., see calculations in Appendix 2).

Commonly, ¹³C-labelled PRCs are obtained dissolved in solvents like nonane. If one adds too much of a solvent like nonane to 80:20 methanol:water (e.g., >10 mL/L), then one will see nonane floating on the PRC loading solution or a cloudy solution if shaking is employed. When PE strips are added to such a multiphase loading solution, the immiscible solvent is likely to (a) accumulate in the PE and change the polymer's affinity for the PRCs and/or (b) remain as a separate phase competing for the PRCs (note that even 1 mL of separate phase nonane is virtually the same volume as 1 g of PE strips, perhaps causing comparable partitioning of the PRCs into this solvent and the LDPE strips.) Consequently, one should be sure to look for the occurrence of a separate solvent phase when spiking the PRC loading solution. For the particular case of nonane, adding less than about 2 mL nonane per liter of the methanol:water loading solution appears to be acceptable. Spiking volumes of other solvents (e.g., hexane) should be tested for their miscibility with the PRC loading solution before use.

After preparing the loading solution, a known mass of pre-cleaned PE is then added and weighted down to insure complete submersion and full exposure of the PE surfaces to the solution. The vessel should be agitated to remove any bubbles/air pockets adhering to the submerged PE. Equilibration times vary for different PRC/PE thickness combinations and the PE-solvent phase ratio, but typically this step is completed within 7 days since methanol swells the PE and thereby speeds PRC diffusion into the polymer sheet (Booij et al., 2002). Generally, the PE is stored in the PRC solution until shortly before it is to be deployed. Before deployment, the PRC-loaded PE is rinsed with ultrapure water, and then it is soaked in ultrapure water for 24 h to remove most of the methanol from the PE, while leaving the more hydrophobic PRCs almost completely in the PE. This leaching step in ultra-pure water is repeated twice to insure complete methanol removal.

QUALITY CONTROL

- 8.1 **PRC Loading Validation:** At least six representative samples of prepared PE should be collected from different parts of the PRC-loaded PE (e.g., 1 cm x 10 cm x 25 μm

pieces weighing about 25 mg each), extracted, and analyzed prior to field deployment to validate that the PRC concentrations are consistent with their intended loadings and these PRCs have uniform concentrations in a batch of PE.

- 8.2 Target HOC Blanks: Subsamples of prepared PE, commensurate in size with the planned environmental PE samples (e.g., 10 cm wide by 5 cm long by 25 μ m thick and therefore weighing about 120 mg), should be collected, extracted, and analyzed prior to field deployment to demonstrate that other substances have not contaminated the PE which would contribute to interfering background for the target HOCs analysis using the intended target analyte detection approach.

METHOD PERFORMANCE

- 9.1 PRC data, obtained from PE samples collected from >six pieces of the prepared PE, should be consistent within about $\pm 10\%$ (i.e., $100 \times \text{standard deviation} / \text{mean}$).
- 9.2 Target HOC concentrations should be undetectable in the prepared PE at the levels of interest. For example, , assuming a target HOC with a level of interest at $10 \text{ pg/L} = 10^{-5} \text{ ng/mL}_{\text{water}}$ and having $K_{PE \text{ water}} = 10^5 \text{ mL}_{\text{water}}/\text{g PE}$, requires background below:

$$(\text{level of interest}) \times K_{LDPE \text{ water}} = 1 \text{ ng HOC /g PE.}$$

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Appendix 1. Suggested Performance Reference Compounds (PRCs), Surrogate Compounds (Recovery Standards), and Injection Standards.

A. PRCs, suitable for polycyclic aromatic hydrocarbon (PAH) determinations when Gas Chromatography-Mass Spectrometry (GCMS) is the preferred method of detection, include, but are not restricted to, deuterated PAH compounds. One subset should be used as PRCs, while reserving others for use as surrogate (recovery) compounds. Still other compounds such as terphenyl can be used as injection standards.

Targets: PAHs Method: EPA 8270d with GCMS-SIM				
PRCs	13C6-phenanthrene	13C6-fluoranthene	13C6-chrysene	13C6-indeno(1,2,3-cd)pyrene
Surrogates	d10-anthracene	d10-fluoranthene	d12-benz(a)anthracene	d12-perylene
Injection Standards	d10-acenaphthene	d14- <i>m</i> -terphenyl		

B. PRCs and surrogate compounds suitable for polychlorinated biphenyl (PCB) determinations when GCMS is the preferred method of detection include, but are not restricted to, ¹³C-labeled or deuterated PCB congeners. One subset, for example including a tri-, tetra-, penta-, hexa-, and heptachloro-biphenyl, can be used as PRCs while reserving different tri-, tetra-, penta-, hexa-, and heptachloro-biphenyl congeners to serve as surrogate compounds (see below) and injection standards.

Targets: PCBs Method: EPA 8270d with GCMS-SIM						
PRCs	¹³ C PCB-37	¹³ C PCB-47	¹³ C PCB-54	¹³ C PCB-111	¹³ C PCB-138	¹³ C PCB-178
log <i>K_{ow}</i>	5.68	5.87	5.32	6.49	6.71	6.98
number Cl's	3	4	4	5	6	7
Surrogates	¹³ C PCB-3	¹³ C PCB-15	¹³ C PCB-28	¹³ C PCB-52	¹³ C PCB-118	¹³ C PCB-153
number Cl's	1	2	3	4	5	6
Surrogates		¹³ C PCB-180	¹³ C PCB-194	¹³ C PCB-208	¹³ C PCB-209	
number Cl's		7	8	9	10	
Injection Standards	¹³ C PCB-19	¹³ C PCB-105	¹³ C PCB-170			

C. When analyzing for organochlorine pesticides such as DDT using GCMS, ¹³C labeled compounds can serve as PRCs and surrogate standards. Since DDT has been shown to degrade to form DDE or DDD in certain situations, one should use the 4,4'- isomer of DDT and the 2,4'- isomers of DDE and DDD as PRCs to allow appearance of ¹³C-labelled 4,4'-DDE or 4,4'-DDD to be interpreted as arising from reaction of the DDT PRC during the deployment. Deuterated or ¹³C labeled PCBs can be used as surrogate (recovery) and injection standards.

Targets: DDTs	Method: GCMS		Detection Limit ~ 200 pg / 100 mg PE
PRCs	¹³ C 2,4'-DDE	¹³ C 2,4'-DDD	¹³ C 4,4'-DDT
Surrogates	¹³ C-PCB111	¹³ C-PCB153	¹³ C 2,4'-DDT
Injection Standards	d6 PCB 77	¹³ C PCB 105	¹³ C PCB 167

Appendix 2. Example of spreadsheet used to design a PRC solution needed to impregnate PE for PCB sampling.

Step 1: Find/estimate PE-spiking solvent partition coefficients for PRCs in solvents of interest (see spreadsheet below). Here 80:20 MeOH:H₂O values from Booi et al. (2002) are used to develop a correlation with K_{ow} values from the literature (Hawker and Connell, 1988); this relation is then used to estimate K_{PE-(80:20)m:w} values for other PCB congeners partitioning between PE and an 80:20 MeOH:water solution.

Step 2: Choose the size of PE needed for the sampling exercise (here a single 1 mil-thick strip of 5 cm width and 68 cm length) and solve for the PE mass (here 0.82 g). Choose a vessel which is large enough to fit the PE inside without extensive PE-PE surface contact, but small enough so that unacceptably expensive masses of the labeled PRCs are not used (here 125 mL ground glass stopped flask). For this PE mass and solution volume, use the PE-solution partition coefficients from step 1 to solve for the fractions of each PRC that will be in the PE at equilibrium using:

$$\text{fraction in PE} = 1 - (1 / (1 + \text{Mass}_{\text{PE}} * K_{\text{PE-solution}} / \text{Volume}_{\text{solution}})) \quad \text{Eq. 1}$$

(e.g., 5.8% for congener #52)

Step 3. Solve for spiking solution concentrations of PRCs that result in desired PRC loadings in the PE (here 100 ng/g_{PE}) using:

$$C_{\text{initial spiking solution}} = C_{\text{desired in PE}} * \text{Mass}_{\text{PE}} / \text{fraction in PE} / \text{Volume}_{\text{solution}} \quad \text{Eq. 2}$$

(e.g., here we find we need about 11.3 ng congener #52 per mL to achieve 100 ng/g PE; this is concentration of the spiking solution that the investigator must make up to prepare PE for subsequent sampling at sites where it is expected that the (pore)water will cause the PE to accumulate about 10 to 100 ng of target PCBs/g_{PE}). Note that the values vary from PRC to PRC, so one might choose to load from a mean solution concentration (*ca.* 5 ng/mL) if the PRCs are supplied at the same concentrations in a stock solution.

PE is stored in the PRC loading solution until shortly before passive sampling use.

Step 4. If spiking solutions contain organic co-solvents like MeOH, this MeOH must be leached out of the PE before the polymer film can be used for passive sampling. To insure that MeOH leaching will not substantially change PRC loading, one may calculate whether substantial fractions of the PRCs will be lost in subsequent steps required to leach the MeOH from the PE. Since the leaching steps involve use of H₂O (with only a little MeOH from the PE), use the PE-water partition coefficients. For PCBs, these coefficients are derived from a linear free energy relationship (LFER) found in the review by Lohmann (2012). With these values, we can solve for the fractional losses of individual PRCs to each batch of the leachate contained in 1000 mL ground glass stoppered flasks, using:

$$\text{fraction of each PRC remaining in PE after a single leach step} = 1 - (1 / (1 + K_{\text{PE-H}_2\text{O}} * \text{Mass}_{\text{PE}} / \text{Volume}_{\text{H}_2\text{O}})) \quad \text{Eq. 3}$$

For example, in the case of congener #52, one finds 99.66% of the PRC remains in the PE after the first leach (see below). Two additional leaches lower this to 99.32% and 98.98%, respectively. More hydrophobic congeners are leached even less in this case.

Example spreadsheet calculation for spiking PCB PRCs into LDPE from a 80:20 methanol-water solution.													
step 1						step 2		step 3		step 4			
								Solution concentration		fraction of PRC left in PE after			
						for PE mass (g) 0.82		(ng/mL) in in order to get		each water soak to remove MeOH			
	Training data for estimation of $K_{PE-(80:20)m:w}$		potential 13C-labelled PCBs to use as PRCs		use correlation to estimate partition coeff'	Volume of MeOH:water (mL) 125		100 ng/g PE		estim log K_{PE-w}	1st leach (Eq. 3)	2nd leach (Eq. 3)	3rd leach (Eq. 3)
PCB congener	log KPE- MeOH:water (ref 1)	log Kow (ref 2)	congener	log Kow (ref 2)	log K_{PE-} (80:20)m:w	fraction of each PRC in PE at equilib' (Eq. 1)		ng/mL MeOH:H2O (Eq. 2)		log Kpew = 1.14*log Kow-1.14 (ref 3)	1000 mL water	1000	1000 mL water
4	0.20	4.65	52	5.84	0.97	5.8%		11.3		5.52	0.997	0.993	0.990
29	1.05	5.6	101	6.38	1.26	10.7%		6.1		6.13	minimal leaching back into water		
155	1.29	6.41	153	6.92	1.55	18.8%		3.5		6.75	1.000		
204	1.67	7.3	180	7.36	1.78	28.4%		2.3		7.25	1.000		
			28	5.67	0.88	4.8%		13.8		5.32	0.995	0.990	0.985
			47	5.85	0.98	5.9%		11.2		5.53	minimal leaching back into water		
			111	6.76	1.46	16.0%		4.1		6.57	1.000		
			153	6.92	1.55	18.8%		3.5		6.75	1.000		
			178	7.14	1.66	23.3%		2.8		7.00	1.000		
use to find following correlation:													
log $K_{PE-(80:20)m:w}$ = 0.532 (± 0.094) * log K_{ow} (Hawker) - 2.133 (± 0.57)						PE mass		5.3	geom ave				
N = 4, R2 = 0.94, S.E. 0.18						number of strips		1					
						PE density (g/cm3)		0.95					
1. Booij, K, Smedes, F., van Weerlee, E.M., Chemosphere 2002, 46, 1157-1161.						PE thickenss (cm)		0.00254	for 1 mil sheet				
2. Hawker DW and Connell DW. 1988. Environ. Sci. Technol. 22: 382-387.						PE length (cm)		68					
3. Lohmann, R. Environ. Sci. & Technol.; 2012, 46, 606–618.						PE width (cm)		5					
						length*width*thickness *number of strips*density							
						mass of PE (g)		0.82					

**Standard Operating Procedure for the
Extraction and Analysis
of Polyethylene (PE) Used
in Polyethylene Devices (PEDs)**

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**Standard Operating Procedure
for the Extraction and Analysis of Polyethylene (PE) Used
in Polyethylene Devices (PEDs)**

SCOPE AND APPLICATION

- 1.1 This method describes procedures for chemical analysis of contaminants contained in polyethylene (PE) that has been deployed in passive samplers used to assess hydrophobic organic compounds (HOCs) in environmental media.
- 1.2 This procedure generates extracts suitable for High Resolution Gas Chromatography/Mass Spectrometry (GCMS) analysis.
- 1.3 This extraction procedure is applicable to PE used in laboratory (ex situ) - or field (in situ)-exposed usage.
- 1.4 Procedures for loading PE with PRCs are discussed in a companion SOP, “Standard Operating Procedure for the Preparation of Polyethylene (PE) Used for Passive Sampling”

SUMMARY OF METHOD

- 2.1 Upon recovery from the field, the PE, while still in the deployment device (e.g., stainless steel mesh or aluminum frame), should be carefully cleaned (e.g., remove adhering sediment) and then cut into appropriate lengths (e.g., to obtain replicates or to acquire sections exposed to varying depths into a sediment bed). The PE pieces, usually 10 to 100 milligram quantities, are placed in pre-cleaned, amber, glass vials with a few drops of water for shipping. Once received by the analytical laboratory, each sample is spiked with Surrogate standards (to assess analyte recoveries) and submerged in a suitable solvent (e.g., methylene chloride) for at least 12 hours. The extract is quantitatively transferred to a large vessel suited for solvent evaporation, and then the PE is re-extracted two more times with methylene chloride, with the extracts combined for evaporative concentration and eventual GCMS (or suitable) instrumental analysis. After extraction, the PE is air-dried and weighed.
- 2.2 A shaker table or other suitable system is recommended for the extractions to facilitate PE-solvent contact.

INTERFERENCES

- 3.1 PE is susceptible to contamination from atmospheric and surficial sources, and so it must be handled using clean techniques.
- 3.2 While the sediment solids, biofilms, and inorganic precipitates on PE surfaces does not prevent HOC accumulation in the PE during in situ deployment, these coatings can substantially complicate subsequent chemical analysis. Careful removal of adhering sediment or surface growths via wiping with a water-wetted Kimwipe® may be necessary. Surface coatings of organic films on PE (e.g., oil or tar residues) can be

removed without compromising the sample by using solvent-saturated wipes (<minute contact times) followed by immediate Surrogate standard addition and solvent extraction.

APPARATUS AND MATERIALS

- 4.1 Extraction vessels: amber glass vials (foil-lined lids)
- 4.2 Concentrating vessels: 100 mL glass, pear-shaped flask with glass stopper; 250 mL glass, round-bottom flask with glass stopper or equivalent
- 4.3 Bottle/jar tumbler, shaker table, bottle roller or equivalent
- 4.4 Analytical balance - capable of weighing to 0.1 mg (i.e., small value relative to samplers weights that are typically between 10 and 100 mg).
- 4.5 Food-grade aluminum foil
- 4.6 Stainless steel forceps
- 4.7 Single-edge razor blades
- 4.8 Teflon (or similar non-contaminating material) cutting board
- 4.9 Glass transfer pipettes
- 4.10 Kimberly-Clark Kimwipe® or equivalent

REAGENTS

- 5.1 Methylene chloride, CH₂Cl₂, pesticide grade or equivalent (other solvent suited to analytes of interest).
- 5.2 Hexane, C₆H₁₄, pesticide grade or equivalent
- 5.3 Organic-free reagent water (as defined in SW-846 Chapter One)
- 5.4 Research grade surrogate and injection standard compounds certified >98+% pure or equivalent.

PREPARATION AND HANDLING

- 6.1 Upon recovery and return to a clean working environment, the PE should be surface cleaned prior to any cutting or extraction. The PE surface should be wiped and rinsed free of surface particles and coatings as much as possible. This may include briefly (< minute) wiping with a hexane-soaked Kimwipe® (or equivalent) to remove oily or tarry exterior staining. If water wet, the PE surface should be blotted dry with a clean wipe.
- 6.2 Laboratory and field personnel should wear nitrile or latex gloves whenever handling PE to avoid cross-contaminating the PE.
- 6.3 Methylene chloride (pesticide grade) rinsed, stainless steel forceps and scissors are used when manipulation of PE is required.
- 6.4 Clean aluminum foil is used to cover any surface that PE may encounter.

PROCEDURE

- 7.1 Solvent Extraction: Laboratory and/or field blank and field-exposed PE is spiked with known quantities of surrogate compounds to assess analytical recoveries and extracted using organic solvents prior to analysis by GC/MS.
- 7.2 The PE is inspected for surface biofilms, particles, mud, or oily coatings. Biofilm mass should be removed as much as possible by using a clean wipe followed by a rinse with organic-free reagent water. Particles and sedimentary debris are removed by rinsing with organic-free reagent water and careful surface scraping if necessary to remove adhered/imbedded material. Oily coatings (e.g., coal tar staining or hydrocarbon slicks) are removed by soaking clean wipes in hexane and using forceps to hold and wipe both PE surfaces. This is not an exhaustive extraction and should be done quickly (<minute) and immediately prior to immersion in solvent. PE surfaces are blotted dry if water wet.
- 7.3 The PE is transferred to a pre-cleaned amber vial (size determined by dimensions of PE, typically 15-40 mL). Vial must be large enough for complete immersion of PE without excessive PE folding.
- 7.4 Known masses of surrogate compounds (Appendix 1) in a methylene chloride- compatible solvent are added to the vial. Typical additions are: 2.5-20 ng for aqueous samples; 50-250 ng for sediment samples, depending on target HOCs and their expected concentrations in the PE.
- 7.5 Methylene chloride is added to the vial to completely submerge the PE for a period of at least 12 hours.
- 7.6 The extract is transferred to a pre-cleaned glass concentration vessel. A second aliquot of methylene chloride is added to the extraction vial and agitated for >10 minutes. This step is repeated two more times.
- 7.7 After the final extract transfer, the PE is dried in air dry in the extraction vial and then weighed on an analytical balance until a consistent PE mass is obtained. This result is used to calculate the final target HOC concentrations measured in the PE sampler in units of HOC mass per PE mass.
- 7.8 Extracts are concentrated using rotary evaporation (or equivalent) down to suitable volumes for GCMS analysis; the resultant concentrated extracts are transferred to smaller vials (e.g., for autosamplers) according to standard laboratory practices. Before analysis, appropriate injection standards are added to the final extracts to allow for evaluation of the total volume of extract analyzed (Appendix 1).
 - a. Typical final extract volumes are:
 - b. 50-250 μ L for water column-exposed PE
 - c. 1-4 mL for contaminated sediment bed-exposed PE

QUALITY CONTROL

- 8.1 Method blanks, field blanks, matrix spikes, and/or replicate samples should be subjected to exactly the same analytical procedures as those used on field/lab-exposed PE samples.

8.2 QA/QC metrics, that are specific to the type of target HOCs of interest and the analytical methods used to quantify them, should be applied. Typical values for targets, like PAHs and PCBs, that are analyzed by capillary gas chromatography-low resolution mass spectrometry, in which picogram/uL detection is common, are:

8.2.1 Freshly prepared polyethylene and trip blanks: <0.1 ng HOC / g PE

Freshly cleaned PE samples, and samples of PE that traveled to and from the field site ("trip blank"), should have no significant peaks where PRCs, surrogate standards, injection standards, and target analytes elute.

8.2.2 PRC-loaded polyethylene reproducibility ($\pm 1\sigma/\text{mean}$, N=6): <10%

Individual batches of PE loaded with PRCs should exhibit reproducible PRC concentrations in the PE before deployment.

:

8.2.3 Recoveries of Surrogate Standards: >70% to < 120%

Surrogate standards should be recovered from PE samples at nearly 100%, plus or minus analytical precision. An exception may be relatively volatile compounds (e.g., mono-, di-chlorobiphenyls, naphthalene) that may be significantly lost when extracts are evaporated (e.g., recovery down to 60%).

8.2.4 Precision of replicate PE extract analyses (N $\geq$ 3): <25%.

The reproducibility of all analytes (injection standards, surrogate standards, PRCs, and target compounds) determined with multiple instrumental analyses of the same PE sample extract, even run on different dates, should fall within suitably narrow bounds.

8.2.5 Detection limits using PE samples: ≤ 1 ng / g PE

Assuming 100 mg PE samples and 100 uL final extract volumes, target analytes, such as PAHs and PCBs, analyzed by GCMS (or methods with like sensitivity) should have <ppb detection limits.

METHOD PERFORMANCE

- 9.1 The method performance is assessed by determining the recovery and reproducibility in analyzing surrogate compounds (Appendix 1). All other lab-specific QA/QC metrics should be adhered to.
- 9.2 Successful PE deployment is achieved when significant (>method precision) losses of PRCs occurred, allowing one to use their behavior to adjust target compound levels in the PE up to equilibrium concentrations (Fernandez et al. 2009; Tcaciuc et al. 2014).

REFERENCES

- Fernandez L.A., Harvey, C.F., and Gschwend, P.M. Using performance reference compounds in polyethylene passive samplers to deduce sediment pore water concentrations for numerous target chemicals. *Environ. Sci. Technol.*, 43, 8888-8894, 2009.
- Tcaciuc, AP, JN Apell, and PM Gschwend. " Passive Sampler PRC Calculation Software and User's Guide". Available at <https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Sediments/ER-200915>. July 2014.

Appendix 1 Suggested Performance Reference Compounds (PRCs), Surrogate Compounds (Recovery Standards), and Injection Standards. The laboratory preparing the PE must coordinate PRC choices with the laboratory doing the PE analyses to avoid conflicting uses.

A. PRCs, suitable for polycyclic aromatic hydrocarbon (PAH) determinations when Capillary Gas Chromatography-Mass Spectrometry (GCMS) is used for analysis include, but are not restricted to, deuterated PAHs. One subset should be used as PRCs, while reserving others for use as surrogate (recovery) and injection standards. Unlabeled compounds such as terphenyl can be used as injection standards if they are readily resolved from the other analytes.

Targets: PAHs Method: GCMS Detection Limit ~ 100 pg / 100 mg PE			
PRCs	¹³ C6-phenanthrene, ¹³ C6-fluoranthene, ¹³ C6-chrysene, ¹³ C6-indeno(1,2,3-cd)pyrene		
Surrogates	d10-anthracene	d10-fluoranthene	d12-benz(a)anthracene
Injection Standards	d10-acenaphthene	d14- <i>m</i> -terphenyl	d12-perylene

B. PRCs and surrogate compounds suitable for polychlorinated biphenyl (PCB) determinations when GCMS is the method separation and detection include, but are not restricted to, ¹³C-labeled or deuterated PCB congeners. One subset, for example including tri-, tetra-, penta-, hexa-, and heptachloro-biphenyls, can be used as PRCs while reserving different tri-, tetra-, penta-, hexa-, and heptachloro-biphenyl congeners to serve as surrogate compounds. Still other compounds such as deuterated PAHs or rare PCBs (not contained in Aroclor/Clophan mixtures such as: PCB-39, PCB-55, PCB-104, PCB-150 and PCB-188) can be used as injection standards.

Targets: PCBs Method: GCMS Detection Limit ~ 100 pg / 100 mg PE	
PRCs	¹³ C labelled PCB congeners: 37, 47, 54, 111, 138, 178
Surrogates	¹³ C labelled PCB congeners: 3, 15, 28, 52, 118, 153, 180, 194, 208, 209
Injection Standards	¹³ C labelled PCB congeners: 19, 105, 170

C. When analyzing for organochlorine pesticides such as DDT using GCMS, ¹³C labeled compounds can serve as PRCs. However, since DDT has been seen to degrade to form DDE or DDD in certain situations, one should use the 4,4'- isomer of DDT and the 2,4'-isomers of DDE and DDD as PRCs to allow appearance of ¹³C-labelled 4,4'-DDE or 4,4'-DDD to be interpreted as arising from reaction the DDT PRC during the deployment. Deuterated or ¹³C labeled PCBs can be used as surrogate (recovery) and injection standards.

Targets: DDTs Method: GCMS Detection Limit ~ 200 pg / 100 mg PE			
PRCs	¹³ C 2,4'-DDE	¹³ C 2,4'-DDD	¹³ C 4,4'-DDT
Surrogates	¹³ C-PCB111	¹³ C-PCB153	¹³ C PCB 178
Injection Standards	d6 PCB 77	¹³ C PCB 105	¹³ C PCB 167

SOP QUESTIONS FROM COMMERCIAL LABORATORIES AND ANSWERS FROM THE POLYMERIC SAMPLER EXPERTS

Question 1: Am I correct in assuming that the sections of the SOP that refer to surrogates or injection standards are not applicable? Each lab is free to use their current SOP listed compounds to support these needs correct?

Response: Yes. Each lab is free to adapt the SOP to the analytical method being used provided the modifications do not interfere with use of the Performance Reference Compounds (PRCs) specified. All labs must correct the polymeric sampler extract concentrations using surrogate recoveries. Use of standardized PRCs and consistent correction for surrogate recoveries is required to ensure different labs that utilize these SOPs produce comparable data.

Question 2: Are the QA and method performance sections applicable? Aren't these SOPs supposed to prescribe sampler loading and extraction procedures – giving the laboratories flexibility to use different analytical methods?

Response: Yes, subject to restrictions noted in response to Question 1 above.

Question 3: Is there flexibility in the methods for labs to make minor changes? For example, in section 7.3.2 of the SPME SOP a volume of 200mL is specified for the spiking solution. Could other volumes be used so long as the 80:20 water/methanol ratio specified in the method is maintained?

Response: Flexibility is allowed within acceptable ranges specified in the EPA method being used. Certainly larger volumes can be used. Here an example with 200 mL is given for a small PDMS segment i.e. 5 cm and small sampling efforts. For PDMS segments of 30 cm a large vessel volume is recommended.

Question 4: Section 7.3.3 of the SPME SOP mentions agitating the PDMS rod at a rate of 130 strokes per minute, which seems high. I would be concerned about the fiber being physically affected by this robust rate. What if my agitating equipment only goes up to 60 strokes per minute?

Response: The vessel should be filled with PRC solution with minimal headspace; in such conditions the movement of PDMS during 1D agitation is very limited, even at high mixing rates (e.g 120 strokes per minute). With an overhead tumbler the risk of PDMS breakage is high so this approach is not recommended.

If fewer than 130 strokes is used, longer PDMS exposure to PRC solution is required. For example, 130 strokes agitation could achieve acceptable loading in 4 weeks but 60 strokes agitation may require 6 weeks.

Question 5: Section 7.3.3 of the SPME SOP states a minimum of 21 days is required for the loading of PCB PRCs. I'm not that familiar with SPME loading but the time frame seems long to me given 7 days is specified for PE?

Response: A key reason the loading time for PE is shorter is because the SOP calls for more solvent in the PRC loading solution, which effectively "opens up" the PE polymer for faster diffusive loading. The PE SOP calls for a 80/20 methanol/water solution whereas the PDMS SOP calls for a 20/80 solvent/water solution. It may be possible to increase the solvent ratio to achieve faster PDMS PRC loading; however, a 21 day loading and 20/80 solvent/water mix is

recommended based on experience. A secondary reason for slower PDMS loading with PRCs is that the PRCs enter the polymer from one side only (diffusion from outside of the PDMS cylinder inward toward the glass core) whereas diffusion into the PE strip occurs from both sides.

Question 6: Section 5.3 of the PE Preparation and Analysis SOP states that surrogates and injection standards must be >98% pure. While we strive to use the purest standards available (within reasonable cost constraints) our corporate QA policy allows us to use >96% purity reagents in this area.

Response: Standards >98% purity are recommended. If standards of lesser purity are used, blanks must be carefully monitored and impurities must be accounted in data reporting and interpretation.

Question 7: Regarding “SOP PE (prep)- 4.1 Extraction vessels:” – are clear or amber jars preferred?

Response: Amber.

Question 8: Regarding “SOP PE (prep) - 7.1 Polyethylene Cleaning Procedures:” - should a differential weight be determined on uncleaned vs. cleaned PE to determine density?

Response: We recommend weighing the polymer after all of the following steps have been completed.

- Sampler retrieval from the sediment exposure
- Gentle sampler cleaning to remove any biofilms etc. (see response to 16 below)
- Sampler extraction in solvent
- Sampler drying to remove solvent

When the sampler is extracted, it “soaks up” solvent and therefore is heavier immediately after extraction than it is normally. We often set the extracted samplers to evaporate in a fume hood for a day or so, periodically weighing the sampler to ensure the weight has stabilized and all solvent has evaporated. We use the final stabilized weight in subsequent computations.

Question 9: Regarding “SOP PE (prep) - 8.1 PRC Loading Validation:” - what should be done with the remaining parts of the strip? Can this be used in another application?

Response: Strips can be stored in the PRC loading solution. It’s critical to collect a portion of the strip for analysis to obtain the PRC concentration at time zero – this must be done for each sampling event.

Question 10: Regarding “SOP PE (extract/analyze) - 2.1 Summary of Method:” - who is responsible for QCing these vessels?

Response: We recommend including a method blank (i.e. an “unloaded” sampler using standard glassware from lab during extraction) to ensure there are no contamination due to laboratory equipment etc. If contamination is encountered, additional diagnostic tests specific to the lab and method would be required.

Question 11: Regarding “SOP PE (extract/analyze) - 2.1 Summary of Method: What is the desired precision?”

Response: Precision in the 5-10% range is desired.

Question 12: Regarding “SOP PE (extractanalyze) - 2.2 Summary of Method:” - when the PRCs are loaded, are they rolled or shaken? Should the same mechanism be used for the extraction?

Response: Either can work. There is no need to be consistent with the loading vs. extraction mechanism. Regarding PE PRC loading, the critical detail is that the polymer is fully submerged. Problems can arise if polymer strips are on top of one another in the loading solution.

Question 13: Regarding “SOP PE (extractanalyze) - 7.1.6 Procedure:” If the initial weight is taken and we are able to determine a differential weight, should we not use desiccators before and after to negate humidity difference?

Response: No. See response to question 8.

Question 14: Regarding “SOP PE (extractanalyze) - 8.1 Quality Control:” - I am not sure of the order of clean, cut and load with PRCs. There is some inconsistency in sections 2.4 and 7.1. We prefer cut, clean and load with PRCs to minimize exposure of the prepared PE.

Response: You can do it in the order you prefer. Cut, clean, and load is fine.

Question 15: Regarding “SOP PE (prep): Section 6.1.” Is cleaned PE stored dry? Or in water? Or ?

Response: It is recommended that the cleaned PE be stored in the bottle and solution used to clean it, with as little air as possible.

Question 16: Regarding “SOP PE (extractanalyze):” Can a soft toothbrush be used to remove biofilm? Section 6.1 and 7.1.1. How far should we go with cleaning?

Response: Yes! It’s critical to remove all of the debris (including any biofilm) such that only the polymer (not polymer + biofilm) is extracted, which permits use of polymer- and contaminant-specific partitioning constant use to convert polymer extract concentrations into sediment porewater concentrations. Cleaning should be done *gently* using a soft bristled toothbrush so as to not damage the sampler. Note that it will not be possible to remove staining and that is OK.

Question 17: Regarding “SOP PE (extractanalyze): section 7.1.3” – it says to add surrogate compounds to the jar. Should this not say pipet onto the PE strip in the jar, and make sure to add before the solvent.

Response: Add surrogate then immediately add the solvent.

Question 18: Regarding “SOP PE (extractanalyze):” Can some allowance be added for cleanup of extracts before GC/MS analysis?

Response: Certainly. It is not typical to require cleanup for PAHs and PCBs using these methods. If using polymeric samplers to measure other organic contaminants (e.g. dioxins), cleanup may be required.

APPENDIX C
Indiana Harbor sediment screening results

Quarterly Progress October 2018 – January 2019

Task 1 results were presented via platform presentation at the SETAC North America 39th Annual Meeting in November 2018, as well as via poster presentation at the ESTCP Symposium in November 2018. Task 2 results are complete and data analysis is underway as of this January 2019 QPR. We anticipate starting Task 3 in March 2019.

A key accomplishment last quarter included selection of a suitable large-quantity sediment sample for use during Task 3. The sediment was collected from Indiana Harbor in 15 individual, 5 gallon buckets, which were stored at 4 °C prior to homogenization. Sediment homogenization was conducted by mechanically mixing the sediment in large drums at the U.S. Engineer Research Development Center (Attachment 1). The homogenized sediment was placed back into the 15 buckets, which had been rinsed clean, and stored at 4 °C. Sediment samples were then collected from the 15 buckets and submitted for total organic carbon (TOC) analysis as an indicator of homogeneity between the buckets. Sediment in buckets #1, #2, and #4 was excluded from further consideration because TOC concentrations in those buckets exhibited greater than 20% relative difference from the global mean TOC concentration value.

Table 1. Total organic carbon (TOC) analysis results for Indiana Harbor sediment samples

Sample	TOC, mg/kg	% moisture	% solids	Relative Percent Difference (RPD) from mean value, %
IHC Bucket #1	120,000	69	31	71%
IHC Bucket #2	85,000	64	36	21%
IHC Bucket #3	63,000	64	36	10%
IHC Bucket #4	52,000	64	36	26%
IHC Bucket #5	80,000	67	33	14%
IHC Bucket #6	65,000	63	37	7%
IHC Bucket #7	62,000	64	36	12%
IHC Bucket #8	72,000	64	36	3%
IHC Bucket #9	64,000	66	34	9%
IHC Bucket #10	58,000	64	36	17%
IHC Bucket #11	57,000	64	36	19%
IHC Bucket #12	58,000	66	34	17%
IHC Bucket #13	56,000	64	37	20%
IHC Bucket #14	79,000	63	37	13%
IHC Bucket #15	80,000	63	37	14%
mean	70,067	65	35	
standard dev.	17,240	2	2	

Next PAHs and PCB congeners (EPA 8270C and 8082, respectively) were measured in the selected sediment samples (Buckets #3, and #5 - #15). Target analytes include the EPA Priority 16 PAHs and the NOAA 18 congeners suite plus congeners 126 and 169 (congeners 195, 206 were not measured for this task).

Table 2. Average PAHs and PCB congeners concentrations across selected subsamples (Buckets #3, and #5 - #15)

PAHs	Average, ug/kg dry weight	Standard Deviation	Relative Standard Deviation	PCBs	Average, ug/kg dry weight	Standard Deviation	Relative Standard Deviation
Naphthalene	415,750	64,385	15%	PCB 8	327	19	6%
Phenanthrene	29,500	4,241	14%	PCB 101	123	8	7%
Anthracene	55,075	3,164	6%	PCB 105	50	3	7%
Fluoranthene	20,483	3,090	15%	PCB 118	73	6	8%
Pyrene	17,575	2,615	15%	PCB 126	ND	--	--
Benzo (a) anthracene	44,267	2,963	7%	PCB 128	ND	--	--
Chrysene	57,058	4,023	7%	PCB 18	689	63	9%
Benzo (b) fluoranthene	32,833	2,186	7%	PCB 138	52	4	8%
Benzo (k) fluoranthene	48,017	6,006	13%	PCB 153	54	5	9%
Benzo (a) pyrene	48,275	3,195	7%	PCB 28	951	69	7%
Indeno (1,2,3-cd) pyrene	20,533	2,110	10%	PCB 169	ND	--	--
Dibenz (a,h) anthracene	6,465	902	14%	PCB 170	19	2	11%
Benzo (g,h,i) perylene	22,625	2,492	11%	PCB 180	44	4	8%
Acenaphthylene	3,724	369	10%	PCB 187	22	2	9%
Acenaphthene	110,508	25,743	23%	PCB 44	309	21	7%
Fluorene	67,550	21,170	31%	PCB 52	275	21	8%
				PCB 66	270	21	8%
Sum, mg/kg dw	1,000			PCB 77	47	4	9%
				Sum, mg/kg dw	3.3		

The average total concentration of PAHs (1,000 mg/kg dw) and PCBs (3.3 mg/kg dw) met our minimum concentration requirements threshold, meaning polydimethylsiloxane (PDMS) and low-density polyethylene (LDPE) polymer samplers and standard analytical methods will be capable of reliably quantifying this range of PAHs and PCBs concentrations in the Indiana Harbor sediment samples. Furthermore, the level of homogeneity achieved in the sediment between buckets was deemed acceptable, with $\leq 11\%$ RSD values for all PCB congeners and $\leq 15\%$ RSD values for all PAHs except acenaphthene and fluorene.

ATTACHMENT 1
Indiana Harbor Sediment Homogenization

Indiana Harbor

Sediment compositing and homogenization

13 Sept 18

Initial bucket homogenization (total 17, partially filled buckets); all buckets were composited into drums by adding 50% volume of each bucket into each drum



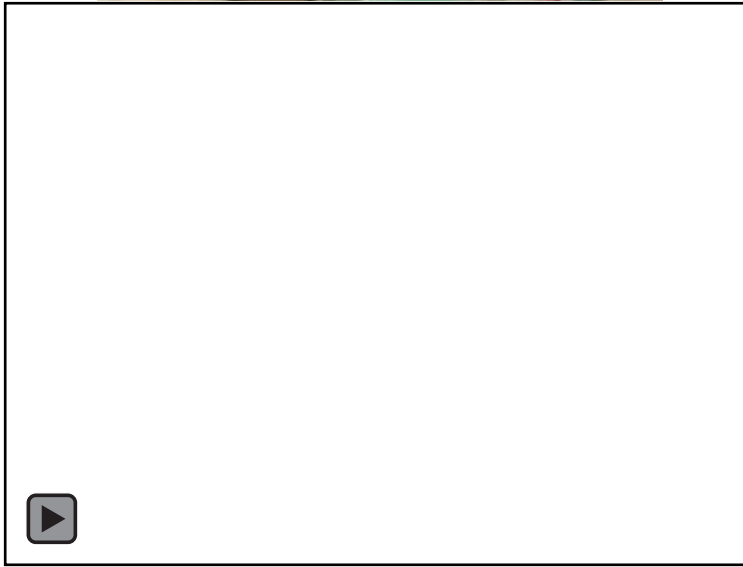
Rinsing of original lids, buckets for material to go back into for cold storage (contaminated rinse water placed in adjacent drum for later disposal)



Homogenization in drums



CLICK FOR VIDEO



Transfer between drums (60% volume, 6 times)

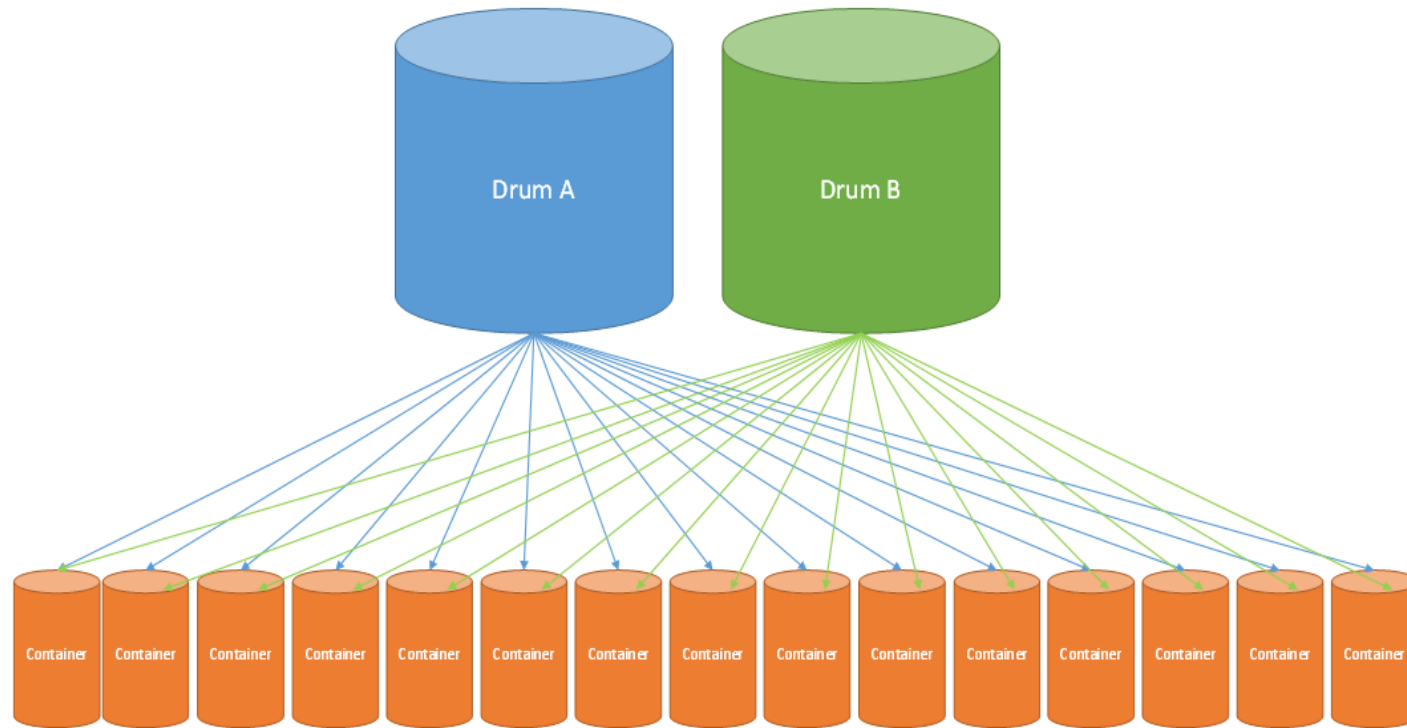


Compositing 2 drums into each of 15 buckets
(total, 2.25 gal from each drum went into each
bucket)



Homogenization after re-allocation to buckets (total of 15 buckets, approx. 4.5 gallons each)

Figure 1. Diagram of compositing. The sediment is to be alternated between each barrel, layered into the jars and repeated until full. This would be repeated for each lab (i.e., all buckets for all labs, repeated until full (note: 15 containers below).



Collecting samples for analytical chemistry
(15 buckets, three 4oz jars each; total 45 sample
containers)



Cold storage



APPENDIX D

Task 1 GO! Memo with appendices

Standardizing Polymeric Sampling for Measuring Freely-Dissolved Organic Contaminants in Sediment Porewater

ESTCP PROJECT ER-201735 Final Task 1 Go/No-Go Memorandum

October 19, 2018

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ATTACHMENT 1	Calibration Check Standard Preparation Methods
~~ATTACHMENT 2~~	~~Calibration Check Standard Results – Data Validation Memo~~
ATTACHMENT 3	Calibration Check Standard Results – Interlab Data Comparability Memo
~~ATTACHMENT 4~~	~~PRC Pre-loaded PDMS Samplers – Data Validation Memo~~
~~ATTACHMENT 5~~	~~PRC Pre-loaded LDPE Samplers – Data Validation Memo~~
ATTACHMENT 6	Pre-loaded Samplers – Interlab Data Comparability Memo

Note: Commercial laboratories are participating in this Interlaboratory method validation study under the condition of anonymity. Accordingly, data validation reports where lab-specific performance was described has been omitted from this publically-released report.

ACRONYM LIST

C_{free}	freely-dissolved organic contaminant concentration
PRC	performance reference compound
PDMS	polydimethylsiloxane
PAH	polycyclic aromatic hydrocarbon
PCB	polychlorinated biphenyl
EPA	Environmental Protection Agency
LDPE	low density polyethylene
USACE	U.S. Army Corps of Engineers
ERDC	Engineer Research Development Center
QA/QC	quality assurance/quality control
HRGC	High Resolution Gas Chromatography
HRMS	High Resolution Mass Spectrometry
LRMS	Low Resolution Mass Spectrometry
RSD	Relative Standard Deviation
RPD	Relative Percent Difference

1. INTRODUCTION

1.1 Project Background

Polymeric samplers sorb hydrophobic organic contaminants present in sediment, whether used actively or passively (i.e. respectively with or without sediment/polymer mixing). The resultant polymer concentrations can then be used to calculate freely-dissolved contaminant concentrations (C_{free}) in the sediment's porewater. Polymeric samplers maybe used as alternatives to (a) Henry samplers and pumping for porewater sample collection or (b) sediment centrifugation with supernatant collection. C_{free} measured by polymeric samplers represents the fraction of contaminants not sorbed to settling solids or associated with suspended colloidal matter. C_{free} is directly linked to sediment-dwelling organism's exposure to contaminants as well as risk for biouptake into the larger foodweb. Therefore, developing standardized methods for obtaining C_{free} measurements using polymeric samplers is critically important.

The objectives of this demonstration are:

1. Develop a standardized methodology for polymeric sampler preparation and analysis of polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) by multiple contract and government laboratories. This methodology will describe how to:
 - a. Prepare polymeric samplers, including loading performance reference compounds (PRCs);
 - b. Expose polymeric samplers to sediment in the laboratory (i.e., *ex situ*);
 - c. Retrieve polymeric samplers from sediment and extract the organic contaminants and PRCs;
 - d. Perform chemical analysis of polymeric sampler extracts; and
 - e. Interpret results and use them to determine the C_{free} present in the sediment porewater.
2. Collaborate with public- and private-sector laboratories to finalize the standardized polymeric sampler methodology, then validate the methodology through a phased interlaboratory comparison.
3. Document the standardized methods and interlaboratory method comparison results in a guidance document prepared following EPA SW846 guidelines, in addition to posting freely available webinars and instructional videos via YouTube and other online platforms.

1.2 Demonstration Performance Objectives

During this demonstration, multiple laboratories will utilize polymeric samplers to quantify freely-dissolved PAHs and PCBs in porewater using a single sediment sample. Demonstration results are intended to document laboratory accuracy and reproducibility of the polymeric sampler method – a key requirement for future acceptance as a SW-846 Method. The demonstration consists of three tasks, each intended to reduce sources of variability extraneous to the polymeric sampler method itself prior to proceeding with subsequent tasks. Performance objectives are described in Table 1 below.

Table 1. Demonstration performance objectives.

Performance Objective	Data Requirements	Success Criteria
Quantitative Performance Objectives		
Interlaboratory analytical variability is low and within acceptable range (Task 1.1)	- Calibration check standards for low- and high-sensitivity methods prepared by one lab - Results of calibration check standard analysis reported as an EPA Stage 4 data package and Electronic Data Deliverable (EDD)	- Data validator confirms analytical data from each lab meets QC criteria (Section 5.4.4) and is of acceptable quality - Each lab reports $\pm 30\%$ of known concentrations for non-isotopically-labeled analytes; $\pm 50\%$ of known concentrations for isotopically-labeled Performance Reference Compounds (PRCs) - Success constitutes “go” to subsequent task.
Laboratories consistently extract and analyze PRCs from PRC-preloaded polymeric samplers provided by expert academic labs (Task 1.3)	- Results of PRC-loaded polymeric samplers (PDMS and LDPE replicates) from the academic laboratories preparing them - Results of PRC-preloaded polymeric samplers (PDMS and LDPE replicates) extracted and analyzed by all labs - Analytical data submitted as EPA Stage 4 data package and EDD	- Data validator confirms analytical data from each lab meets QC criteria (Section 5.4.4) and is of acceptable quality - Each lab reports $\geq \pm 50\%$ of known concentrations for the isotopically-labeled PRCs - Percent Relative Standard Deviation (% RSD) $\leq 20\%$ for replicate analyses; tolerance beyond this range will be considered on basis of collective results - Success constitutes “go” to subsequent task.
Laboratories achieve target PRC concentrations in polymeric samplers following standardized methods specific to each polymer (Task 2)	- Extract analysis results from polymeric samplers (PDMS and LDPE replicates) independently loaded by labs following standard method. - Analytical data submitted as EPA Stage 4 data package and EDD	- Data validator confirms analytical data meets QC criteria (Section 5.4.4) and is of acceptable quality - Each lab achieves within $\pm 50\%$ of target PRC concentrations immediately after loading is complete (i.e. $PRC_{T=0}$); Collective results will be used to establish target $PRC_{T=0}$ concentration criteria for Task 3 %RSD $\leq 20\%$ for replicate analyses performed; tolerance beyond this range will be considered on basis of collective results - Success constitutes “go” to subsequent task.
Laboratories measure target contaminants in homogenized sediment sample using “active” and “passive” sampling/exposure methods (as described in Section 5.3.3) following standardized methods specific to each polymer (Task 3)	- All analytical data from the polymeric sampler measurements submitted as EDD - Analytical data resulting from sediment porewater analysis via polymeric samplers, the Hawthorne method^{8,9}, and the air-bridge method¹⁰ - Analytical data submitted as EPA Stage 4 data package and EDD	- Data validator confirms analytical data meets QC criteria (Section 5.4.4) and is of acceptable quality - Achieve %RSD $\leq 20\%$ for $PRC_{T=0}$ concentration - Establish interlaboratory variability in resulting estimates of fractional approach to equilibrium and $C_{polymer}$ for both “active” and “passive” exposures; identify to the extent possible contributing sources of interlaboratory variability - Establish intermethod variability by comparing C_{free} estimates determined using polymeric samplers compared to alternative Hawthorne^{8,9} and air-bridge methods; variability as a function of target compound hydrophobicity will also be established
Quantitative Performance Objectives		
Meet minimum commercial laboratory participation required to fulfill method validation requirements for SW-846 standardized method application	Responsiveness, flexibility, commitment to identify and resolve technical issues so that maximum participation is retained during demonstration	At least 3 commercial laboratories successfully complete all demonstration tasks

1.3 Document Organization and Purpose

Task 1 was completed in three subtasks (Tasks 1.1 – 1.3). The purpose of this Go/No-Go memorandum is to document the methods and results of all Task 1 subtasks, document results compared to performance objectives, and to recommend a Go/No-Go decision to proceed with Task 2. Section 2 presents Task 1 methods; Section 3 presents Task 1 results; Section 4 presents discussion and the Go/No-Go recommendation. Supporting information is attached.

2. METHODS

2.1 Task 1.1 – “Calibration Check Standard” Preparation and Analysis

As a first order of business, all commercial laboratories identified the standard EPA method they preferred to use to measure PCBs and PAHs during the project. Methods and associated QC criteria were documented in the Final Demonstration Plan (USACE, February 2018). Performance Reference Compounds (PRCs) are isotopically-labeled versions of the target organic contaminants of interest, which are loaded into the samplers prior to deployment. PRC loss from the polymer during deployment provides a measure of its progress toward equilibrium with contaminants in the sediment porewater. While there are many commercially available isotopically-labeled PAH and PCB candidates for PRCs, commercial laboratories already use many of these as internal standards in their analytical methods. A key achievement of the demonstration thus far was reaching consensus amongst all participating laboratories on a set of PRCs listed below. The PAH PRCs are independent of the analytical method the laboratories use; thus, there is only one suite of PRCs for each method. PCB PRCs vary by analytical method and such there are two suites of PCB PRCs: one for regular sensitivity (low resolution mass spectrometry) and one for high sensitivity (high resolution mass spectrometry) methods.

- PAH PRCs: $^{13}\text{C}_6$ -phenanthrene, $^{13}\text{C}_6$ -fluoranthene, $^{13}\text{C}_6$ -chrysene, $^{13}\text{C}_6$ -indeno(1,2,3-cd)pyrene
- PCBs PRCs (Regular Sens): ^{13}C -labeled PCB congeners 37, 47, 54, 111, 138, 178
- PCBs PRCs (High-Sen): ^{13}C -labeled PCB congeners 28, 47, 70, 80, 111, 141, 182

Calibration check standards were prepared by the Texas Technical University (TTU) laboratory to contain method-specific PRCs and method-appropriate concentrations. Attachment 1 includes the SOP for calibration check standard preparation.

Each laboratory analyzed the method-specific calibration check standards they received using their chosen analytical methods. Data packages received from commercial laboratories were subject to a complete (Level IV) data validation by Mr. Mingta Lin. The Data Validation Report (Attachment 2) identified no data quality deficiencies in

calibration check standard data packages submitted by commercial laboratories. University laboratories used their standard or high-sensitivity analytical procedures to quantify concentrations of PAHs and PCBs in the calibration check standards as well. University data were not subject to validation; however, as documented in the Data Comparability Memorandum (Attachment 3) Mr. Lin determined that it was appropriate to present and evaluate data generated by commercial and university laboratories collectively.

2.2 Task 1.2 – Standardization of Polymeric Sampler Procedures

Danny Reible's group at Texas Technical University (TTU) and Phil Gschwend's group at the Massachusetts Institute of Technology (MIT) – respective subject matter experts for use of polydimethylsiloxane (PDMS) and low-density polyethylene (LDPE) polymeric samplers – shared their standard operating procedures (SOPs) for the preparation and extraction of PDMS and PE samplers with each other and with commercial laboratories to solicit questions and input. The resulting updated polymer-specific SOPs and Frequently Asked Questions (FAQs) from commercial laboratories were included as an attachment to the Final Demonstration Plan. The final polymer-specific SOPs were utilized by the commercial and university laboratories to complete Task 1.3.

2.3 Task 1.3 – “PRC Pre-Loaded Polymeric Sampler” Preparation and Analysis

Expert university laboratories followed the polymer-specific SOPs to load method-specific PAHs and PCBs into replicate polymeric samplers. TTU prepared PRC pre-loaded PDMS fiber segments; MIT prepared PRC pre-loaded LDPE fiber segments. TTU and MIT each sent triplicate pre-loaded samplers to all participating laboratories, which then followed the polymer-specific SOPs to extract PRCs from the samplers and analyze them using their preferred methods and instrumentation. Data packages received from commercial laboratories were subject to a complete (Level IV) data validation by Mr. Mingta Lin. The Data Validation Reports (Attachment 4 for PDMS, Attachment 5 for LDPE) identified no data quality deficiencies that would preclude data use for intended purpose. University data were not subject to validation; however, as documented in the Data Comparability Memorandum (Attachment 6) Mr. Lin determined that it was appropriate to present and evaluate data generated by commercial and university laboratories collectively.

As of May 31, 2018, two of six participating commercial laboratories had not submitted Task 1.3 data packages. The first tardy laboratory (ALS Kelso) withdrew from the project on May 31, 2018, citing significant laboratory organizational challenges and inability to meet project requirements. The second tardy laboratory (Vista Analytical) withdrew from the project in July 2018. Four commercial laboratories will proceed to Task 2. We expect all four remaining laboratories will participate fully through project completion.

3. RESULTS

3.1 Task 1.1 – “Calibration Check Standard” Preparation and Analysis

Commercial laboratories are participating in this project under the condition of anonymity. Accordingly, identities of laboratories that submitted calibration check standard results have been obscured by assigning each a random number (Table 2).

Table 2. Tests Performed by Laboratories

Test	GC/MS Sensitivity	Check Standard (ng/L)	Laboratory Number (Randomly-Assigned) that Performed Test	
			University	Commercial
PCBs	High Sensitivity	5	40, 75, 84	25, 62, 11
	Regular Sensitivity	50	0, 87, 94	35, 69, 17
PAHs	High Sensitivity	5	58, 82	91
	Regular Sensitivity	100	9, 74, 98	3, 6, 28, 37, 47

Calibration check standard results reported by labs were within $\pm 30\%$ of known concentrations for PCB and PAH natives 83% of the time, and were within $\pm 50\%$ of known concentrations for PCB and PAH PRCs 96% of the time (Figure 1, Table 3). Labs 98 and 28 reported 1 or 2 out of range results for native PAHs ($\leq \pm 38\%$, Table 3). Lab 62 reported 2 out of range results for native PCB congeners ($\leq \pm 36\%$); Lab 11 reported 1 out of range ($\leq \pm 32\%$) result. A significantly out-of-target-range result (-91%) for PAH PRC indeno(1,2,3-cd)pyrene was reported by Lab 74.

Table 3. Summary of Task 1.1 performance against objectives.

Method	Analyte	Total Labs Performing	Lab Response Rate	Pass	Fail	Pass Rate	Exceedance Summary
EPA 1625B/8270D or EPA 8270D	PAH Natives	10	100%	8	2	80%	Lab 98 ^a achieved +38% for naphthalene Lab 28 ^b achieved -38% for dibenz[a,h]anthracene and -32% for indeno[1,2,3-cd]pyrene
	PAH PRCs	10	100%	9	1	90%	Lab 74 ^c achieved -91% for indeno[1,2,3-cd]pyrene
EPA 8270D	PCB Natives	6	100%	6	0	100%	
	PCB PRCs	6	100%	6	0	100%	
EPA 1668C	PCB Natives	7	100%	5	2	71%	Lab 62 ^d achieved -36% and -32% for PCB-128 and PCB-138, respectively; Lab 11 ^e achieved -32% for PCB-44
	PCB PRCs	7	100%	7	0	100%	
Totals		46		41	5	89%	

a) Naphthalene contamination in lab's internal standard mix, new contaminant-free standard mix prepared; b) check standard solvent (isooctane) likely interfered with lab's internal standard solvent (methylene chloride), issue isolated to Task 1.1; c) suspected column "bleed" for PRC indeno(1,2,3-cd)pyrene-¹³C6 on low-resolution GC/MS used by Lab 74, deuterated or fully-labeled PRC would be more appropriate PRC for low-res GC/MS; d&e) apparent experimental error, which will be monitored going forward.

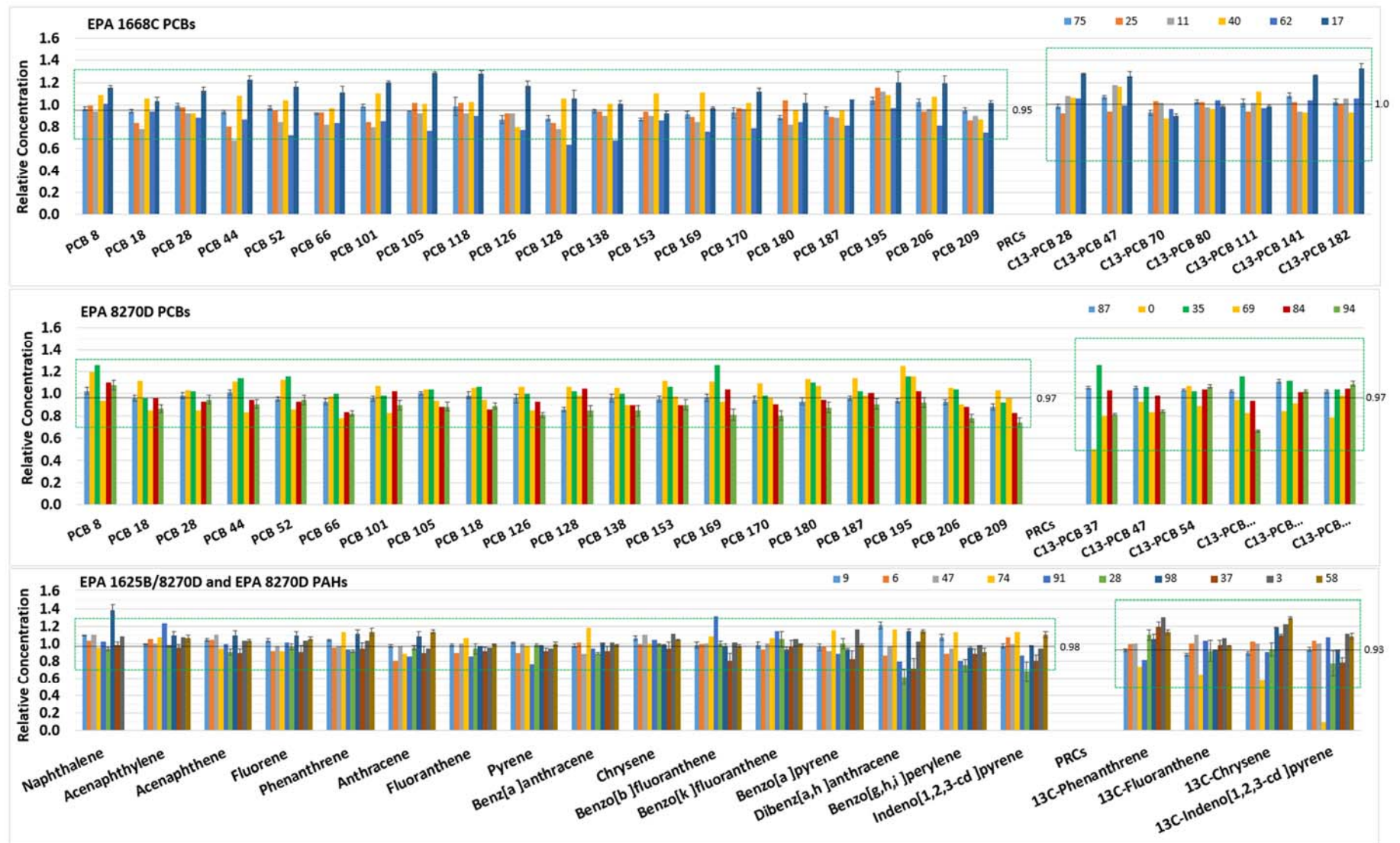


Figure 1. Calibration check standards results in relative units (Creported/Cknown). PAHs analyzed by regular- and high-sensitivity methods are shown at the bottom, PCB congeners analyzed by high-sensitivity and regular-sensitivity method are respectively shown at the top and middle of the figure. The acceptable range for native and PRC results (respectively $\pm 30\%$ and $\pm 50\%$) is highlighted in green. Average results for each data set are shown as black lines with average values to right.

3.2 Task 1.3 – “PRC Pre-Loaded Polymeric Sampler” Preparation and Analysis

Identities of laboratories that submitted results for PRC pre-loaded PDMS and LDPE polymeric samplers were obscured by assigning each a random number (Table 4). TTU and MIT prepared the PRC pre-loaded polymeric samplers for all labs. Concentrations reported by TTU and MIT were considered the “known” concentrations; accordingly, TTU and MIT identities were not obscured.

Table 4. PRC Concentrations achieved in pre-loaded samplers and labs performing tests

Test	GC/MS Sensitivity	Known Concentration Range for PRC Loaded Samplers (ng/g-LDPE or ng/mL-PDMS)	Laboratory
PDMS PCBs	High Sensitivity	1400 – 1700	76, 85, 93, 10, TTU
	Regular	8700 – 9200	44, 46, 20, TTU
PDMS PAHs	High Sensitivity	600 – 840	14, TTU
	Regular	7000 – 8500	71, 15, 23, 55, 38, 63, 81, TTU
LDPE PCBs	High Sensitivity	31 – 36	93, 18, 72, 60, MIT
	Regular	110 – 160	40, 86, 17, MIT
LDPE PAHs	High Sensitivity	27 – 51	MIT only
	Regular	140 – 200	MIT, 91, 16, 90, 72, 44, 32

PRC pre-loaded sampler results reported by labs were within $\pm 50\%$ of known concentrations for PAH and PCB PRCs loaded in PDMS and LDPE samplers 96 % of the time (Figures 2 and 3, Table 5). Lab 38 reported 1 out of range result for PAH PRC indeno(1,2,3-cd)pyrene in the PDMS samplers (-58%; Figure 2). Lab 86 reported 3 out of range results for PCB PRCs PCB-111, PCB-138 and PCB-178 (respectively -53%, -60%, and -71%; Figure 3).

Table 5. Summary of Task 1.3 performance against objectives.

Method	Analyte	Total Labs Performing	Lab Response Rate	Pass	Fail	Pass Rate	Exceedance Summary
PDMS	EPA 1625B/8270D or EPA 8270D PAH PRCs	9	100%	8	1	89%	Lab 38 ^a achieved -58% for indeno[1,2,3-cd]pyrene
	EPA 8270D PCB PRCs	4	100%	4	0	100%	
	EPA 1668C PCB PRCs	5	100%	5	0	100%	
LDPE	EPA 1625B/8270D or EPA 8270D PAH PRCs	8	100%	8	0	100%	
	EPA 8270D PCB PRCs	4	100%	3	1	67%	Lab 86 ^b achieved -53%, -60%, 71% for PCB congeners 111, 138, 178
	EPA 1668C PCB PRCs	5	100%	5	0	100%	
Total		35		33	2	94%	

a) detailed investigation identified no explanation for low result; b) not an analytical issue, suspect LDPE material variability in pre-loaded samplers provided to Lab 86, see discussion.

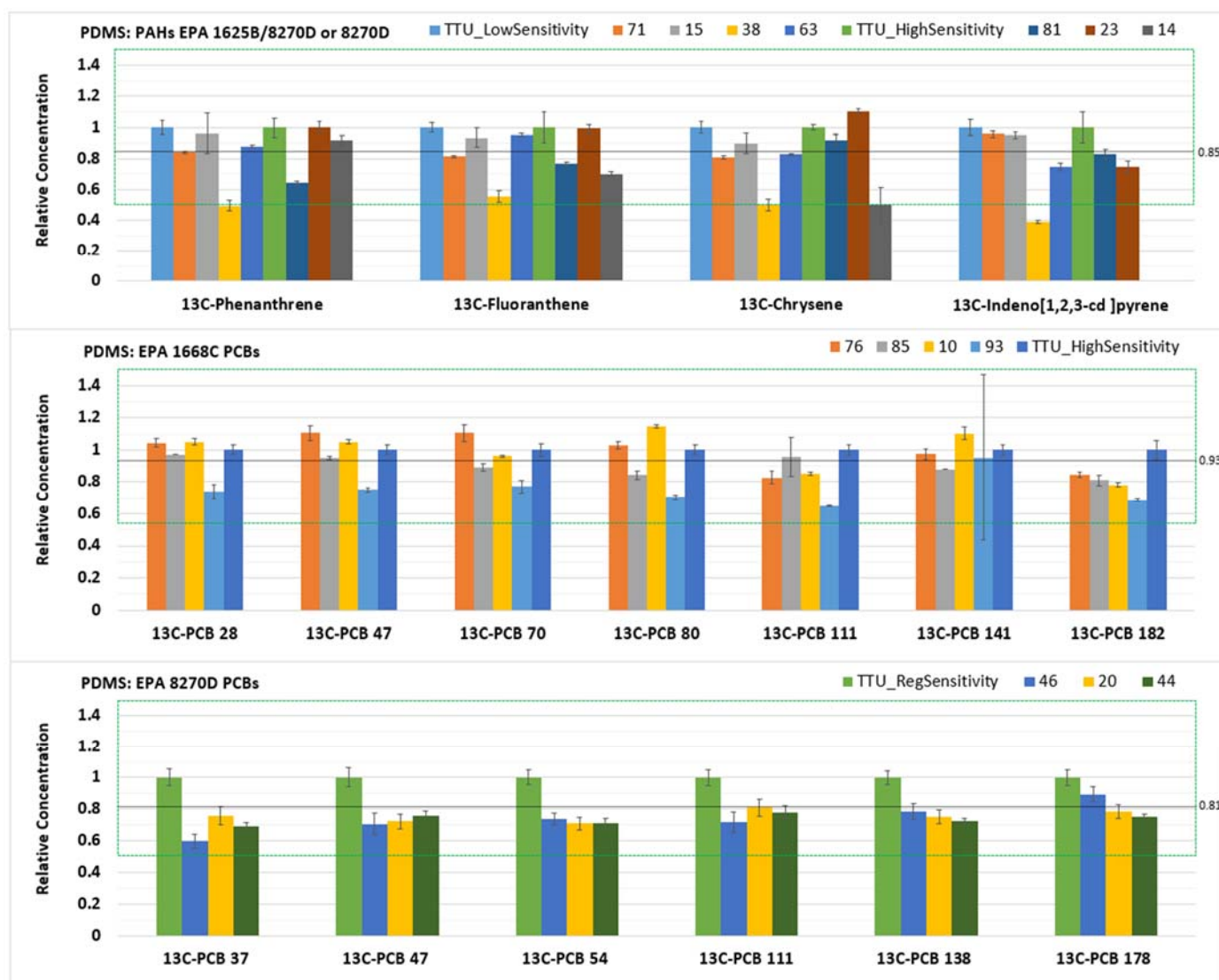


Figure 2. PRC Pre-loaded PDMS polymeric sampler results in relative units (Creported/Cknown). PCB congeners analyzed by high-sensitivity and regular-sensitivity methods are respectively shown in the middle and bottom; PAHs analyzed by regular- and high-sensitivity methods are shown at the top of the figure. The $\pm 50\%$ of known concentration performance criteria is highlighted in green. Average results for each data set are shown as black lines with average values to right.

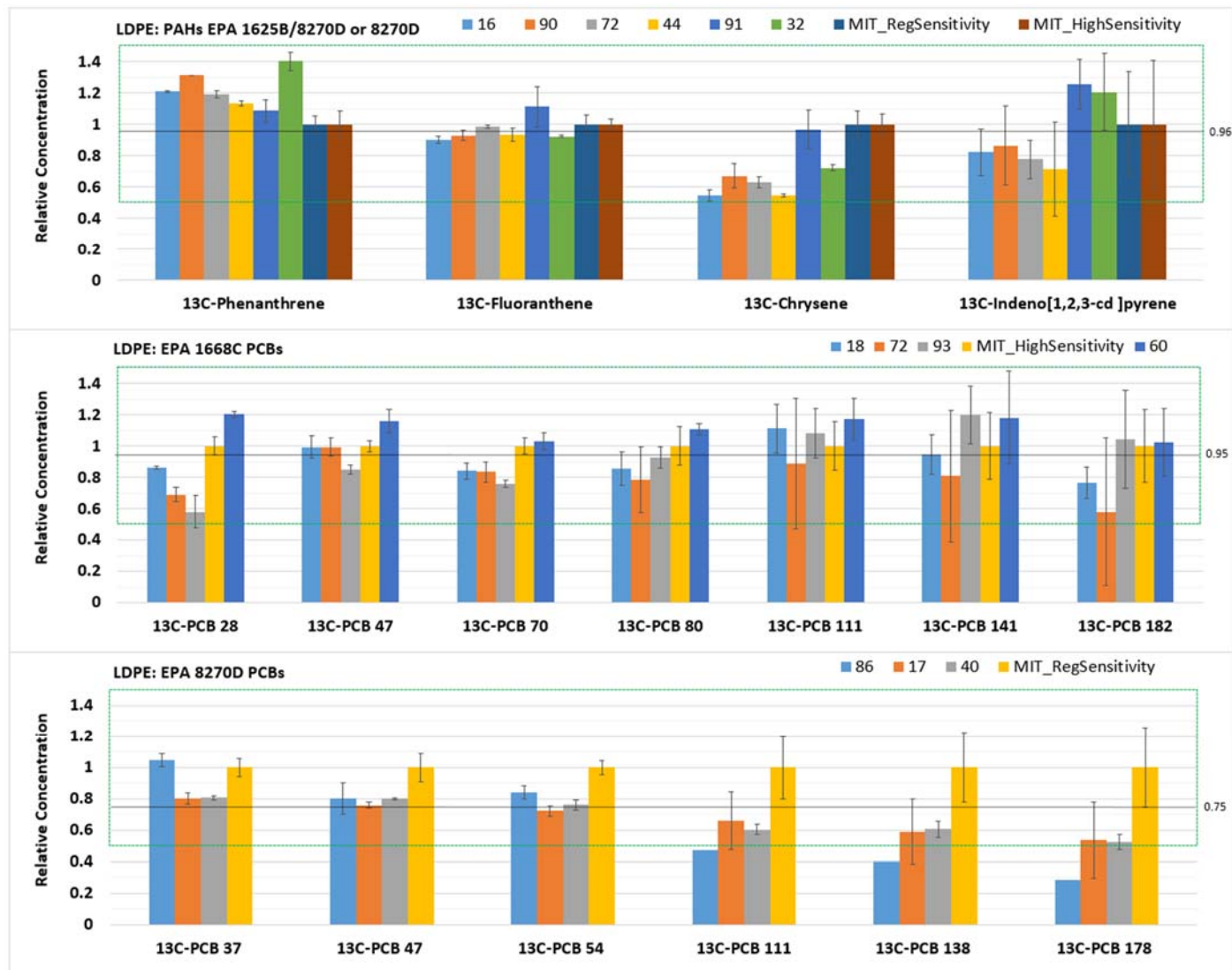


Figure 3. PRC Pre-loaded LDPE polymeric sampler results in relative units ($C_{reported}/C_{known}$). PCB congeners analyzed by high-sensitivity and regular-sensitivity methods are respectively shown in the middle and bottom; PAHs analyzed by regular- and high-sensitivity methods are shown at the top of the figure. The $\pm 50\%$ of known concentration performance criteria is highlighted in green. Average results for each data set are shown as black lines with average values to right.

4. DISCUSSION AND GO! RECOMMENDATION

Task 1.1. Interlaboratory analysis of the calibration check standard (Task 1.1) showed most labs met the acceptance criteria of $\pm 30\%$ for all of the native target analytes and $\pm 50\%$ for all of the PRCs. A few labs reported results for a few analytes that were slightly out-of-range (e.g. $\pm 38\%$ for one or two natives; $\pm 58\%$ for one or two PRCs). These minor exceedances were due to naphthalene contamination in an internal standard and calibration check standard solvent (isooctane) interference with lab standard solvent (methylene chloride); both of which were resolved as of Task 1.1 conclusion. The cause of minor accuracy exceedances for one or two PCB congeners by Labs 62 and 11 were not identified in QC documents or through data validation. Experimental errors such as these will be monitored for and documented going forward. A significantly out-of-target-range result (-91%) for PAH PRC indeno[1,2,3-cd]pyrene- $^{13}\text{C}_6$ was reported by university Lab 74. This consensus PRC choice worked well for all labs except university Lab 74, which elected to use a low resolution GC/MS. No corrective action was taken as this result was simply a limit of Lab 74's instrumentation. **A key lesson learned: PAH PRC indeno[1,2,3-cd]pyrene- $^{13}\text{C}_6$ does not provide sufficient m/z distinction for low resolution GC/MS analysis.** Labs performing analysis on a low resolution GC/MS should consider fully- ^{13}C -labeled or deuterated PRCs. Lab 74 will continue to use preferred low resolution GC/MS analysis and associated performance issues will be documented. **Task 1.1. acceptance criteria exceedances were occasional, not systemic, and thus support a "Go" recommendation.**

Task 1.3. Interlaboratory analysis of the PRC pre-loaded samplers (Task 1.3) showed most labs met the $\pm 50\%$ acceptance criteria for all the individual PCBs and PAHs. A single lab reported an exceedance (-58%) for a single PAH PRC ($^{13}\text{C}_6$ -indeno[1,2,3-cd]pyrene) in PDMS. This exceedance reported by Lab 38 was investigated by the lab chemist and by Mr. Lin. No explanation was found; this anomalous result was deemed insufficient grounds for data or lab exclusion. Lab 86 also reported exceedances for congeners PCB-111, PCB-138, and PCB-178 in LDPE samplers (respectively -53% , -60% , and -71%). These LDPE PCB exceedances appeared not to be actual exceedances by Lab 86 but rather intrinsic variations in the pre-loaded LDPE sampler concentrations. Upon review at MIT where the Task 1.3 samplers were prepared, it was discovered that pre-loaded samplers provided to Lab 86 were likely a different LDPE material, which contained different steady-state PRC masses. **A key lesson learned: labs preparing PRC-loaded LDPE strips should ensure that the area/weight ratios of the LDPE strips are consistent prior to adding the LDPE strips to the PRC loading solution.** **Task 1.3. acceptance criteria exceedances were occasional, not systemic, and thus support a "Go" recommendation.**

Task 1 results collectively support a "Go" decision to proceed to Task 2. Results of Task 1.1 showed 89% of lab submittals passed accuracy criteria. Of the 11% that did not, almost

all of these were accounted for through corrective actions and lessons learned listed below. In the end only 2 submittals out of 46 had unexplained apparent experimental issues, which resulted in minor acceptance criteria exceedances for Task 1.1. Only 2 out of 35 lab submittals for Task 1.3 failed to meet accuracy criteria, and only 1 was due to unexplained experimental issues. As summarized herein and detailed in Tasks 1.1 and 1.3 data comparability memos (Attachments 3 and 6, respectively), criteria exceedances observed during Task 1 were not basis for data exclusion and were considered suitable for intended use. Therefore, we recommend a Go decision to proceed to Task 2.

The following Task 2 activities have been completed or are in-progress as of October 2018.

- TTU and MIT will ship “blank” PDMS and LDPE samplers, respectively, to labs.
- Labs utilized the finalized polymeric sampler SOPs included in the finalized demonstration plan to independently load PRCs into the “blank” samplers, extract the PRCs from the samplers after loading was complete, and quantify the PRC concentrations in the sampler extracts using lab-specific methods.
- Results will be summarized in a Task 2 Go/No-Go memorandum submitted for review and approval by ESTCP.

Key Lessons Learned:

- Ensure internal standards are free of contaminants that could interfere with quantifying target analytes.
- Solvent variations can impact method performance; if varied solvent use is being considered as part of new extraction/analysis protocol be sure to investigate potential interferences ahead of required analysis.
- PAH PRC indeno[1,2,3-cd]pyrene-¹³C6 does not provide sufficient m/z distinction for low resolution GC/MS analysis; corrective measures associated with use of this PRC will be considered during Task 2/prior to Task 3.
- Labs preparing PRC-loaded LDPE strips should ensure that the area/weight ratios of the LDPE strips are consistent *prior* to adding the strips to the PRC loading solution.
- Surrogate compounds mimic behaviors of target compounds during sample analysis procedures, e.g., sample extraction, extract cleanup, solvent exchange, etc. For analytical methods using injection standards (as opposed to isotope dilution) for analyte quantitation, these standards are added to final extract prior to instrument analysis so as to assess the fraction of the extract volume analyzed; the injection standard does not reflect potential analyte loss during sample preparation. To quantitate analyte concentrations in a sample, the results should be normalized with surrogate spike recovery. We have taken care during this project to ensure data sets generated by different labs are comparable with respect to surrogate recoveries.

ATTACHMENT 1

Calibration Check Standard Preparation

Preparation of check standards

1. APPARATUS AND MATERIALS

- 1.1. 50 mL and 500 mL graduated flasks
- 1.2. 60 mL certified vials (amber and clear) for check standard transfer with screw caps
- 1.3. 2 mL GC vials amber and clear
- 1.4. PTFE lined solid screw caps for GC vials
- 1.5. Micropipettes: (0.2-10 uL) and (10-100 uL)
- 1.6. Pasteur pipettes
- 1.7. Kimwipes®
- 1.8. Food-grade aluminum foil
- 1.9. Parafilm
- 1.10. Freezer boxes
- 1.11. Cooler shipping boxes

2. REAGENTS

- 2.1. Dichloromethane (methylene chloride, CH_2Cl_2) for cleaning the graduated flasks
- 2.2. Acetone for cleaning the graduated flasks
- 2.3. Hexane for cleaning the graduated flasks
- 2.4. Nonane (AlfaAesar)
- 2.5. Iso-octane (SupraSolv)
- 2.6. MiliQ Water (Barnstead, GenPure Pro) or equivalent
- 2.7. ^{13}C labeled PCB and PAH stock solutions in nonane from Cambridge Isotope Laboratories (CIL)
- 2.8. PCB stock solutions in iso-octane from Accustandard
- 2.9. PAH stock solution from Accustandard

3. PROCEDURE

- 3.1. Wash glassware in glassware washer with soap followed with ultrapure water rinse
- 3.2. Rinse the glassware with methylene chloride, hexane and acetone each
- 3.3. **To prepare 50 mL of the check standard PRC MIX containing ^{13}C CB28/47/70/80/111/141/182 @ 5 ng/mL (High Res) in iso-octane**
 - 3.3.1. Add 20 mL of iso-octane into the graduated flask
 - 3.3.2. Add 6.25 uL of the stock solution (40000 ng/mL) of each compound to the flask and rinse with a small volume of solvent in case the stock becomes in contact with the flask's wall.
 - 3.3.3. Fill up the flask up to 50 mL with **iso-octane**.
 - 3.3.4. Close the flask with stopper
 - 3.3.5. Mix the flask head-over-head
 - 3.3.6. Transfer the content into a clean certified 60 mL vial with crew cap
 - 3.3.7. Transfer 1.5 mL of the check standard to GC vial with Pasteur pipette and close with a black solid screw cap with aluminum foil liner
 - 3.3.8. Cover the outer part of the cap with parafilm

- 3.3.9. Place the vials in a freezer box and secure with tape
- 3.3.10. Place the freezer box in a cooler box with icepack for shipping

3.4. To prepare 50 mL of the check standard PRC MIX containing ¹³C CB37/47/54/111/138/178 @ 50 ng/mL (Low Res) in iso-octane:

- 3.4.1. Add 20 mL of iso-octane into the graduated flask
- 3.4.2. Add 62.5 µL of the stock solution (40000 ng/mL) of each compound to the flask and rinse with a small volume of iso-octane in case the stock becomes in contact with the flask's wall
- 3.4.3. Fill up the flask up to 50 mL with iso-octane.
- 3.4.4. Close the flask with stopper
- 3.4.5. Mix the flask head-over-head
- 3.4.6. Transfer the content into a clean certified 60 mL vial with crew cap with aluminum foil liner
- 3.4.7. Transfer 1.5 ml of the check standard to GC vial with Pasteur pipette and close with a black solid screw cap
- 3.4.8. Cover the outer part of the cap with parafilm
- 3.4.9. Place the vials in a freezer box and secure with tape
- 3.4.10. Place the freezer box in a cooler box with icepack for shipping

Notes:

All components are added together in one flask.

Micropipettes are used for standard transfer.

¹³C PCB PRCs

High Res PCBs	stock solution in nonane ng/mL	volume of stock solution µl	check standard MIX ng/mL in ISO-OCTANE
13C-28	40000	1200	5
13C-47	40000	1200	5
13C-70	40000	1200	5
13C-80	40000	1200	5
13C-111	40000	1200	5
13C-141	40000	1200	5
13C-182	40000	1200	5

Low Res PCBs

13C-37	40000	1200	50
13C-47	40000	1200	50
13C-54	40000	1200	50
13C-111	40000	1200	50
13C-138	40000	1200	50
13C-178	40000	1200	50

3.5. To prepare 500 mL of the check standard MIX containing non-labelled CB8/18/28/44/52/66/101/105/118/126/128/138/153/169/170/180/187/195/206/209 @ 5 ng/mL in iso-octane (High Res).

- 3.5.1. Add 200 mL of iso-octane into the graduated flask
- 3.5.2. Add 25 uL of the stock solution (100000 ng/mL) of each compound to the flask and rinse with a small volume of iso-octane in case the stock becomes in contact with the flask's wall.
- 3.5.3. Fill up the flask up to 500 mL with iso-octane.
- 3.5.4. Close the flask with stopper
- 3.5.5. Mix the flask head-over-head
- 3.5.6. Transfer part of the check standard into a clean certified 60 mL vial with crew cap with aluminum foil liner
- 3.5.7. Transfer 1.5 ml of the check standard to GC vial with Pasteur pipette and close with a black solid screw cap
- 3.5.8. Cover the outer part of the GC solid cap with parafilm
- 3.5.9. Place the vials in a freezer box and secure with tape
- 3.5.10. Place the freezer box in a cooler box with icepack for shipping

3.6. To prepare 50 mL of the check standard MIX containing non-labelled CB8/18/28/44/52/66/101/105/118/126/128/138/153/169/170/180/187/195/206/209 @ 50 ng/mL in iso-octane (Low Res)

- 3.6.1. Add 20 mL of iso-octane into the graduated flask
- 3.6.2. Add 25 uL of the stock solution (100000 ng/mL) of each compound to the flask and rinse with a small volume of solvent in case the stock becomes in contact with the flask's wall.
- 3.6.3. Fill up the flask up to 500 mL with iso-octane.
- 3.6.4. Close the flask with stopper
- 3.6.5. Mix the flask head-over-head
- 3.6.6. Transfer the check standard into a clean certified 60 mL vial with crew cap
- 3.6.7. Transfer 1.5 ml of the check standard to GC vial with Pasteur pipette and close with a black solid screw cap
- 3.6.8. Cover the outer part of the cap with parafilm
- 3.6.9. Place the vials in a freezer box and secure with tape
- 3.6.10. Place the freezer box in a cooler box with icepack for shipping

Non-Labeled PCBs:

High Res PCBs	stock solution in iso- octane ng/mL	volume of stock solution μ l	check standard MIX ng/mL in ISO-OCTANE
8	100000	1200	5
18	100000	1200	5
28	100000	1200	5
44	100000	1200	5
52	100000	1200	5
66	100000	1200	5
101	100000	1200	5
105	100000	1200	5
118	100000	1200	5
126	100000	1200	5
128	100000	1200	5
138	100000	1200	5
153	100000	1200	5
169	100000	1200	5
170	100000	1200	5
180	100000	1200	5
187	100000	1200	5
195	100000	1200	5
206	100000	1200	5
209	100000	1200	5
Low Res PCBs			
8	100000	1200	50
18	100000	1200	50
28	100000	1200	50
44	100000	1200	50
52	100000	1200	50
66	100000	1200	50
101	100000	1200	50
105	100000	1200	50
118	100000	1200	50
126	100000	1200	50
128	100000	1200	50
138	100000	1200	50
153	100000	1200	50
169	100000	1200	50
170	100000	1200	50
180	100000	1200	50
187	100000	1200	50
195	100000	1200	50
206	100000	1200	50
209	100000	1200	50

3.7. To prepare 50 mL of the check standard MIX containing non-labeled PAH16 and ¹³C labeled PAHs @ 100 ng/mL in iso-octane (Low Res)

- 3.7.1. Prepare an intermediate working standard containing 16 PAHs at 20000 ng/mL from original stock solution (2000 µg/mL)
 - 3.7.1.1. Add 20 mL of iso-octane into 50 mL graduated flask
 - 3.7.1.2. Add 500 µL of 2000 µg/mL stock solution containing PAH16 into the flask and rinse with a small volume of iso-octane in case the stock solution becomes in contact with the flask's wall
 - 3.7.1.3. Fill up the flask up to 50 mL with iso-octane
 - 3.7.1.4. Close the flask with stopper
 - 3.7.1.5. Mix the flask head-over-head
 - 3.7.1.6. Transfer the working standard into a clean certified 60 mL vial with crew cap with aluminum foil liner
 - 3.7.1.7. Use the working standard in further steps
- 3.7.2. Add 20 mL of iso-octane into 50 mL graduated flask
- 3.7.3. Add 250 µL of the working standard (20000 ng/mL) containing PAH16 and 50 µL of ¹³C-phenanthrene, ¹³C-fluoranthene, ¹³C-chrysene and ¹³C-indeno[1,2,3-CD]pyrene stock solution (100000 ng/mL) to the 50 mL flask and rinse with a small volume of iso-octane in case the stock becomes in contact with the flask's wall.
- 3.7.4. Fill up the flask up to 50 mL with iso-octane.
- 3.7.5. Close the flask with stopper
- 3.7.6. Mix the flask head-over-head
- 3.7.7. Transfer the check standard into a clean certified 60 mL amber vial with crew cap with aluminum foil liner
- 3.7.8. Transfer 1.5 ml of the check standard to amber GC vial with Pasteur pipette and close with a black solid screw cap
- 3.7.9. Cover the outer part of the GC solid cap with parafilm
- 3.7.10. Place the vials in a freezer box and secure with tape
- 3.7.11. Place the freezer box in a cooler box with icepack for shipping

3.8. To prepare 250 mL of the check standard MIX containing non-labeled PAH16 and ¹³C labeled PAHs @ 5 ng/mL in iso-octane (High Res)

- 3.8.1. Prepare an intermediate working standard containing 16 PAHs at 20000 ng/mL from original stock solution (2000 µg/mL)
 - 3.8.1.1. Add 20 mL of iso-octane into 50 mL graduated flask
 - 3.8.1.2. Add 500 µL of 2000 µg/mL stock solution containing PAH16 into the flask and rinse with a small volume of iso-octane in case the stock solution becomes in contact with the flask's wall
 - 3.8.1.3. Fill up the flask up to 50 mL with iso-octane
 - 3.8.1.4. Close the flask with stopper

- 3.8.1.5. Mix the flask head-over-head
- 3.8.1.6. Transfer the working standard into a clean certified 60 mL vial with crew cap with aluminum foil liner
- 3.8.1.7. Use the working standard in further steps

- 3.8.2. Add 50 mL of iso-octane into 250 mL graduated flask
- 3.8.3. Add 62.5 μ L of the working standard (20000 ng/mL) containing PAH16 and 12.5 μ L of ^{13}C -phenanthrene, ^{13}C -fluoranthene, ^{13}C -chrysene and ^{13}C -indeno[1,2,3-CD]pyrene stock solution (100000 ng/mL) to the 250 mL flask and rinse with a small volume of iso-octane in case the stock becomes in contact with the flask's wall.
- 3.8.4. Fill up the flask up to 250 mL with iso-octane.
- 3.8.5. Close the flask with stopper
- 3.8.6. Mix the flask head-over-head
- 3.8.7. Transfer part of the check standard into a clean certified 60 mL amber vial with crew cap with aluminum foil liner
- 3.8.8. Transfer 1.5 ml of the check standard to amber GC vial with Pasteur pipette and close with a black solid screw cap
- 3.8.9. Cover the outer part of the GC solid cap with parafilm
- 3.8.10. Place the vials in a freezer box and secure with tape
- 3.8.11. Place the freezer box in a cooler box with icepack for shipping

Non-Labeled PAHs

	check standard MIX ng/mL in ISO-OCTANE
High Res PAHs	
Naphthalene	5
Acenaphthylene	5
Acenaphthene	5
Fluorene	5
Phenanthrene	5
Anthracene	5
Fluoranthene	5
Pyrene	5
Benz[a]anthracene	5
Chrysene	5
Benzo[b]fluoranthene	5
Benzo[k]fluoranthene	5
Benzo[a]pyrene	5
Dibenz[a,h]anthracene	5
Benzo[g,h,i]perylene	5
Indeno[1,2,3-cd]pyrene	5
Low Res PAHs	
Naphthalene	100
Acenaphthylene	100
Acenaphthene	100
Fluorene	100
Phenanthrene	100
Anthracene	100
Fluoranthene	100
Pyrene	100
Benz[a]anthracene	100
Chrysene	100
Benzo[b]fluoranthene	100
Benzo[k]fluoranthene	100
Benzo[a]pyrene	100
Dibenz[a,h]anthracene	100
Benzo[g,h,i]perylene	100
Indeno[1,2,3-cd]pyrene	100

¹³C PAH PRCs:

High Res PAHs	check standard MIX ng/mL in ISO-OCTANE
C13PHENANTHRENE	5
C13FLUORANTHENE	5
C13CHRYSENE	5
C13INDENO[1,2,3-CD]PY	5
Low Res PAHs	
C13PHENANTHRENE	100
C13FLUORANTHENE	100
C13CHRYSENE	100
C13INDENO[1,2,3-CD]PY	100

ATTACHMENT 3

Task 1.1 Interlaboratory Data Comparability Memorandum

Data Comparability Analysis Memorandum:

Task 1.1 Calibration Check Standard

1. Introduction

This memo presents and discusses data comparability of the polycyclic aromatic hydrocarbon (PAH) and polychlorinated biphenyl (PCB) check standard analyses performed by six commercial laboratories and three university research laboratories participating in this study. Commercial laboratories used standard EPA-approved analytical methods to analyze PAHs and PCBs; resulting data were subject to a Stage 4 (full) data validation. A Data Validation Report (DVR, Pyron 2018) was prepared separately (Attachment 2) to document the scope and findings of the validation. University laboratories used variations of EPA-approved analytical methods to analyze PAHs and PCBs; resulting university data were not subject to data validation. Per the final Demonstration Plan, each laboratory quantified PAHs using a high or low sensitivity analytical method (EPA Method 1625 or EPA Method 8270D-SIM, respectively) and PCBs using a high or low sensitivity analytical method (EPA Method 1668C or EPA Method 8270D-SIM, respectively). A total of four calibration check standards were prepared containing method-appropriate concentrations of target analytes (see below). Each commercial laboratory analyzed one calibration check standard for PAHs and one for PCBs, each containing appropriate concentrations for their chosen analytical method. University research laboratories, in most cases, analyzed all four calibration check standards using university lab-specific analytical method standard operating procedures. To obscure laboratory identity, participating laboratories were assigned randomly-assigned numbers (Table 1).

- **PCBs by high sensitivity GC/MS:** A check standard containing 5 ng/mL of target PCB congeners and ¹³C-labelled PCBs (as Performance Reference Compounds, PRCs) was prepared for high sensitivity GC/MS analysis. Three commercial laboratories and all three university research laboratories chose to analyze/report results for this check standard. The commercial laboratories primarily followed EPA Method 1668C for this analysis.
- **PCBs by regular GC/MS (EPA Method 8270-SIM):** A check standard containing 50 ng/mL target PCB congeners and ¹³C-labelled PCBs (PRCs) was prepared for this analysis. Three commercial laboratories and all three university research laboratories chose to analyze/report results for this check standard. The commercial laboratories primarily followed EPA Method 8270D-SIM for this analysis.
- **PAHs by high sensitivity GC/MS:** A check standard containing 5 ng/mL of target PAHs and ¹³C₆-labelled PAHs (as PRC) was prepared for this analysis. One commercial laboratory and two university research laboratories chose to analyze/report results for this check standard. The commercial laboratories primarily follow EPA Method 1625 for this analysis.

- **PAHs by regular GC/MS:** A check standard containing 100 ng/mL of regular target PAHs congeners and $^{13}\text{C}_6$ -labelled PAHs was prepared for this analysis. Five commercial laboratories and all three university research laboratories chose to analyze/report results for this check standard. The commercial laboratories primarily followed EPA Method 8270D-SIM for this analysis. Two commercial laboratories chose to use an isotope dilution technique (as referenced to EPA Method 1625) for analyte quantitation, whereas the other three commercial laboratories chose to use an internal standard technique (as referenced in EPA Method 8270D). Only one laboratory chose to correct results for surrogate recovery as noted in each method results section.

Table 1. Tests Performed by Laboratories (Identified by Randomly-Assigned Numbers)

Test	GC/MS Sensitivity	Check Standard (ng/L)	Laboratory Performing Test	
			Commercial	University
PCBs	High Sensitivity	5	25, 62, 11	40, 75, 17
	Regular	50	35, 69, 84	0, 87, 94
PAHs	High Sensitivity	5	91	58, 82
	Regular	100	3, 6, 28, 37, 47	9, 74, 98

The calibration check standard DVR found no notable procedural or quality control issues that deviated from the analytical methods and the laboratories' SOPs. This data comparability memo for the calibration check standard analysis (Demonstration Task 1.1) thus confidently concludes that analytical results submitted by participating commercial laboratories herein are representative analytical results generated by each laboratory's standard practices under optimal conditions of their instrumentation.

Data submitted by university laboratories were not subject to an independent data validation. Analytical methodologies used by university laboratories have been consistently applied to their research relevant to the passive sampling studies and results published over the years. While university methodologies generally follow standard analytical approaches (e.g. Method 8270 SIM for low res MS), some laboratory-specific deviations exist. In particular, quality control components such as the frequencies and acceptance criteria for instrument tuning, initial calibration, calibration verification, and analyte quantitation (e.g., surrogate spike recovery corrections on sample results) may be different or not documented rigorously as done by commercial laboratories. University laboratory data were included in this analysis to document its comparability with data generated via EPA methods produced by commercial laboratories.

2. Data Comparability Assessment Methods

Data comparability was evaluated based on accuracy, precision, and sensitivity.

Accuracy was determined by comparing the analytical results to the NIST true values of the pre-made check standards submitted to each of the laboratories. As established in the Demonstration Plan, a criterion of $\pm 30\%$ for regular PCB congener (*i.e.*, non- ^{13}C -labelled PCBs) and $\pm 50\%$ for performance reference compounds (PRCs, *i.e.*, ^{13}C -labelled PCBs) were applied for accuracy evaluation. A regular PCB value outside $\pm 30\%$ (*i.e.* 70-130%) or a PRC value outside $\pm 50\%$ (*i.e.* 50-150%) of the respective true value was considered an exceedance.

Precision was determined by the relative percent difference (RPD) if only two measurements performed by a laboratory were available. RPD is the difference divided by the average of two values expressed as a percentage. In cases where more than two measurements were reported, the percent relative standard deviation (%RSD) was used to evaluate variation with the group of data. RSD is the standard deviation divided by the mean of a group of values expressed as a percentage. According to EPA Method 1668C, Method 8270D, and Method 1625C, replicate analysis precision within a laboratory is evaluated by comparing the %RSD value for replicate analyses to the criteria of $\leq 20\%$. To show variations of results reported by commercial vs. university laboratories, average and %RSD values were calculated and presented for each group. It is important to note that precision acceptance criteria of $\leq 20\%$ applies only to *intralab* results; *interlab* average and %RSD values were provided for context only.

Method sensitivity is evaluated based on reporting limits (MRLs) or Practical Quantitation Limits (PQLs) a laboratory achieved given a sample matrix under the laboratory's standard operating conditions. MRLs for commercial laboratories were mostly based on their lowest-point of initial calibration that was customized for this calibration check standard analysis. Because of the solvent difference between this check standard and actual extraction solvent used in various commercial laboratories, method sensitivity was not evaluated here but will be evaluated in Task 1.3 based on representative analysis conditions.

3. Assessment Findings

PCBs by high sensitivity GC/MS

Three commercial and three university laboratories analyzed the PCB check standard by high sensitivity GC/MS (Table 2). Laboratories 62 and 11 respectively had two and one exceedances (out of 27 total analytes) of the $\pm 30\%$ accuracy criteria for PCBs. The low bias of these two laboratories did not indicate a systematic bias of their PCB analyses. Data validation did not identify specific QC issues with these analyses for Labs 62 and 11 either. Therefore, these exceedances were assumed to be experimental errors, which will be monitored in future analyses. These laboratories reported co-elutions of the target analytes with adjacent PCBs, which likely contributed to the few exceedances observed. All the university laboratories met the accuracy criteria. No laboratories had exceedances for PRCs.

All commercial and university laboratory %RSD values were $\leq 20\%$, indicating overall good precision across the commercial and university laboratories. The ^{13}C -labelled PRCs showed slightly better accuracy and precision, again suggesting co-elutions of unlabeled PCB congeners contributed to the few accuracy exceedances observed.

In general, inter-laboratory comparison showed that PCB analyses by high sensitivity GC/MS methodologies was carried out with satisfactory inter-laboratory comparability across the six commercial and university laboratories.

PCBs by regular sensitivity GC/MS

Three commercial and three university laboratories analyzed the PCB check standard by regular sensitivity GC/MS (Table 3). None of the laboratories exceeded the 70-130% accuracy criteria for regular PCBs or the 50-150% accuracy criteria for PRC PCBs.

Percent RSD values for commercial laboratories were less than 20% for natives, with a maximum of 23% observed for labeled PRCs.

Based on the accuracy and precision analyses, methodologies used by the three commercial laboratories (using standardized methodology) and three university laboratories (using in-house research methods) showed satisfactory comparability.

PAHs by high sensitivity GC/MS

One commercial and two university laboratories analyzed the PAH check standard formulated for high sensitivity GC/MS, as shown in Table 4. All PAHs results reported by commercial Laboratory 91 met the accuracy criteria. The university laboratories reported five exceedances.

The significantly elevated level of naphthalene reported by university Laboratory 58 was caused by contamination in the lab's internal standard mix. Laboratory 58 subsequently prepared a contaminant-free internal standard as the corrective measure. Laboratory 82 analyzed the high sensitivity check standard using a low resolution GC/MS. Multiple exceedances reported by Lab 82 indicate (a) low resolution GC/MS is not suitable for detecting low concentrations of dibenzo(a,h)anthracene, and (b) $^{13}\text{C}_6$ PRCs provide insufficient m/z distinction on the low resolution GC/MS; deuterated PRCs or fully-labeled PRCs would be a more appropriate choice for low resolution GC/MS analysis. University Laboratory 82 analyzed the high sensitivity standard using their preferred low sensitivity method in the spirit of completeness only for Task 1.1.

Since Laboratory 82 used a low resolution GC/MS, only results from single labs were available; therefore, no Interlaboratory precision evaluation was performed.

Excluding exceptions discussed above, and based on minimal accuracy exceedances by Labs 91 and 58, the data was considered appropriate to compare and consider collectively.

PAHs by regular sensitivity GC/MS

Five commercial and three university laboratories analyzed the PAH check standard by regular sensitivity GC/MS, as shown in Table 5. Although each laboratory was required to analyze and report the check standard once, Laboratories 9, 28, and 98 chose to analyze the check standard three times and report the triplicate results. Laboratory 37 analyzed the check standard four times, each at a different dilution factor (1:2, 1:3, 1:10, and 1:50; respectively), and reported results from all four analyses. Results of only the first three dilutions were featured in the average and standard deviations reported here. Commercial Laboratories 3, 28, and 37 used an internal standard approach for analyte quantitation, while commercial Laboratories 6 and 47 used an isotope dilution technique. The results at highest dilution factor (a 10-fold dilution) submitted by Laboratory 37 were omitted from this analysis due to low recovery of higher-molecular-weight PAHs from over-dilution. Average values of the multiple results reported by these laboratories were used for this comparison.

Low recovery of indeno(1,2,3-cd)pyrene and dibenzo(a,h)anthracene by Laboratory 28 caused two accuracy exceedances. This lower recovery was likely a result of the solvent (iso-octane) interference of the check standard, which differed from the laboratory's standard solvent (methylene chloride). This effect is not expected in future analyses in this study since iso-octane will not be used as solvent moving forward to the future tasks. The three university laboratories had only one exceedance: indeno(1,2,3-cd)pyrene-¹³C6 was reported at 9.4 ng/mL (as opposed to the true value of 100 ng/mL) by university Laboratory 74. This consensus PRC choice (indeno(1,2,3-cd)pyrene-¹³C6) worked well for all labs except Lab 74, which elected to use a low resolution GC/MS. Labs that choose to perform this analysis on a low resolution GC/MS would need to choose PRCs that provide sufficient m/z distinction, i.e. deuterated PRCs or fully-¹³C-labeled PRCs. No corrective action will be taken to resolve this issue; however, any exceedances encountered due to low resolution GC/MS analysis will be documented.

Interlaboratory %RSD values were typically well below 20% and all less than 25% across commercial and university laboratories, with one exception: 39%RSD for indeno(1,2,3-cd)pyrene-¹³C6 by university labs. This was due to low recovery of this analyte by Laboratory 74 as discussed above.

Overall %RSD values and the minimal accuracy exceedances, the methodologies used by commercial and university laboratories are expected to generate data with satisfactory comparability.

Table 2. PCBs by High Sensitivity Methodology

Compounds	True Value (ng/mL)	Lower Limit (ng/mL)	Upper Limit (ng/mL)	Commercial Laboratories (ng/mL)			University Laboratories (ng/mL)			Commercial Laboratory		University Laboratory	
				25	62	11	40	75	17	Average	%RSD ^(A)	Average	%RSD ^(A)
Native PCBs													
PCB-008	5.0	3.5	6.5	5.0	5.1	4.7	5.5	4.8	5.8	4.9	3%	5.3	9%
PCB-018	5.0	3.5	6.5	4.2	4.7	3.9	5.3	4.7	5.2	4.3	12%	5.1	6%
PCB-028	5.0	3.5	6.5	4.9	4.4	4.6	4.6	5.0	5.7	4.6	6%	5.1	9%
PCB-044	5.0	3.5	6.5	4.0	4.3	3.4	5.4	4.7	6.1	3.9	17%	5.4	14%
PCB-052	5.0	3.5	6.5	4.7	3.6	4.2	5.2	4.9	5.8	4.2	15%	5.3	9%
PCB-066	5.0	3.5	6.5	4.6	4.2	4.1	4.8	4.6	5.6	4.3	10%	5.0	10%
PCB-101	5.0	3.5	6.5	4.2	4.3	4.0	5.5	4.9	6.0	4.2	11%	5.5	10%
PCB-105	5.0	3.5	6.5	5.1	3.8	4.6	5.1	4.7	6.4	4.5	13%	5.4	16%
PCB-118	5.0	3.5	6.5	5.1	4.5	4.6	5.1	4.9	6.4	4.7	6%	5.5	14%
PCB-126	5.0	3.5	6.5	4.6	3.9	4.6	4.0	4.3	5.8	4.4	11%	4.7	18%
PCB-128	5.0	3.5	6.5	4.2	3.2	3.9	5.3	4.4	5.3	3.8	20%	5.0	11%
PCB-138	5.0	3.5	6.5	4.7	3.4	4.5	5.1	4.7	5.1	4.2	17%	4.9	4%
PCB-153	5.0	3.5	6.5	4.7	4.3	4.5	5.5	4.3	4.6	4.5	7%	4.8	9%
PCB-169	5.0	3.5	6.5	4.5	3.8	4.2	5.6	4.6	4.8	4.2	12%	5.0	8%
PCB-170	5.0	3.5	6.5	4.9	4.0	4.8	5.1	4.6	5.6	4.5	11%	5.1	10%
PCB-180	5.0	3.5	6.5	5.2	4.2	4.1	4.8	4.4	5.1	4.5	12%	4.8	9%
PCB-187	5.0	3.5	6.5	4.4	4.1	4.4	4.7	4.8	5.2	4.3	9%	4.9	5%
PCB-195	5.0	3.5	6.5	5.8	4.9	5.6	5.4	5.2	6.0	5.4	8%	5.5	9%
PCB-206	5.0	3.5	6.5	4.7	4.1	4.8	5.4	5.1	6.0	4.5	9%	5.5	9%
PCB-209	5.0	3.5	6.5	4.3	3.7	4.5	4.3	4.7	5.1	4.2	13%	4.7	6%
Labeled PRC													
¹³ C-PCB-28	5.0	2.5	7.5	4.6	5.3	5.4	5.3	4.9	6.4	5.1	7%	5.6	13%
¹³ C-PCB-47	5.0	2.5	7.5	4.7	5.0	5.9	5.8	5.4	6.3	5.2	10%	5.8	8%
¹³ C-PCB-70	5.0	2.5	7.5	5.2	4.8	5.1	4.4	4.6	4.5	5.0	3%	4.5	3%
¹³ C-PCB-80	5.0	2.5	7.5	5.1	5.2	4.9	4.8	5.1	4.9	5.1	3%	5.0	3%
¹³ C-PCB-111	5.0	2.5	7.5	4.7	4.9	5.1	5.6	5.1	4.9	4.9	4%	5.2	5%
¹³ C-PCB-141	5.0	2.5	7.5	5.1	5.2	4.7	4.7	5.4	6.3	5.0	4%	5.5	11%
¹³ C-PCB-182	5.0	2.5	7.5	5.1	5.3	5.3	4.6	5.1	6.6	5.2	3%	5.5	16%

- Each laboratory was randomly assigned a number to obscure laboratory identity.
 - Shaded number indicates that the result is outside the accuracy control limit for regular PCBs (70-130%, or 3.5-6.5 ng) or ¹³C-labelled PCBs (50-150%, or 2.5-7.5 ng).
 - Results reported by university laboratory 40 were corrected with surrogate spike recovery.
- ^(A) – %RSD criteria is ≤20%.

Avg – Laboratories 8 and 9 each submitted three sets of results; the values listed herein are means of the replicates.

ng/mL – Nanogram per milliliter

PRC – Performance reference compound

%RSD – Percent relative standard deviation

Table 3. PCBs by Regular Sensitivity Methodology

Compounds	True Value (ng/mL)	Lower Limit (ng/mL)	Upper Limit (ng/mL)	Commercial Laboratories (ng/mL)			University Laboratories (ng/mL)			Commercial Laboratory		University Laboratory	
				35	69	84	0	87	94	Average	%RSD ^(A)	Average	%RSD ^(A)
Native PCBs													
PCB-008	50.0	35.0	65.0	63.0	46.7	55.1	59.7	51.1	53.9	54.9	17%	54.9	6%
PCB-018	50.0	35.0	65.0	48.0	42.5	48.0	55.7	47.9	43.1	46.2	6%	48.9	10%
PCB-028	50.0	35.0	65.0	51.0	42.3	46.5	51.6	49.1	47.2	46.6	8%	49.3	4%
PCB-044	50.0	35.0	65.0	57.0	41.7	47.3	55.5	50.6	45.3	48.7	13%	50.5	8%
PCB-052	50.0	35.0	65.0	58.0	43.0	46.4	56.3	47.6	47.2	49.1	13%	50.4	7%
PCB-066	50.0	35.0	65.0	50.0	38.9	41.6	48.9	46.4	41.1	43.5	11%	45.5	8%
PCB-101	50.0	35.0	65.0	49.0	41.1	51.3	53.4	47.8	44.8	47.1	9%	48.7	7%
PCB-105	50.0	35.0	65.0	52.0	46.9	43.9	52.0	50.2	44.0	47.6	7%	48.7	8%
PCB-118	50.0	35.0	65.0	53.0	47.3	43.0	52.7	49.3	44.4	47.8	9%	48.8	7%
PCB-126	50.0	35.0	65.0	50.0	42.4	46.4	53.1	47.8	40.4	46.3	8%	47.1	11%
PCB-128	50.0	35.0	65.0	51.0	49.3	52.2	53.0	42.8	42.4	50.8	6%	46.1	10%
PCB-138	50.0	35.0	65.0	50.0	44.7	44.8	52.7	48.1	42.3	46.5	6%	47.7	9%
PCB-153	50.0	35.0	65.0	53.0	48.7	44.8	56.0	47.4	44.9	48.8	7%	49.5	9%
PCB-169	50.0	35.0	65.0	63.0	46.3	51.9	55.6	48.2	40.4	53.7	14%	48.1	13%
PCB-170	50.0	35.0	65.0	49.0	47.8	45.3	54.6	47.3	40.0	47.4	9%	47.3	13%
PCB-180	50.0	35.0	65.0	55.0	53.3	47.1	56.5	46.5	43.7	51.8	9%	48.9	10%
PCB-187	50.0	35.0	65.0	51.0	49.1	50.3	57.1	47.9	45.3	50.1	7%	50.1	9%
PCB-195	50.0	35.0	65.0	58.0	58.0	51.2	62.7	46.8	46.1	55.7	9%	51.9	13%
PCB-206	50.0	35.0	65.0	52.0	45.2	44.2	52.8	46.3	38.9	47.1	7%	46.0	12%
PCB-209	50.0	35.0	65.0	46.0	47.8	41.2	51.5	44.1	36.8	45.0	8%	44.1	14%
Labeled PRC													
¹³ C-PCB-37	50.0	25.0	75.0	63.0	40.2	51.5	25.2	52.8	40.6	51.6	18%	39.5	23%
¹³ C-PCB-47	50.0	25.0	75.0	53.0	41.6	49.2	46.4	52.7	42.1	47.9	11%	47.1	11%
¹³ C-PCB-54	50.0	25.0	75.0	51.0	44.3	52.0	53.4	51.7	53.2	49.1	7%	52.8	2%
¹³ C-PCB-111	50.0	25.0	75.0	58.0	41.1	46.6	47.3	51.1	33.2	48.6	17%	43.9	21%
¹³ C-PCB-138	50.0	25.0	75.0	56.0	45.5	50.8	42.0	55.6	50.9	50.8	8%	49.5	9%
¹³ C-PCB-178	50.0	25.0	75.0	52.0	49.1	52.1	39.2	51.0	54.3	51.1	9%	48.1	11%

- Each laboratory was randomly assigned a number to obscure laboratory identity.
 - Shaded number indicates that the result is outside the accuracy control limit for regular PCBs (70-130%, or 35.0-65.0 ng) or ¹³C-labelled PCBs (50-150%, or 25.0-75.0 ng); or %RSD is >20%. Possible causes and corrective actions for the outliers were discussed in the corresponding section in the text.
 - Results reported by university laboratory 0 were corrected with surrogate spike recovery.
- ^(A) – %RSD criteria is ≤20%.

Avg – Laboratory 1 submitted two sets of results; laboratories 87 and 94 each submitted three sets of results. The values listed herein are means of the duplicates.
 ng/mL – Nanogram per milliliter
 PRC – Performance reference compound
 %RSD – Percent relative standard deviation

Table 4. PAHs by High Sensitivity Methodology

Compounds	True Value (ng/mL)	Upper Limit (ng/mL)	Lower Limit (ng/mL)	Commercial Laboratory (ng/mL)	University Laboratories (ng/mL)	
				91	58	82 ^(B)
Native PAHs						
Naphthalene	5.0	3.5	6.5	5.1	38	4.5
Acenaphthylene	5.0	3.5	6.5	6.1	5.3	4.2
Acenaphthene	5.0	3.5	6.5	5.0	5.1	3.9
Fluorene	5.0	3.5	6.5	5.1	5.3	3.7
Phenanthrene	5.0	3.5	6.5	4.7	5.7	3.7
Anthracene	5.0	3.5	6.5	4.3	5.7	3.8
Fluoranthene	5.0	3.5	6.5	4.3	4.9	4.0
Pyrene	5.0	3.5	6.5	3.8	5.0	3.9
Benz(a)anthracene	5.0	3.5	6.5	4.7	4.9	4.0
Chrysene	5.0	3.5	6.5	5.2	5.2	4.2
Benzo(b)fluoranthene	5.0	3.5	6.5	6.6	4.9	4.4
Benzo(k)fluoranthene	5.0	3.5	6.5	5.7	5.0	4.5
Benzo(a)pyrene	5.0	3.5	6.5	4.4	4.9	5.3
Indeno(1,2,3-cd)pyrene	5.0	3.5	6.5	4.0	5.7	4.9
Dibenzo(a,h)anthracene	5.0	3.5	6.5	4.0	4.5	ND (0.0)
Benzo(g,h,i)perylene	5.0	3.5	6.5	4.3	5.5	5.1
Labeled PRC						
Phenanthrene- ¹³ C ₆	5.0	2.5	7.5	4.1	5.6	2.3
Fluoranthene- ¹³ C ₆	5.0	2.5	7.5	5.2	4.9	2.7
Chrysene- ¹³ C ₆	5.0	2.5	7.5	4.5	6.5	2.2
Indeno(1,2,3-c,d)pyrene- ¹³ C ₆	5.0	2.5	7.5	5.4	5.4	ND (0.0)

- Each laboratory was randomly assigned a number to obscure laboratory identity.
- Shaded number indicates that the result is outside the 70-130% (regular PAHs) or 50-150% (¹³C-labelled PAHs) accuracy control limit; or %RSD is >20%. Possible causes and corrective actions for the outliers were discussed in the corresponding section in the text.
- Laboratories 91 used isotope dilution (EPA Method 1625A) technique for this study.
- Results reported by university laboratory 82 were corrected with surrogate spike recovery.

(A) – %RSD criteria is ≤20%.

(B) – Lab 82 analyzed the high sensitivity standard using a low resolution GC/MS; because the method was different, Lab 82 results were not featured in the precision evaluation

Avg - Laboratory 58 submitted three sets of results; average values of the multiple results were used for this comparison.

ND – The compound was not detected at or above the quantitation limit; the result was assumed as 0 for data comparability analysis.

ng/mL – Nanogram per milliliter

PRC – Performance reference compound

RPD – Relative percent difference

%RSD – Percent relative standard deviation

Table 5. PAHs by Regular Sensitivity Methodology

Compounds	True Value (ng/mL)	Upper Limit (ng/mL)	Lower Limit (ng/mL)	Commercial Laboratories (ng/mL)					University Laboratories (ng/mL)			Commercial Laboratory		University Laboratory	
				28	37	6	3	47	74	9	98	Average	%RSD ^(A)	Average	%RSD ^(A)
Native PAHs															
Naphthalene	100	70.0	130	94.0	98.2	103	108	110	95.3	109	138	103	7%	114	15%
Acenaphthylene	100	70.0	130	96.7	95.6	105	107	100	107	99.0	109	101	5%	105	6%
Acenaphthene	100	70.0	130	89.0	89.7	104	103	110	94.2	104	109	99.2	9%	102	6%
Fluorene	100	70.0	130	95.0	90.4	91.6	103	97.0	91.8	104	109	95.5	6%	101	7%
Phenanthrene	100	70.0	130	90.7	94.1	95.7	103	97.0	113	104	111	96.2	6%	110	5%
Anthracene	100	70.0	130	94.0	89.0	80.3	94.4	97.0	88.0	97.0	108	90.9	7%	97.6	8%
Fluoranthene	100	70.0	130	90.7	91.2	89.1	95.8	100	107	98.7	96.9	93.3	6%	101	3%
Pyrene	100	70.0	130	99.0	91.1	89.5	94.7	100	97.7	101	97.8	94.9	5%	98.8	2%
Benzo(a)anthracene	100	70.0	130	88.0	91.3	101	101	88.0	118	97.8	99.8	93.9	7%	105	7%
Chrysene	100	70.0	130	98.7	94.4	99.1	111	110	100	106	98.0	103	7%	101	4%
Benzo(b)fluoranthene	100	70.0	130	98.3	80.8	99.0	101	100	108	98.3	97.5	95.8	11%	101	4%
Benzo(k)fluoranthene	100	70.0	130	101	96.5	93.4	105	100	106	98.3	93.4	99.1	7%	99.4	5%
Benzo(a)pyrene	100	70.0	130	96.7	82.3	96.0	116	91.0	115	96.0	93.3	96.4	13%	101	8%
Indeno(1,2,3-cd)pyrene	100	70.0	130	58.0	71.7	86.7	101	97.0	116	121	115	83.1	24%	117	3%
Dibenzo(a,h)anthracene	100	70.0	130	71.3	87.9	88.5	98.4	94.0	113	107	95.7	88.0	13%	105	7%
Benzo(g,h,i)perylene	100	70.0	130	62.7	80.6	107	94.6	99.0	113	97.3	97.3	88.8	22%	103	6%
Labeled PRC															
Phenanthrene- ¹³ C ₆	100	50.0	150	113	119	99.4	129	100	73.3	92.2	105	112	9%	90.3	13%
Fluoranthene- ¹³ C ₆	100	50.0	150	85.3	98.4	100	106	110	64.4	87.2	92.4	99.9	12%	81.3	12%
Chrysene- ¹³ C ₆	100	50.0	150	94.7	109	102	122	100	58.7	89.2	118	106	10%	88.6	23%
Indeno(1,2,3-c,d)pyrene- ¹³ C ₆	100	50.0	150	69.7	78.8	103	111	100	9.44	93.4	91.9	92.5	21%	64.9	39%

Notes:

- Each laboratory was randomly assigned a number to obscure laboratory identity.
- Shaded number indicates that the result is outside the 70-130% (regular PAHs) or 50-150% (¹³C-labelled PAHs) accuracy control limit; or %RSD is >20%. Possible causes and corrective actions for the outliers were discussed in the corresponding section in the text.
- Laboratories 28, 37 and 3 used internal standard approach for quantitation (EPA Method 8270-SIM); laboratories 6 and 47 used isotope dilution (EPA Method 1625A); and Laboratory 5 used HRGC/MS and isotope dilution technique for the study.
- Results reported by university laboratory 74 were corrected with surrogate spike recovery.

(A) – %RSD criteria is ≤20%.

Avg - Laboratory 28 submitted three sets of results, and Laboratory 37 submitted four sets of results at various dilution factors respectively. The results at highest dilution factor (a 10-fold dilution) submitted by Laboratory 37 were omitted as a result of the low recovery of higher-molecular-weight PAHs due to over-diluting. Average values of the multiple results reported by Laboratories 1 and 2 were used for this comparison.

ng/mL – Nanogram per milliliter

PRC – Performance reference compound

%RSD – Percent relative standard deviation

References

- USEPA. 2010. *Method 1668C: Chlorinated Biphenyl Congeners in Water, Soil, Sediment, Biosolids, and Tissue by HRGC/HRMS*. April 2010. USEPA-820-R-10-005.
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ATTACHMENT 6

Task 1.3 Interlaboratory Data Comparability Memorandum

DATA COMPARABILITY ANALYSIS MEMORANDUM

Task 1.3 Pre-Loaded Solid-Phase Microextraction (SPME) and Low-Density Polyethylene (LDPE) Polymetric Samplers

1. INTRODUCTION

This memo presents and discusses data comparability of the polycyclic aromatic hydrocarbon (PAH) and polychlorinated biphenyl (PCB) analyses performed by four commercial laboratories and three university research laboratories participating in this study. The PAHs and PCBs analyzed here were isotopically-labeled performance reference compounds (PRCs), which were pre-loaded into polydimethylsiloxane (PDMS) and low-density polyethylene (LDPE) polymer segments at known concentrations, then extracted per the standardized polymeric sampler standard operating procedures (attachments to final Demonstration Plan) and quantified using standard EPA methods. Danny Reible’s group at Texas Tech University (TTU) and Phil Gschwend’s group at the Massachusetts Institute of Technology (MIT), respective subject matter experts for use of PDMS and LDPE samplers, prepared the PRC pre-loaded samplers in triplicate for all participating labs to analyze.

The PAH PRCs are independent of the analytical method the laboratories use; thus, there is only one suite of PRCs for each method. PCB PRCs vary by analytical method and as such there are two suites of PCB PRCs: one for regular sensitivity (low resolution mass spectrometry) and one for high sensitivity (high resolution mass spectrometry) methods.

- PAH PRCs: ¹³C₆-phenanthrene, ¹³C₆-fluoranthene, ¹³C₆-chrysene, ¹³C₆-indeno(1,2,3-cd)pyrene
- PCBs PRCs (Low-Sensitivity Methods): ¹³C-labeled PCB congeners 37, 47, 54, 111, 138, and 178
- PCBs PRCs (High-Sensitivity Methods): ¹³C-labeled PCB congeners 28, 47, 70, 80, 111, 141, 182

Four commercial laboratories and three university research laboratories participated in Task 1.3. Per the final Demonstration Plan, each laboratory quantified PAHs using a high or low sensitivity analytical methods (EPA Method 1625 or EPA Method 8270D-SIM, respectively) and PCBs using a high or low sensitivity analytical methods (EPA Method 1668C or EPA Method 8270D-SIM, respectively). To obscure laboratory identity, participating laboratories were identified by randomly-assigned numbers. See Table 1 for a list of which laboratories performed each analysis.

Table 1. Tests Performed by Laboratories

PRCs	Method Sensitivity	Target Concentration Range ^(A)		PDMS Laboratory ^(B)		LDPE Laboratory ^(B)	
		PDMS	LDPE	Commercial	University	Commercial	University
PAHs	Low	7006 - 8541	137 - 198	15, 38, 63, 71	18, 23, 81	16, 44, 72, 90	25, 32, 91
	High	602 - 844	27 – 50	None	14, 72	None	52
PCBs	Low	9168 -8671	89 - 155	20, 46	44, 82	17, 86	20, 40
	High	1431 - 1677	31 - 36	76, 85	10, 40, 93	18, 72	41, 60, 93

Notes:
^(A) – Target concentrations were determined by university laboratories that prepared the samples; concentration for each PRC varies, and thus is presented as concentration range; PDMS units are ng/mL-PDMS; LDPE units are ng/g-LDPE.
^(B) – Each laboratory was assigned a random number for each analysis.

Resulting data submitted by participating commercial laboratories were subject to a Stage 4 (full) data validation. Data Validation Reports (DVR, Pyron 2018) for PDMS and LDPE

sample analysis were prepared separately (Attachment 4) to document the scope and findings of the validation. The DVRs found no notable procedural or quality control issues that deviated from the analytical methods and the laboratories' SOPs. This data comparability memo for the pre-loaded sampler analytical data (Demonstration Task 1.3) thus confidently assumes that analytical results submitted by participating commercial laboratories herein are representative analytical results generated by each laboratory's standard practices under optimal conditions of their instrumentation.

Data submitted by university laboratories were not subject to an independent data validation. Analytical methodologies used by university laboratories have been consistently applied to their research relevant to the passive sampling studies and results published over the years. While university methodologies generally follow standard analytical approaches (e.g. Method 8270 SIM for low res MS), some laboratory-specific deviations exist. In particular, quality control components such as the frequencies and acceptance criteria for instrument tuning, initial calibration, calibration verification, and analyte quantitation (e.g., surrogate spike recovery corrections on sample results) can be different from protocols used by commercial laboratories. University laboratory data were included in this analysis to document its comparability with data generated via EPA methods produced by commercial laboratories. The "known" concentrations of PRCs were established as the average of replicate PAHs and PCBs concentrations provided by the preparing laboratories TTU for PDMS and by MIT for LDPE and were compared to each commercial lab's results, as described in more detail below.

Note that the analytical results for PDMS were reported as nanogram per milliliter of PDMS (ng/mL-PDMS), where results for LDPE samplers were reported as nanogram per gram of LDPE (ng/g-LDPE). Conversion conventions for these reporting units were provided by TTU and MIT, respectively.

2. DATA COMPARABILITY ASSESSMENT METHODS

Data comparability was evaluated based on accuracy, precision, and sensitivity.

2.1 Accuracy

Accuracy was determined by comparing the analytical results to the target concentrations determined by university laboratories that prepared the pre-loaded PDMS (by TTU) and LDPE (by MIT) samplers. As established in the Demonstration Plan (USACE *et al.*, 2018), a criterion of $\pm 50\%$ of the known value was established for PRC concentrations reported; any reported PRC concentration outside of this range was considered an exceedance. This acceptance criteria was based on EPA 1668C: $\pm 50\%$ of known concentrations for isotopically-labeled laboratory control samples/verification samples (LCS/VS); $\pm 30\%$ of known concentrations for non-isotopically-labeled LCS/VS.

2.2 Precision

Precision was determined by the relative percent difference (RPD) if only two measurements performed by a laboratory were available. RPD is the difference divided by the average of two values expressed as a percentage. In cases where more than two measurements were reported, the percent relative standard deviation (%RSD) was used to evaluate variation with the group of data. RSD is the standard deviation divided by the mean of a group of values expressed as a percentage. According to EPA Method 1668C, Method 8270D, and Method 1625C, replicate analysis precision within a laboratory is evaluated by comparing the %RSD value for replicate analyses to the criteria of $\leq 20\%$. To show variations of results reported by commercial vs. university laboratories, average and %RSD values were calculated and presented for each group. It is important to note that precision acceptance criteria of $\leq 20\%$ applies only to *intralab* results; *interlab* average and %RSD values were provided for context only. *Interlab* variability could be $\pm 50\%$ of known concentrations for isotopically-labeled laboratory control samples/verification

samples (LCS/VS); $\pm 30\%$ of known concentrations for non-isotopically-labeled LCS/VS and still be within the accuracy standard of 1668C.

2.3 Sensitivity

Method sensitivity was evaluated based on the Method Reporting Limits (MRLs) or Practical Quantitation Limits (PQLs) that a laboratory achieved given a sample matrix under the laboratory's standard operation. In some cases where the commercial laboratories did not report sample-specific MRLs (*i.e.* MRLs that are specific determined for the PRCs), the lowest-point of the initial calibration standard was used for this comparison.

3. ASSESSMENT FINDINGS FOR PDMS RESULTS

3.1 PAH PRCs by Low-Sensitivity GC/MS

Four commercial and three university laboratories analyzed the PAH PRCs pre-loaded in PDMS with low-sensitivity GC/MS. As shown in Table 2, all results reported by commercial and university laboratories met the accuracy criteria of 50-150% target concentrations, with the exception of a single analyte by a single commercial laboratory: 39% of target for $^{13}\text{C}_6$ -indeno[1,2,3-cd]pyrene by laboratory 38. An in-depth investigation was conducted by laboratory 38 leading chemist and project chemist Mingta Lin. No anomalies were identified that would have contributed to the low-bias PAHs results for this analyte. Mr. Lin and team determined this accuracy exceedance was not basis for exclusion of this data from comparison.

All laboratory replicate analysis %RSD values were well below the $\leq 20\%$ criteria, which demonstrated acceptable precision within each laboratory. The interlaboratory %RSD values for commercial laboratories ranged from 19% to 27% and 7% to 20% for university laboratories.

MRLs reported by the commercial laboratories indicated sufficient sensitivity to detect and quantitate the expected levels of target analytes in this analysis.

Low-sensitivity GC/MS PAHs data produced by the four commercial laboratories (using standardized methodology) and three university laboratories (using in-house research methods) was deemed acceptable and suitable for comparison based on accuracy and precision evaluation findings. Note that commercial laboratories 38 and 63; and university laboratories 18, 23, and 81 used an internal standard technique (as opposed to isotope dilution) for analyte quantitation. Only university laboratory 23 normalized their results with surrogate spike recovery.

3.2 PAH PRCs by High-Sensitivity GC/MS

None of the commercial laboratories participated in the analysis of PAH PRCs in PDMS by high-sensitivity GC/MS. Two of the university laboratories performed this analysis. However, one of the laboratories, laboratory 14, actually used low-sensitivity GC/MS to perform this analysis. As shown in Table 3, instrumentation for both laboratories was not capable of detecting $^{13}\text{C}_6$ -indeno[1,2,3cd]pyrene. Data were insufficient for comparability evaluation. This analytical method will not be utilized going forward on the project.

3.3 PCB PRCs by Low-Sensitivity GC/MS

Two commercial and two university laboratories analyzed the PCB PRCs pre-loaded in PDMS with low-sensitivity GC/MS methods. As shown in Table 4, all results reported by commercial and university laboratories met the accuracy criteria of 50-150% target concentrations.

All laboratory replicate analysis %RSD values were well below the $\leq 20\%$ criteria, which demonstrated acceptable precision within each laboratory. The inter-laboratory RPD values for PCB PRCs ranged from 7% to 15% for commercial laboratories and 11% to 15% for university laboratories.

MRLs reported by the commercial laboratories indicated sufficient sensitivity to detect and quantitate the expected levels of target analytes in this analysis.

Low-sensitivity GC/MS PCBs data produced by the four commercial laboratories (using standardized methodology) and three university laboratories (using in-house research methods) was deemed acceptable and suitable for comparison based on accuracy and precision evaluation findings. Note that results reported by university laboratory 44 were corrected with surrogate spike recovery. Commercial laboratories 20 and 46 and university laboratories 44 and 82 used internal standard technique (as opposed to isotope dilution) for analyte quantitation.

3.4 PCB PRCs by High-Sensitivity GC/MS

Two commercial and three university laboratories analyzed the PCB PRCs pre-loaded in PDMS with high-sensitivity GC/MS. As shown in Table 5, all results reported by commercial and university laboratories met the accuracy criteria of 50-150% target concentrations.

All laboratory replicate analysis %RSD values were below the $\leq 20\%$ criteria, which demonstrated acceptable precision within participating laboratories. The inter-laboratory RSD values for PCB PRCs ranged from 4% to 12% for commercial laboratories; RSD values ranged from 9% to 15% for university laboratories.

MRLs reported by the commercial laboratories indicated sufficient sensitivity to detect and quantitate the expected levels of target analytes in this analysis.

High-sensitivity GC/MS PCBs data produced by the two commercial laboratories (using standardized methodology) and three university laboratories (using in-house research methods) was deemed acceptable and suitable for comparison based on accuracy and precision evaluation findings. Only university laboratory 44 normalized their results with surrogate spike recovery. Note that results for analytes ^{13}C -PCB 28 and ^{13}C -PCB 111 reported by commercial laboratory 85 corrected for method blank contamination; these concentrations are therefore considered estimated but suitable for comparison here (Pyrone 2018).

4. ASSESSMENT FINDINGS FOR LDPE SAMPLER ANALYSIS

4.1 PAH PRCs by Low-Sensitivity GC/MS

Four commercial and three university laboratories analyzed the PAH PRCs pre-loaded in LDPE samplers with low-sensitivity GC/MS. As shown in Table 6, all results reported by commercial and university laboratories met the accuracy criteria of 50-150% target concentrations.

All laboratory replicate analysis %RSD values were within the $\leq 20\%$ criteria, except for $^{13}\text{C}_6$ -indeno[1,2,3cd]pyrene reported by commercial laboratories 44 and 90 and university laboratories 25 and 32. Insufficient m/z distinction of this partially-labeled PRC may have contributed to the frequent precision exceedances observed by both commercial and university labs for this compound. Although the chemist and team determined these precision exceedances were not basis for exclusion of this data from comparison, this PRC will be reevaluated carefully during Task 2, with corrective actions identified; $^{13}\text{C}_6$ -indeno[1,2,3cd]pyrene may be replaced with a fully-labeled ^{13}C -indeno[1,2,3cd]pyrene or a deuterated version (if needed and pending consultation with commercial labs and

consensus decision to do so). Inter-laboratory RSD values for PCB PRCs ranged from 4% to 25% for commercial laboratories and ranged from 9% to 25% for university laboratories. Results reported by laboratory 91 were corrected by surrogate spike recovery, in particular to compensate potential analyte loss during solvent exchange. The solvent exchange step was unnecessary and will be eliminated in subsequent analyses.

MRLs reported by the commercial laboratories indicated sufficient sensitivity to detect and quantitate the expected levels of target analytes in this analysis.

Low-sensitivity GC/MS PAHs data produced by four commercial laboratories (using standardized methodology) and three university laboratories (using in-house research methods) was deemed acceptable and suitable for comparison based on accuracy and precision evaluation findings, subject to future evaluation and corrective action for PRC $^{13}\text{C}_6$ -indeno[1,2,3cd]pyrene. Note that commercial laboratories 44 and 72; and university laboratories 25, 32, and 91 used internal standard technique (as opposed to isotope dilution) for analyte quantitation. Only university laboratory 91 (discussed above) and university laboratory 25 normalized their results with surrogate spike recovery.

4.2 PAH PRCs by High-Sensitivity GC/MS

Only one university laboratory, laboratory 52, performed the analysis of PAH PRCs that were pre-loaded at concentration for high-sensitivity GC/MS analysis. Laboratory 52 actually used a low-sensitivity GC/MS for this analysis (Table 7). Precision issues (%RSD of 41%) for $^{13}\text{C}_6$ -indeno[1,2,3cd]pyrene (41%) were observed on low-sensitivity data, where the analysis was interfered with the column bleed noise. Insufficient data were available for data comparability analysis for Task 1.3; this method will not be utilized during future demonstration tasks.

4.3 PCB PRCs by Low-Sensitivity GC/MS

Two commercial and two university laboratories analyzed the PCB PRCs pre-loaded in LDPE samplers with low-sensitivity GC/MS methods. As shown in Table 8, all results reported by commercial and university laboratories met the accuracy criteria of 50-150% target concentrations, except for ^{13}C -PCB 111, ^{13}C -PCB 138 and ^{13}C -PCB 178 by laboratory 86.

All laboratory replicate analysis %RSD values for ^{13}C -PCB 37, ^{13}C -PCB 47, and ^{13}C -PCB 54 were less than the criterion of $\leq 20\%$. Replicate analysis %RSD values for higher molecular weight PRCs, ^{13}C -PCB 111, ^{13}C -PCB 138, and ^{13}C -PCB 138, exceeded 20% for both commercial laboratories and one of the two university laboratories (laboratory 20). These precision exceedances may be related to loading efficiency of the high molecular weight PCBs, particularly if material variations (area/weight consistency) in a given batch of samplers is not identified. Ensuring uniform LDPE material *before* preparing PRC-loaded LDPE samplers was a key lesson learned during task 1.

MRLs reported by the commercial laboratories indicated sufficient sensitivity to detect and quantitate the expected levels of target analytes in this analysis.

Low-sensitivity GC/MS PCBs data produced by two commercial laboratories (using standardized methodology) and two university laboratories was deemed acceptable and suitable for comparison based on accuracy and precision evaluation findings, given variations in the LDPE material identified subsequent to task completion. Material consistency will be ensured during all future demonstration tasks. Note that commercial laboratories 17 and 86; and university laboratories 20 and 40 used internal standard technique (as opposed to isotope dilution) for analyte quantitation. University laboratories 20 and 40 normalized their results with surrogate spike recovery.

4.4 PCB PRCs by High-Sensitivity GC/MS

Two commercial and three university laboratories analyzed the PCB PRCs pre-loaded in LDPE samplers with high-sensitivity GC/MS methods. As shown in Table 9, all results reported by commercial and university laboratories met the accuracy criteria of 50-150% target concentrations.

Replicate analysis %RSD values met the $\leq 20\%$ criteria for low molecular weight PCB congeners for all labs but multiple exceedances were observed for high molecular weight PCB congeners. There was not significant variability across participating laboratories, except for commercial laboratory 72, which reported RSD exceedances for four of the seven PRCs. No data quality issues were identified via data validation; the root causes of these precision exceedances for laboratory 72 were unclear but may have been due to LDPE material variations. However, laboratory 72 exceedances were not deemed sufficient basis for data exclusion from comparison.

MRLs reported by the commercial laboratories indicated sufficient sensitivity to detect and quantitate the expected levels of target analytes in this analysis.

High-sensitivity GC/MS PCBs data produced by two commercial laboratories (using standardized methodology) and three university laboratories was deemed acceptable and suitable for comparison based on accuracy and precision evaluation findings, given that most RSD values were $\leq 25\%$. Note that laboratory 93 reported results that were normalized with surrogate spike recovery to compensate potential analyte loss due to solvent exchange during extraction; solvent exchange will not be performed in future.

Table 2. PAH PRCs in PDMS by Low-Sensitivity Methods

PRCs	Target Concentration ng/mL-PDMS	50% Low	50% High	Commercial Laboratory								University Laboratory								Commercial Laboratory		University ^(B) Laboratory	
				15		38		63		71		18		23 ^(A)		81							
				Avg	RSD	Avg	RSD	Avg	RSD	Avg	RSD	Avg	RSD	Avg	RSD	Avg	RSD	Avg	RSD	Avg	RSD	Avg	RSD
¹³ C ₆ -Phenanthrene	7010	3500	10500	6740	14%	3460	7%	6150	1%	5880	1%	7010	5%	7020	4%	4500	2%	6260	22%	6180	20%		
¹³ C ₆ -Fluoranthene	7670	3840	11500	7160	7%	4270	7%	7300	1%	6230	1%	7670	3%	7610	3%	5900	1%	6900	19%	7060	12%		
¹³ C ₆ -Chrysene	7620	3810	11400	6850	7%	3800	8%	6300	1%	6150	1%	7620	4%	8410	2%	7000	4%	6430	19%	7680	7%		
¹³ C ₆ -Indeno[1,2,3-cd]pyrene	8540	4270	12800	8110	2%	3320	3%	6380	3%	8170	2%	8540	5%	6380	5%	7080	4%	7550	27%	7330	13%		

Notes:

Shaded number indicated that the value did not meet the accuracy evaluation criterion; the italicized value met the criteria at two significant digits and was therefore not counted as an exceedance

^(A): Results were corrected with surrogate spike recovery

^(B): Average value of multiple analyses was used for laboratory 23 for RSD calculation.

Avg: Average value; based on three replicates analyzed/reported by each laboratory, except laboratory 18. Laboratory 18 analyzed and reported six replicates.

ng/mL-PDMS: nanogram per milliliter of polydimethylsiloxane

PAH: Polycyclic aromatic hydrocarbon

PRCs: Performance reference compounds

RSD: Relative standard deviation; criterion was set at ≤20% as guideline for intralab precision evaluation

Table 3. PAHs in PDMS by High-Sensitivity Methods

PRCs	Target Concentration ng/mL-PDMS	50% Low	50% High	University Laboratory				University ^(B) Laboratory	
				14		72 ^(A)		Average	RSD
				Average	RSD	Average	RSD		
¹³ C ₆ -Phenanthrene	602	301	903	554	3%	602	6%	578	7%
¹³ C ₆ -Fluoranthene	836	418	1250	587	2%	836	10%	711	17%
¹³ C ₆ -Chrysene	722	361	1080	358	24%	722	2%	540	26%
¹³ C ₆ -Indeno[1,2,3-cd]pyrene	844	422	1270	<250	NC	NC	NC	NC	NC

Notes:

This analytical method is not being used by participating commercial labs and will not be utilized going forward on the project.

Shaded number indicated that the value did not meet the evaluation criterion.

^(A): Laboratory 72 actually used low-sensitivity instrumentation to analyze the pre-loaded SPME samplers; the results were corrected with surrogate spike recovery. Data are included in this table for comparability analysis between the high-sensitivity method (performed by Laboratory 14) and the low-sensitivity method performed by laboratory 72.

^(B): Average value of multiple analyses was used for laboratory 14 for RSD calculation.

Avg: Average value; based on three replicates analyzed/reported by each laboratory, except laboratory 14. Laboratory 14 analyzed and reported six replicates.

NC: Not calculated

ng/mL-PDMS: nanogram per milliliter of polydimethylsiloxane

PAH: Polycyclic aromatic hydrocarbon

PRCs: Performance reference compounds

RPD: Relative percent difference

RSD: Relative standard deviation; criterion was set at ≤20% as guideline for intralab precision evaluation

Table 4. PCBs in PDMS by Low-Sensitivity Methods

PRCs	Target Concentration ng/mL-PDMS	50% Low	50% High	Commercial Laboratory				University Laboratory				Commercial Laboratory		University ^(B) Laboratory	
				20		46		44 ^(A)		82					
				Avg	RSD	Avg	RSD	Avg	RSD	Avg	RSD	Avg	RSD		
¹³ C-PCB 37	8670	4340	13000	6570	7%	5170	7%	6010	3%	8670	5%	5870	15%	7340	15%
¹³ C-PCB 47	9030	4520	13600	6540	7%	6360	10%	6840	4%	9030	6%	6450	8%	7930	12%
¹³ C-PCB 54	9170	4580	13800	6500	6%	6770	5%	6520	5%	9170	5%	6630	7%	7840	14%
¹³ C-PCB 111	8900	4450	13400	7220	7%	6390	9%	6960	5%	8910	5%	6800	10%	7930	11%
¹³ C-PCB 138	9310	4650	14000	7000	6%	7320	6%	6750	2%	9310	5%	7160	7%	8030	13%
¹³ C-PCB 178	8750	4380	13100	6900	5%	7830	5%	6550	3%	8750	5%	7350	9%	7650	12%

Notes:

Shaded number indicated that the value did not meet the accuracy evaluation criterion.

Avg: Average value; based on three replicates analyzed/reported by each laboratory, except laboratory 18. Laboratory 18 analyzed and reported six replicates.

^(A): Results were corrected with surrogate spike recovery

^(B): Average value of multiple analyses was used for laboratory 44 for RSD calculation.

ng/mL-PDMS: nanogram per milliliter of polydimethylsiloxane

PCB: Polychlorinated biphenyl

PRCs: Performance reference compounds

RPD: Relative percent difference

RSD: Relative standard deviation; criterion was set at $\leq 20\%$ as guideline for intralab precision evaluation

Table 5. PCBs in PDMS by High-Sensitivity Methods

PRCs	Target Concentration ng/ml-PDMS	50% Low	50% High	Commercial Laboratory				University Laboratory						Commercial Laboratory		University ^(B) Laboratory	
				76		85		10		40 ^(A)		93		Avg	RSD	Avg	RSD
				Avg	RSD	Avg	RSD	Avg	RSD	Avg	RSD	Avg	RSD				
¹³ C-PCB 28	1630	813	2440	1700	2%	1580	0%	1710	2%	1630	3%	1200	6%	1640	4%	1610	9%
¹³ C-PCB 47	1680	838	2520	1850	4%	1590	1%	1760	1%	1680	3%	1260	2%	1720	9%	1660	9%
¹³ C-PCB 70	1570	784	2350	1730	5%	1400	2%	1510	1%	1570	4%	1210	5%	1570	12%	1520	8%
¹³ C-PCB 80	1450	724	2170	1490	2%	1220	3%	1660	1%	1450	3%	1020	2%	1360	11%	1470	13%
¹³ C-PCB 111	1540	768	2310	1270	5%	1470	13%	1310	1%	1540	3%	996	0%	1370	12%	1410	13%
¹³ C-PCB 141	1430	716	2150	1400	3%	1260	0%	1580	4%	1430	3%	1360	4%	1330	6%	1470	6%
¹³ C-PCB 182	1460	729	2190	1230	2%	1180	4%	1140	2%	1460	6%	1000	1%	1210	4%	1320	15%

Notes:

Shaded number indicated that the value did not meet the accuracy evaluation criterion.

Bolded and boxed results were corrected for method blank contamination, and are therefore considered estimated values (Pyron, 2018a).

^(A): Results were corrected with surrogate spike recovery

^(B): Average value of multiple analyses was used for laboratory 93 for RSD calculation.

Avg: Average value; based on three replicates analyzed/reported by each laboratory, except laboratory 18. Laboratory 18 analyzed and reported six replicates.

ng/mL-PDMS: nanogram per milliliter of polydimethylsiloxane

PCB: Polychlorinated biphenyl

PRCs: Performance reference compounds

RSD: Relative standard deviation; criterion was set at ≤20% as guideline for intralab precision evaluation

Table 6. PAH PRCs in LDPE by Low-Sensitivity Methods

PRCs	Target Concentration ng/g-PE	50% Low	50% High	Commercial Laboratory								University Laboratory						Commercial Laboratory		University Laboratory	
				16		44		72		90		25 ^(A)		32		91 ^(A)					
				Avg	RSD	Avg	RSD	Avg	RSD	Avg	RSD	Avg	RSD	Avg	RSD	Avg	RSD	Avg	RSD		
¹³ C ₆ -Phenanthrene	137	68.6	206	166	1%	155	1%	164	2%	180	0%	137	5%	193	4%	149	7%	166	6%	137	15%
¹³ C ₆ -Fluoranthene	176	87.8	263	158	2%	164	4%	173	1%	163	4%	176	6%	162	1%	196	11%	165	4%	148	9%
¹³ C ₆ -Chrysene	198	99.1	297	109	7%	108	2%	124	6%	133	11%	198	9%	144	3%	192	13%	119	11%	149	16%
¹³ C ₆ -Indeno[1,2,3-cd]pyrene	173	86.6	260	142	18%	124	42%	134	15%	150	29%	173	34%	209	21%	217	13%	138	25%	167	25%

Notes:

Shaded number indicated that the value did not meet the evaluation criterion.

^(A): Results were corrected with surrogate spike recovery.

Avg: Average value; based on three replicates reported by each laboratory, except laboratory 25. Laboratory 25 reported seven replicates.

LDPE: Low density polyethylene sampler

ng/g-PE: nanogram per gram of low-density polyethylene sampler

PAH: Polycyclic aromatic hydrocarbon

PRCs: Performance reference compounds

RSD: Relative standard deviation; criterion was set at ≤20% as guideline for intralab precision evaluation

Table 7. PAHs in LDPE by High-Sensitivity Methods

PRCs	Target Concentration ng/g-PE	50% Low 50% High		University Laboratory	
				52 ^(A)	
				Average	RSD
¹³ C ₆ -Phenanthrene	27.1	13.6	40.7	27.1	9%
¹³ C ₆ -Fluoranthene	40.8	20.4	61.1	40.8	3%
¹³ C ₆ -Chrysene	42.4	21.2	63.5	42.4	7%
¹³ C ₆ -Indeno[1,2,3-cd]pyrene	50.7	25.3	76.0	50.7	41%

Notes:

This analytical method is not being used by participating commercial labs and will not be utilized going forward on the project.

Shaded number indicated that the value did not meet the evaluation criterion.

^(A): Laboratory 52 actually used low-sensitivity instrumentation to analyze the pre-loaded PE samplers for high-sensitivity methods. Results were corrected with surrogate spike recovery.

Avg: Average value; based on eight replicates reported by laboratory 52.

LDPE: Low density polyethylene sampler

ng/g-PE: nanogram per gram of polyethylene sampler

PAH: Polycyclic aromatic hydrocarbon

PRCs: Performance reference compounds

RSD: Relative standard deviation; criterion was set at ≤20% as guideline for intralab precision evaluation

Table 8. PCBs in LDPE by Low-Sensitivity Methods

PRCs	Target Concentration ng/g-PE	50% Low50% High		Commercial Laboratory				University Laboratory				Commercial Laboratory		University Laboratory	
				17		86		20 ^(A)		40 ^(A)					
				Avg	RSD	Avg	RSD	Avg	RSD	Avg	RSD	Avg	RSD		
¹³ C-PCB 37	126.0	63.0	189	101.0	4%	129.0	0%	126.0	6%	102.0	3%	115.0	13%	114.0	12%
¹³ C-PCB 47	112.0	56.0	168	85.0	3%	84.0	9%	112.0	9%	89.5	0%	84.5	4%	101.0	13%
¹³ C-PCB 54	89.2	44.6	134	64.5	5%	72.9	1%	89.2	5%	67.8	2%	68.7	7%	78.5	14%
¹³ C-PCB 111	154.0	76.8	230	101.0	28%	72.4	22%	154.0	20%	92.8	6%	86.9	30%	123.0	31%
¹³ C-PCB 138	148.0	73.9	222	87.4	35%	59.8	20%	148.0	22%	89.8	8%	73.6	36%	119.0	33%
¹³ C-PCB 178	155.0	77.5	232	83.4	45%	44.6	21%	155.0	26%	81.6	9%	64.0	54%	118.0	41%

Notes:

Shaded number indicated that the value did not meet the accuracy evaluation criterion.

^(A): Results were corrected with surrogate spike recovery.

Avg: Average value; based on three replicates reported by each laboratory, except laboratories 86 and 20. Analyses performed by laboratory 86 were likely affected by the loading efficiency of the LDPE samplers. Laboratory 20 reported six replicates.

LDPE: Low density polyethylene sampler

ng/g-PE: nanogram per gram of polyethylene sampler

PCB: Polychlorinated biphenyl

PRCs: Performance reference compounds

RSD: Relative standard deviation; criterion was set at $\leq 20\%$ as guideline for intralab precision evaluation

Table 9. PCBs in LDPE by High-Sensitivity Methods

PRCs	Target Concentration ng/g-PE	50% Low	50% High	Commercial Laboratory				University Laboratory						Commercial Laboratory		University Laboratory	
				18		72		41 ^(A)		60		93 ^(A)		Avg	RSD	Avg	RSD
				Avg	RSD	Avg	RSD	Ave	RSD	Avg	RSD	Avg	RSD				
¹³ C-PCB 28	35.3	17.6	52.9	30.5	1%	24.3	6%	35.3	6%	42.4	2%	20.5	18%	27.4	13%	32.7	26%
¹³ C-PCB 47	31.2	15.6	46.8	31.0	7%	31.0	6%	31.2	4%	36.1	6%	26.5	3%	31.0	6%	31.2	12%
¹³ C-PCB 70	36.4	18.2	54.6	30.6	6%	30.3	8%	36.4	5%	37.4	5%	27.6	3%	30.5	6%	33.8	14%
¹³ C-PCB 80	36.0	18.0	54.1	30.8	12%	28.3	27%	36.0	12%	40.0	3%	33.4	7%	29.6	19%	36.4	13%
¹³ C-PCB 111	31.5	15.8	47.3	35.1	14%	28.0	47%	31.5	16%	37.0	11%	34.1	15%	31.5	31%	34.2	24%
¹³ C-PCB 141	33.4	16.7	50.0	31.6	13%	27.0	52%	33.4	21%	39.4	25%	40.0	15%	29.3	33%	37.6	38%
¹³ C-PCB 182	35.7	17.8	53.5	27.3	13%	20.7	81%	35.7	23%	36.5	21%	37.2	30%	24.0	48%	36.4	76%

Notes:

Shaded number indicated that the value did not meet the accuracy evaluation criterion.

^(A): Results were corrected with surrogate spike recovery.

Avg: Average value; based on three replicates reported by each laboratory, except laboratory 41. Laboratory 41 analyzed and reported six replicates.

LDPE: Low density polyethylene sampler

ng/g-PE: nanogram per gram of polyethylene sampler

PCB: Polychlorinated biphenyl

PRCs: Performance reference compounds

RPD – Relative percent difference

RSD: Relative standard deviation; criterion was set at $\leq 20\%$ as guideline for intralab precision evaluation

References

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APPENDIX E

Task 2 GO! Memo with appendices

April 3, 2019

Dr. Andrea Leeson
Deputy Director & Environmental Restoration Program Manager
SERDP & ESTCP
4800 Mark Center Drive, Suite 17D08
Alexandria, VA, 22350-3605

Re: Standardizing Polymeric Sampling for Measuring Freely-Dissolved Organic Contaminants
in Sediment Porewater, ESTCP Project ER-201735 – Draft Task 2 Go/No-Go Memorandum

Dear Dr. Leeson:

The subject ESTCP Project seeks to demonstrate a standardized methodology for polymeric sampler preparation and analysis of polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) by multiple contract and academic laboratories. Task 2 of the project required laboratories to demonstrate the ability to load polymeric samplers with performance reference compounds (PRCs) in preparation for Task 3. A Go/No-Go decision was included in the project to ensure successful completion of Task 2 before proceeding to Task 3. On the basis of the participating laboratories' performance during Task 2, a Go! decision is recommended to proceed to Task 3. The basis for our recommend Go! decision is summarized below.

- ALL laboratories achieved measurable loading and acceptable precision ($\leq 20\%$ RSD in replicated PRC-loaded samplers) during Task 2. This is the critical factor in employing PRCs in that the fractional depletion of this initial concentration allows estimation of the extent of equilibrium.
- Variations in solvent type and proportions in intermediate solutions used to prepare the PRC loading solution caused variations in the PRC loading concentrations in different laboratories. While not interfering with the primary need to achieve acceptable precision in PRC loading at any given laboratory, the variability did suggest that improvements in the PRC loading SOPs were needed to recognize the importance of appropriate solvents and proportions in the spiking solutions. These revisions to SOPs were implemented and provided to all participating laboratories.

Acceptable precision in the $C_{\text{PRC},t=0}$ results reported by all laboratories during Task 2, coupled with the corrective action of refining SOPs, support our Go! recommendation to proceed with Task 3. The enclosed memorandum documents methods and details of the conduct, laboratory performance, and overall results of Task 2. If you have any questions or require additional information about the information presented above, please give me a call at 206-764-3324 or email at mandy.m.michalsen@usace.army.mil.

We look forward to your review and your Go/No-Go decision.

Thank you,



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Standardizing Polymeric Sampling for Measuring Freely-Dissolved Organic Contaminants in Sediment Porewater

ESTCP PROJECT ER-201735 Task 2 Go/No-Go Memorandum

April 3, 2019

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ATTACHMENT 1	Updated polymeric sampler SOPs
ATTACHMENT 2	Low-Density Polyethylene (LDPE) Polymeric Samplers, ~~Task 2 Data Validation Report~~
ATTACHMENT 3	Polydimethylsiloxane (PDMS) Polymeric Samplers, ~~Task 2 Data Validation Report~~
ATTACHMENT 4	Interlaboratory Data Comparability Memo, Task 2

Note: Commercial laboratories are participating in this Interlaboratory method validation study under the condition of anonymity. Accordingly, data validation reports where lab-specific performance was described has been omitted from this publically-released report.

ACRONYM LIST

C _{free}	freely-dissolved organic contaminant concentration
PRC	performance reference compound
PDMS	polydimethylsiloxane
PAH	polycyclic aromatic hydrocarbon
PCB	polychlorinated biphenyl
EPA	Environmental Protection Agency
LDPE	low density polyethylene
USACE	U.S. Army Corps of Engineers
ERDC	Engineer Research Development Center
QA/QC	quality assurance/quality control
HRGC	High Resolution Gas Chromatography
HRMS	High Resolution Mass Spectrometry
LRMS	Low Resolution Mass Spectrometry
RSD	Relative Standard Deviation
RPD	Relative Percent Difference

1. INTRODUCTION

1.1 Project Background

Polymeric samplers sorb hydrophobic organic contaminants present in sediment, whether used actively or passively (i.e. respectively with or without sediment/polymer mixing). The resultant polymer concentrations can then be used to calculate freely-dissolved contaminant concentrations (C_{free}) in the sediment's porewater. Polymeric samplers may be used as alternatives to (a) Henry samplers and pumping for porewater sample collection or (b) sediment centrifugation with supernatant collection. C_{free} measured by polymeric samplers represents the fraction of contaminants not sorbed to settling solids or associated with suspended colloidal matter. C_{free} is directly linked to sediment-dwelling organism's exposure to contaminants as well as risk for bioaccumulation into the larger foodweb. Therefore, developing standardized methods for obtaining C_{free} measurements using polymeric samplers is critically important for assessing the risk contaminated sediments represent to ecological and human health (e.g., consumption of contaminated fish and shellfish).

The objectives of this demonstration are as follows.

1. Develop a standardized methodology for polymeric sampler preparation and analysis of polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) by multiple contract and government laboratories. Two polymeric samplers are included: low-density polyethylene (LDPE) samplers and polydimethylsiloxane (PDMS) samplers. This methodology will describe how to:
 - Prepare polymeric samplers, including loading performance reference compounds (PRCs);
 - Expose polymeric samplers to sediment in the laboratory (i.e., *ex situ*);
 - Retrieve polymeric samplers from sediment and extract the organic contaminants and PRCs;
 - Perform chemical analysis of polymeric sampler extracts; and
 - Analyze raw chemical data and interpret results using them to determine the C_{free} present in the sediment porewater.
2. Collaborate with public- and private-sector laboratories to finalize the standardized polymeric sampler methodology, then validate the methodology through a phased interlaboratory comparison.
3. Document the standardized methods and interlaboratory method comparison results in a guidance document prepared following EPA SW846 guidelines, in addition to posting freely available webinars and instructional videos via YouTube and other online platforms.

1.2 Demonstration Performance Objectives

During this demonstration, multiple laboratories will utilize polymeric samplers to quantify freely-dissolved PAHs and PCBs in porewater using a single sediment sample. Demonstration results are intended to document laboratory accuracy and reproducibility of the polymeric sampler method – a key requirement for future acceptance as a SW-846 Method. The demonstration consists of

three tasks, each intended to reduce sources of variability extraneous to the polymeric sampler method itself prior to proceeding with subsequent tasks. Performance objectives are described in Table 1.

Table 1. Demonstration Performance Objectives.

Performance Objective	Data Requirements	Success Criteria
Quantitative Performance Objectives		
Interlaboratory analytical variability is low and within acceptable range (Task 1.1)	- Calibration check standards for low- and high-sensitivity methods prepared by one lab - Results of calibration check standard analysis reported as an EPA Stage 4 data package and Electronic Data Deliverable (EDD)	- Data validator confirms analytical data from each lab meets QC criteria (Section 5.4.4) and is of acceptable quality - Each lab reports $\pm 30\%$ of known concentrations for non-isotopically-labeled analytes; $\pm 50\%$ of known concentrations for isotopically-labeled Performance Reference Compounds (PRCs) - Success constitutes "go" to subsequent task.
Laboratories consistently extract and analyze PRCs from PRC-preloaded polymeric samplers provided by expert academic labs (Task 1.3)	- Results of PRC-loaded polymeric samplers (PDMS and LDPE replicates) from the academic laboratories preparing them - Results of PRC-preloaded polymeric samplers (PDMS and LDPE replicates) extracted and analyzed by all labs - Analytical data submitted as EPA Stage 4 data package and EDD	- Data validator confirms analytical data from each lab meets QC criteria (Section 5.4.4) and is of acceptable quality - Each lab reports $\geq \pm 50\%$ of known concentrations for the isotopically-labeled PRCs - Percent Relative Standard Deviation (% RSD) $\leq 20\%$ for replicate analyses; tolerance beyond this range will be considered on basis of collective results - Success constitutes "go" to subsequent task.
Laboratories achieve target PRC concentrations in polymeric samplers following standardized methods specific to each polymer (Task 2)	- Extract analysis results from polymeric samplers (PDMS and LDPE replicates) independently loaded by labs following standard method. - Analytical data submitted as EPA Stage 4 data package and EDD	- Data validator confirms analytical data meets QC criteria (Section 5.4.4) and is of acceptable quality - Each lab achieves within $\pm 50\%$ of target PRC concentrations immediately after loading is complete (i.e. $PRC_{t=0}$); Collective results will be used to establish target $PRC_{t=0}$ concentration criteria for Task 3 %RSD $\leq 20\%$ for replicate analyses performed; tolerance beyond this range will be considered on basis of collective results - Success constitutes "go" to subsequent task.
Laboratories measure target contaminants in homogenized sediment sample using "active" and "passive" sampling/exposure methods (as described in Section 5.3.3) following standardized methods specific to each polymer (Task 3)	- All analytical data from the polymeric sampler measurements submitted as EDD - Analytical data resulting from sediment porewater analysis via polymeric samplers, the Hawthorne method^{8,9}, and the air-bridge method¹⁰ - Analytical data submitted as EPA Stage 4 data package and EDD	- Data validator confirms analytical data meets QC criteria (Section 5.4.4) and is of acceptable quality - Achieve %RSD $\leq 20\%$ for $PRC_{t=0}$ concentration - Establish interlaboratory variability in resulting estimates of fractional approach to equilibrium and $C_{polymer}$ for both "active" and "passive" exposures; identify to the extent possible contributing sources of interlaboratory variability - Establish intermethod variability by comparing C_{free} estimates determined using polymeric samplers compared to alternative Hawthorne^{8,9} and air-bridge methods; variability as a function of target compound hydrophobicity will also be established
Quantitative Performance Objectives		
Meet minimum commercial laboratory participation required to fulfill method validation requirements for SW-846 standardized method application	Responsiveness, flexibility, commitment to identify and resolve technical issues so that maximum participation is retained during demonstration	At least 3 commercial laboratories successfully complete all demonstration tasks

1.3 Document Organization and Purpose

Task 1 of this project involved a "round robin" analysis of standards containing known concentrations of PAHs and PRCs in order to confirm that all participating laboratories could obtain comparable results using their preferred EPA certified methods. Task 1 results were successful so the project proceeded on to Task 2, which involved each laboratory following the

polymer sampler standard operating procedures (SOPs) to independently load performance reference compounds (PRCs) into the samplers, followed by extracting and quantifying the PRCs in sampler extracts. PRCs are isotopically-labeled versions of the target organic contaminants of interest. PRC loss from the polymer during deployment provides a measure of its progress toward equilibrium with contaminants in the sediment porewater. Thus, the objective of Task 2 was to confirm all laboratories could successfully follow the polymeric sampler SOPs to successfully load PRCs into the samplers, then extract and quantify PRCs in the sampler extracts prior to proceeding to the “round robin” analysis of a reference sediment sampler during Task 3.

This “Go/No-Go” memorandum documents Task 2 methods and results, evaluates results against performance objectives, and recommends a “Go/No-Go” decision to proceed to Task 3. Section 2 presents Task 2 methods; Section 3 presents Task 2 results; and Section 4 presents discussion and the “Go/No-Go” recommendation. Supporting information is included in Attachments 1 – 4.

2. METHODS

Dr. Danny Reible’s group at Texas Tech University (TTU) and Dr. Phil Gschwend’s group at the Massachusetts Institute of Technology (MIT), respective subject matter experts for use of PDMS and LDPE samplers, each prepared 7 pre-cleaned “blank” polymeric samplers for participating laboratories to use in Task 2. Laboratories loaded PRCs into the samplers following the SOPs (Attachment 1) provided by TTU and MIT, respectively, for PDMS and LDPE. Once PRC loading was completed (minimum 1 month for PDMS and minimum 7 days for LDPE), the PRC-loaded samplers (and the method blank samplers) were extracted per the SOPs and the extracts were analyzed using standard EPA methods.

The PAH PRCs are independent of the EPA analytical method the laboratories use; thus, there is only one suite of PRCs for each method. PCB PRCs vary by EPA analytical method and as such there are two suites of PCB PRCs: one for regular sensitivity (low resolution mass spectrometry) and one for high sensitivity (high resolution mass spectrometry) methods.

- PAH PRCs: ¹³C6-phenanthrene, ¹³C6-fluoranthene, ¹³C6-chrysene, ¹³C6-indeno(1,2,3-cd)pyrene
- PCBs PRCs (Low-Sensitivity Methods): ¹³C-labeled PCB congeners 37, 47, 54, 111, 138, and 178
- PCBs PRCs (High-Sensitivity Methods): ¹³C-labeled PCB congeners 28, 47, 70, 80, 111, 141, 182

Four commercial laboratories and three university research laboratories participated in Task 2 under the condition of anonymity with each laboratory being assigned a random numeric identifier. These random identifiers are used through-out this document. Table 1 provides a list of which laboratories performed each analysis using LDPE and PDMS polymeric samplers. Per the final Demonstration Plan, each laboratory quantified PAHs using a low sensitivity analytical method (EPA Method 8270D-SIM) and PCBs using a high or low sensitivity analytical method (EPA Method 1668C or EPA Method 8270D-SIM, respectively).

Table 2. Analysis Performed by Laboratories during Task 2

PRCs	Method Sensitivity	Target Concentration Range ^(A)		SPME Laboratory		LDPE Laboratory	
		SPME	LDPE	Commercial	University	Commercial	University
PAHs	Low	1184 – 5922	500 – 1000	19, 48, 83, 98	9, 64	34, 52, 58, 84	15, 50
PCBs	Low	1184 – 5922	500 – 1000	14, 17	4, 55	11, 91	5, 52
	High	1184 – 1000	500 – 1000	37, 95	2	86, 93	69

Notes: SPME sampler results were reported in ng/mL-SPME; LDPE results were reported in ng/g-LDPE. ^(A)Target concentrations were computed based on volumes and concentrations of PRCs in the loading solutions the samplers were exposed to; concentration for each PRC varied between laboratories and are thus presented as a concentration range. Attachment 4 provides laboratory-, sampler-, and analysis-specific target concentration details.

Data packages received from commercial laboratories were subject to a complete (Level IV) data validation by Mr. Mingta Lin. The Data Validation Reports (Attachments 2 and 3) identified no data quality deficiencies in the data packages submitted by commercial laboratories. In addition, university laboratories used their standard or high-sensitivity analytical procedures to quantify concentrations of PAHs and PCBs. University data were not subject to validation; however, as documented in the Data Comparability Memorandum (Attachment4), Mr. Lin determined that it was appropriate to present and evaluate data generated by commercial and university laboratories collectively.

3. RESULTS

3.1 Low-Density Polyethylene (LDPE) Polymeric Samplers

PAH PRCs by Low-Sensitivity GC/MS. Four commercial laboratories (34, 52, 58, and 84) and two university laboratories (15 and 50) loaded and analyzed the PAH PRCs in LDPE samplers with low-sensitivity GC/MS. As illustrated in Figure 1, results reported by commercial and university laboratories met the accuracy criteria ($\pm 50\%$ of target concentrations), with the following exceptions:

- Commercial laboratory 34: ¹³C6-Phenanthrene (<50% of target concentration)
- Commercial laboratory 52: ¹³C6-indeno[1,2,3cd]pyrene (>150% of target concentration)
- Commercial laboratory 84: ¹³C6-Phenanthrene ¹³C6-Fluoranthene, ¹³C6-Chrysene (<50% of target concentration) and ¹³C6-indeno[1,2,3cd]pyrene (>150% of target concentration)
- University laboratory 15: ¹³C6-Phenanthrene ¹³C6-Fluoranthene, and ¹³C6-indeno[1,2,3cd]pyrene (>150% of target concentration)

All laboratory replicate analysis %RSD values met the precision criteria of $\leq 20\%$.

PCB PRCs by High-Sensitivity GC/MS. Two commercial laboratories (86 and 93) and one university laboratory (69) loaded and analyzed the PCB PRCs in LDPE samplers with high-sensitivity GC/MS methods (Figure 1). Most PCB PRC concentrations exceeded the upper limit of the accuracy criteria ($\pm 50\%$ of target concentrations), as follows:

- Commercial laboratory 86: ¹³C-PCB 80 and 13C-PCB 111 (>150% of the target concentration)

- Commercial laboratory 93: ^{13}C -PCB 28 and ^{13}C -PCB 80 (>150% of the target concentration)
- University laboratory 69: All PCB PRCs (>150% of the target concentration)

All laboratory replicate analysis %RSD values met the precision criteria of $\leq 20\%$.

PCB PRCs by Low-Sensitivity GC/MS. Two commercial laboratories (11 and 91) and two university laboratories (5 and 52) loaded and analyzed the PCB PRCs in LDPE samplers with low-sensitivity GC/MS methods (Figure 1). All results reported by commercial and university laboratories met the accuracy criteria ($\pm 50\%$ of target concentrations), with the following exceptions:

- Commercial laboratory 11: ^{13}C -PCB 47 and ^{13}C -PCB 111 (>150% of the target concentration)
- Commercial laboratory 91: ^{13}C -PCB 37, ^{13}C -PCB 47, ^{13}C -PCB 111, ^{13}C -PCB 138, and ^{13}C -PCB 178 All PCB PRCs except ^{13}C -PCB 54 (>150% of the target concentration)
- University laboratory 5: ^{13}C -PCB 37, ^{13}C -PCB 47, ^{13}C -PCB 54, and ^{13}C -PCB 111 All PCB PRCs except ^{13}C -PCB 138 and ^{13}C -PCB 178 (>150% of the target concentration)
- University laboratory 52: ^{13}C -PCB 37, ^{13}C -PCB 47, ^{13}C -PCB 111, ^{13}C -PCB 138, and ^{13}C -PCB 178 All PCB PRCs except ^{13}C -PCB 54 (>150% of the target concentration)

All laboratory replicate analysis %RSD values met the precision criteria of $\leq 20\%$.

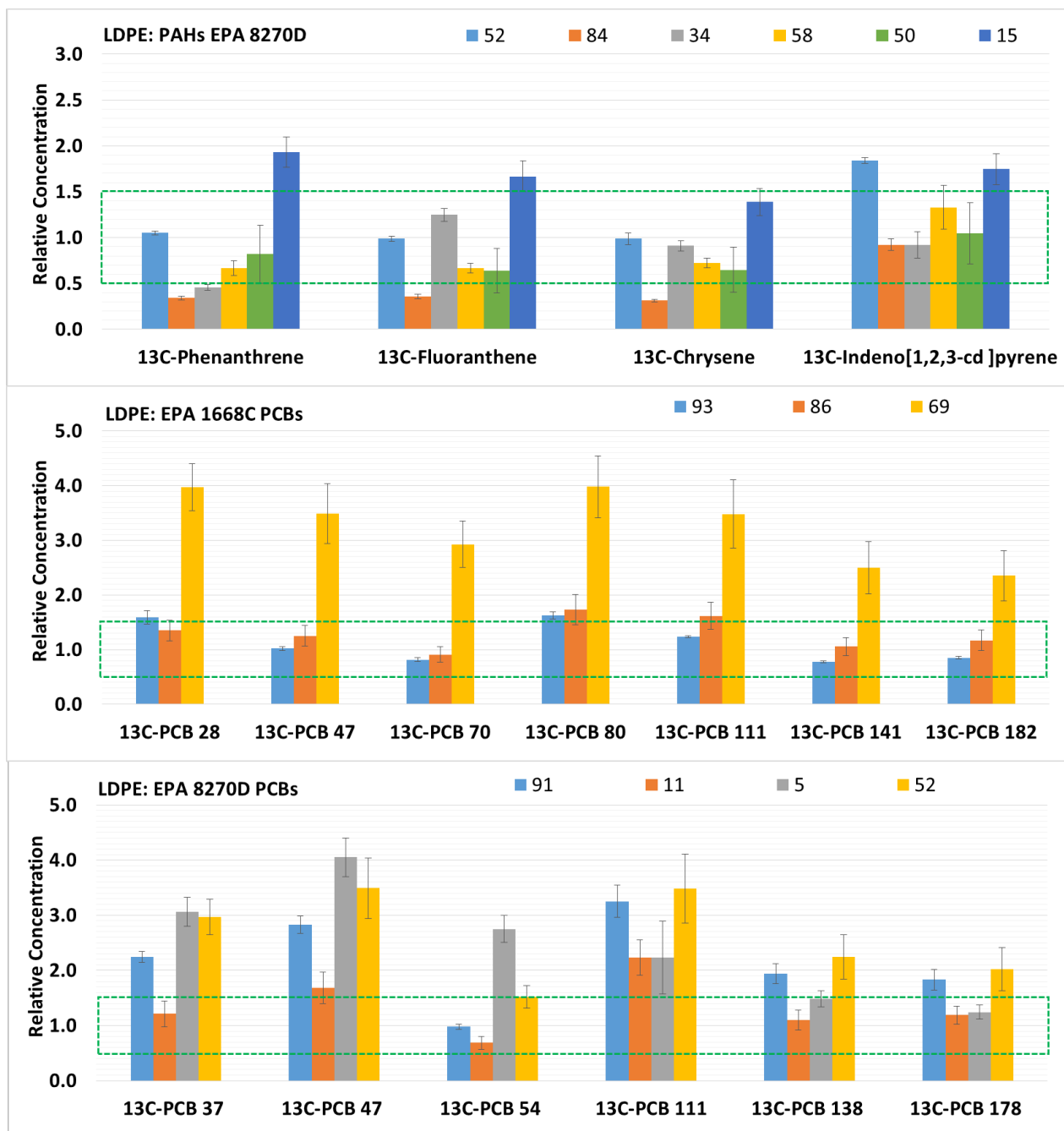


Figure 1. LDPE PRC loading and analysis results in relative units ($C_{\text{reported}}/C_{\text{known}}$). PAHs analyzed by the low sensitivity (8270D) method are shown at the top, PCB congeners analyzed by high-sensitivity (1668C) and low-sensitivity (8270D) methods are respectively shown at the middle and bottom of the figure. The acceptable range for PRC results ($\pm 50\%$) is highlighted within the green rectangle.

3.2 Task 2 Loading and Analysis of Polydimethylsiloxane (PDMS) Samplers

PAH PRCs by Low-Sensitivity GC/MS. Four commercial laboratories (19, 48, 83, and 98) and two university laboratories (9 and 64) analyzed the PAH PRCs loaded in PDMS with low-sensitivity GC/MS. As illustrated in Figure 2, results reported by commercial and university laboratories met the accuracy criteria ($\pm 50\%$ of target concentrations), with the following exceptions:

- Commercial laboratory 48: $^{13}\text{C}_6$ -Phenanthrene
- Commercial laboratory 83: $^{13}\text{C}_6$ -Phenanthrene and $^{13}\text{C}_6$ -Indeno[1,2,3-cd]pyrene
- Commercial laboratory 98: $^{13}\text{C}_6$ -Phenanthrene
- University laboratory 9: $^{13}\text{C}_6$ -Fluoranthene

All laboratory replicate analysis %RSD values met the precision criteria of $\leq 20\%$.

PCB PRCs by High-Sensitivity GC/MS. Two commercial laboratories (37 and 95) and one university laboratory (2) analyzed the PCB PRCs loaded in PDMS with high-sensitivity GC/MS. As shown in Figure 2, all results reported by commercial and university laboratories met the accuracy criteria ($\pm 50\%$ of target concentrations) indicating satisfactory accuracy. All laboratory replicate analysis %RSD values were less than the criterion of $\leq 20\%$, demonstrating acceptable precision within each of the participating laboratories.

PCB PRCs by Low-Sensitivity GC/MS. Two commercial laboratories (14 and 17) and two university laboratories (4 and 55) analyzed the PCB PRCs loaded in PDMS with low-sensitivity GC/MS methods. As illustrated in Figure 2, all results reported by commercial and university laboratories met the accuracy criteria ($\pm 50\%$ of target concentrations), with the following exceptions:

- Commercial laboratory 19: ^{13}C -PCB 37
- Commercial laboratory 17: ^{13}C -PCBs 54, 111, 138, and 178
- University laboratory 4: ^{13}C -PCB 54

All laboratory replicate analysis %RSD values met the precision criteria of $\leq 20\%$.

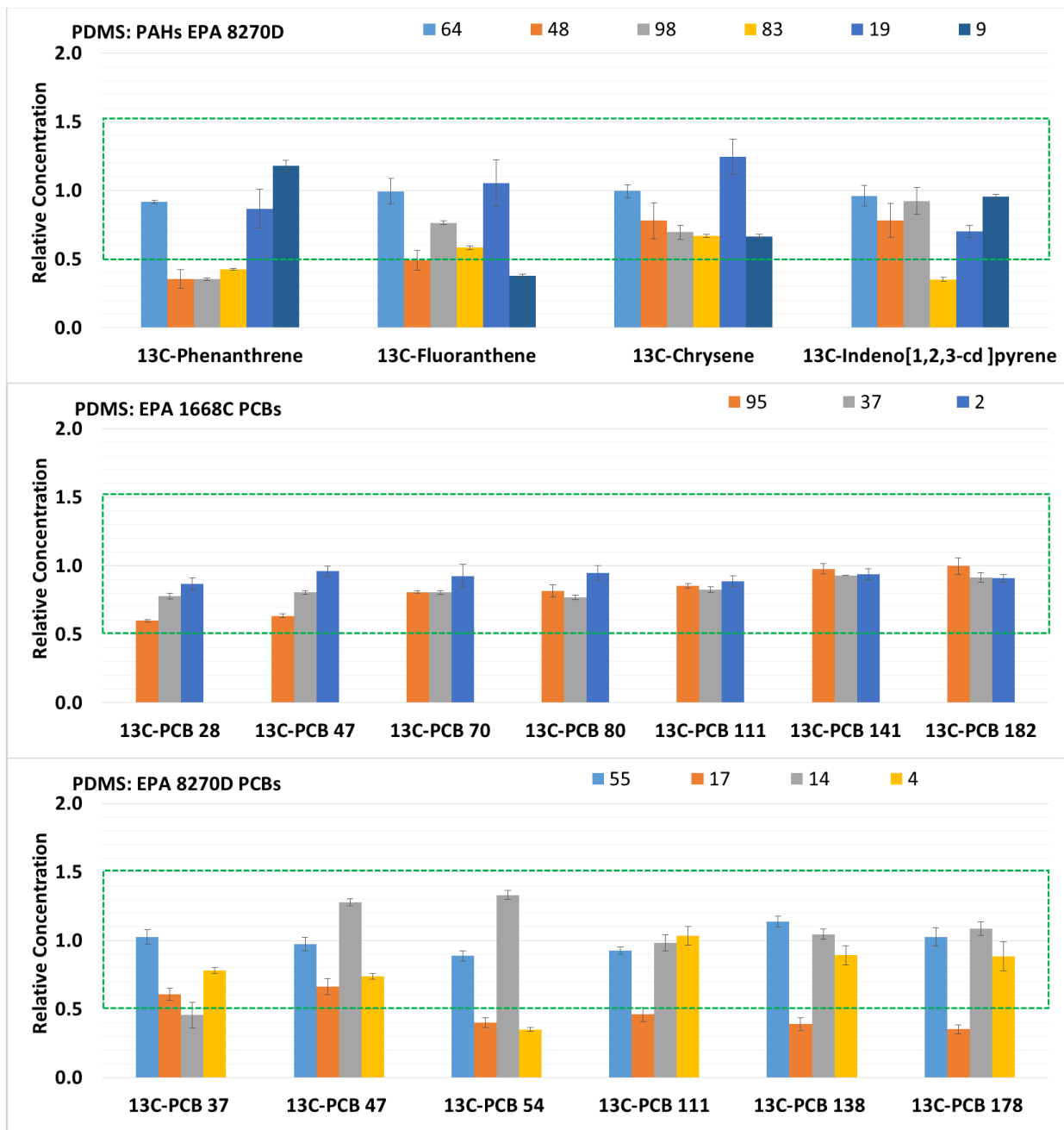


Figure 2. PDMS PRC loading and analysis results in relative units ($C_{\text{reported}}/C_{\text{known}}$). PAHs analyzed by the low sensitivity method (8270D) is shown at the top, PCB congeners analyzed by high-sensitivity (1668C) and low-sensitivity (8270D) methods are respectively shown at the middle and bottom of the figure. The acceptable range for PRC results ($\pm 50\%$) is highlighted within the green rectangle.

4. DISCUSSION AND GO! RECOMMENDATION

ALL laboratories achieved measurable loading and acceptable precision ($\leq 20\%$ RSD in replicated PRC-loaded samplers) during Task 2. Achieving acceptable precision in the PRC concentrations loaded into the polymeric samplers prior to deployment (i.e. $C_{\text{PRC}, t=0}$) is critical because this value is used to correct measured concentrations of PAHs and PCBs in sediment porewater for their progress towards equilibrium during field deployments. As long as the $C_{\text{PRC}, t=0}$ result is precise and the loaded PRC concentration is detectable by the standard analytical method being used, the PRCs may be used to correct for equilibrium conditions.

Variations in solvent type and volumetric proportions used to prepare the PRC loading solution led to variations in loaded PRC concentration achieved by different laboratories. All laboratories prepared their PRC loading solutions (referred to below and in the SOPs as the “working standard”) in 80:20 methanol:water for LDPE and in 20:80 methanol:water for PDMS, consistent with the polymeric sampler SOPs. However, composition of the “spiking standard” varied for each lab. Spiking standard contains high concentrations of PRCs in a solvent, which is “spiked” into the working standard to achieve the final PRC concentrations in the PRC loading solution. Varied PRC concentrations in the spiking standard caused variations in the spike standard volume added to the working standard; varied volumes added coupled with varied solvent types used to prepare the spiking standard resulted in differences in final loaded PRC concentrations achieved by the different labs. Spiking standards with high nonane content (i.e., solvent used by the vender to store the PRCs) were particularly problematic. It is important to ensure spiking standard and working standard solvent miscibility and also best to minimize the ratio of nonane to solvent in the working standard. We recommended acetone as the spiking standard solvent; problems were encountered when alternative solvents were used. As a result, the LDPE and PDMS SOPs were updated (Attachment 1) to feature more stringent requirements regarding spiking standard solvent types and proportions. **Acceptable method performance across laboratories will be obtained so long as laboratories follow updated SOPs to (1) use miscible carrier solvents to form a uniform PRC loading solution, (2) use an appropriate volume of loading solution per mass of polymeric samplers being prepared, (3) ensure the samplers have sufficient time in the loading solution to achieve equilibrium, and (4) analyze replicate PRC-loaded samplers after the samplers have equilibrated to ensure acceptable precision on the PRC-loaded sampler $C_{t=0}$ measurement *before* using the PRC-loaded samplers to characterize sediment porewater concentrations.**

Acceptable precision in the $C_{\text{PRC}, t=0}$ results reported by all laboratories during Task 2, coupled with refined SOPs and corrective actions described below, support our GO! recommendation to proceed with Task 3. All laboratories were provided copies of the updated SOPs, which feature more stringent PRC loading solution requirements and agreed to follow the revised requirements during PRC loading of blank samplers during Task 3. Further, participating laboratories will be required to provide their Task 3 $C_{\text{PRC}, t=0}$ results for co-PI review and approval so that acceptable accuracy and precision is verified prior to proceeding with the round robin sediment measurement. If Task 3 $C_{\text{PRC}, t=0}$ results do not meet accuracy and precision criteria, ESTCP would

be notified of this occurrence and the team would pause for additional SOP trouble shooting until $C_{PRC, t=0}$ success criteria have been achieved by all participating laboratories.

ATTACHMENT 1
Polymeric Sampler SOPs



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

1. SCOPE AND APPLICATION

- 1.1. This method is an operating procedure for handling and loading solid phase micro-extraction polydimethylsiloxane (SPME-PDMS) fibers with performance reference compounds (PRCs) for measuring environmental contaminant concentrations in sediment pore water and overlying water.
- 1.2. The method is applicable to hydrophobic organic contaminants (HOCs) and the focus herein is on polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs).
- 1.3. This procedure generates extracts suitable for High Performance Liquid Chromatography (HPLC) and gas chromatography with mass spectroscopy detection GC-MS analysis for priority and alkyl PAHs (PAH-38); and GC-MS/MS and gas chromatography with electron capture detection (GC-ECD) for PCBs.
- 1.4. 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. SUMMARY OF METHOD

- 2.1. A specific length of PDMS-coated fiber is cleaned by consecutive extraction with dichloromethane, hexane, methanol and ultrapure water.
- 2.2. Performance reference compounds are loaded onto cleaned PDMS fiber in water-methanol (80:20%) solution.
- 2.3. A shaker table is required to facilitate well-mixing of the PRC spiking solution and contact with the PDMS fibers.
- 2.4. The PDMS fibers are kept in the PRC solution until preparation for deployment.
- 2.5. 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 into the water column.
- 2.6. 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 atmospheric and surficial sources, 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 MilliQ 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 non-aqueous 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 phase 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.
- 4.2. Solid phase micro-extraction polydimethylsiloxane fibers – commercially available through suppliers like Polymicro Technologies™ (Molex, Phoenix, AZ, USA) and Fiberguide (Stirling, NJ, USA).
- 4.3. Extraction vessels – 2 mL amber (for PAHs) or clear glass (for PCBs) autosampler vials.
- 4.4. 300 µL glass inserts with springs for ultra-low solvent volumes.
- 4.5. PTFE/Silicone/PTFE screw caps and PTFE lined solid tops for long-term storage.
- 4.6. Kimwipes®
- 4.7. Food-grade aluminum foil
- 4.8. Tweezers
- 4.9. Ceramic Cutter or nippers
- 4.10. Shaker table or overhead tumbler

5. REAGENTS

- 5.1. Dichloromethane (i.e., methylene chloride, CH₂Cl₂)
- 5.2. Hexane
- 5.3. Acetonitrile
- 5.4. Methanol
- 5.5. MilliQ Water (Barnstead, GenPure Pro) or equivalent
- 5.6. Research grade deuterated or ¹³C labeled compounds as performance reference compounds (PRCs) from Ultra Scientific and Cambridge Isotope Laboratories (**Appendix 1**).
- 5.7. Research grade deuterated or ¹³C labeled compounds as surrogates (**Appendix 1**) or internal standards for GC-MS or GC-MS/MS analysis: d-acenaphthene, d-phenanthrene and d-perylene for PAHs (working standard concentration of 1000 ng/mL in hexane),

and ^{13}C mix containing PCBs 9/118/188 (working standard concentration of 1000 ng/mL in hexane).

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/column cutter or nippers 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 thicknesses 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 2.
- 7.2. PDMS washing procedure
 - 7.2.1. The cut PDMS fibers are placed in the 120 ml glass vessel and cleaned by washing consecutively by soaking in three solvents (i.e., dichloromethane (2x), hexane (2x) and methanol (2x)) for 30 minutes each on a shaker table. Larger vessels and volumes are recommended for large sampling efforts. Care should be taken to avoid PDMS breakage during washing with solvents especially if the vessel is filled with solvent half way. 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 MilliQ water 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 cleaned PDMS fibers should be stored closed in the glass vessel 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. 100 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

(**Appendix 1**) at working concentration of 2500 ng/ml in acetone or methanol are added to the water-20% methanol solution.

Note: Acetone must be used for preparation of diluted working standards to ensure miscibility with stock solutions purchased in nonane. When stock solutions are purchased in methanol, working standards should be prepared in methanol. Deviations could lead to phase separation in the working standard causing potential loss of control of PRC loading concentrations. If unsure, preliminary testing should be conducted to make sure that the standard solvent and working solution solvents are miscible. Example calculations for preparation of working standards and the fraction of nonane is provided as **Appendix 1**. The levels of PRCs on PDMS should be similar to the target analytes after uptake from the environment and can be predetermined by using PDMS-water partition coefficients (see PRC spiking calculation in **Appendix 2**). 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. PRCs should be loaded onto fibers targeting a final extract concentration at least 10 times practical quantification limits to ensure detection after losses during exposure.

7.3.3. The spiking solution with PDMS is agitated (approximately 120-130 strokes per minute) using a shaker table for a minimum of 7 days with deuterated PAHs and a minimum of three weeks with C¹³ labeled PCBs before using the PRC loaded PDMS. Longer equilibration times may be required for thicker samplers. Note, with minimal headspace the movement of PDMS during 1D agitation at 130 strokes per minute is not vigorous even at high mixing rates. If fewer than 130 strokes is used, longer PDMS exposure to PRC solution is required. For example, 130 strokes agitation achieves acceptable loading of PCBs in 3 weeks but 60 strokes agitation may require 5 weeks. Alternatively, effective loading of PRCs onto PDMS within 3 weeks can be achieved using a roller mixer with ca. 45-50 rpm. A horizontal placement of the loading vessel in a tumbler and mixing at 45 rpm may also be used but in this case the vessel should allow unobstructed movement of the PDMS to avoid breakage. Overhead tumbling of the vessel is not recommended as PDMS at both ends may break.

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 via the methods in Section 7.7. At least 6 PRC loaded PDMS fibers should be analyzed for initial PRC concentrations.

7.4. Deployment of PDMS in sediment samples

7.4.1. The loaded PDMS fiber (5 cm) is withdrawn from the PRC solution using clean tweezers, rinsed with MilliQ water and liquids blotted on Kimwipes® and allowed to evaporate

- 7.4.2. The 5 cm loaded PDMS fiber is deployed in sediment and the sediment placed on a shaker table if desired. A shaker tool can speed equilibration if the sediment contains sufficient moisture (e.g. above the liquid limit)
- 7.5. Retrieval
- 7.5.1. All surfaces that the PDMS fiber will come into contact with must be covered with clean food grade aluminum foil.
- 7.5.2. 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.
- 7.5.3. All laboratory and field personnel must wear nitrile or powder-free gloves when handling the PDMS fiber.
- 7.5.4. After 21-28 d the vials are removed from the shaker table and the 5 cm PDMS fiber is carefully withdrawn from the sediment. Any adhering sediment, particles, biofilm, or residue is removed from the PDMS fiber using a MilliQ water wetted Kimwipe®. After cleaning, the fiber should be blotted dry prior to segmentation and extraction.
- 7.5.5. Segmentation of the 5 cm PDMS fiber should be performed as quickly as possible to minimize volatilization of more volatile analytes of concern.
- 7.5.6. The 5 cm PDMS fibers are segmented using a ceramic column cutter into 2+2+1 cm lengths.
- 7.6. 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 sufficient for the complete immersion of the PDMS fiber segments. 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.
- 7.6.1. 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
- 7.6.2. The PDMS fiber segments are left in the solvent overnight and stored at -17°C to avoid any losses if employing a volatile solvent (e.g. hexane).
- 7.6.3. Following overnight extraction, vials with inserts containing SPME segments and solvent are sonicated for 1 min to ensure homogenization.
- 7.6.4. 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. Extracts in GC vials without inserts can be vortexed before transfer and IS addition.
- 7.6.5. Priority pollutant PAHs can be analyzed without cleanup steps by EPA Method 8310 or 8270 and PCB congeners by EPA Method 8082/8270 or modified Method 1668. Cleanup steps can be optional when complex matrices are analyzed.

8. QUALITY CONTROL & METHOD PERFORMANCE

- 8.1. PRC loading before deployment: at $t=0$ i.e. after withdrawing PDMS from PRC solution: 6 samples of loaded PDMS (5 cm segments) must be collected from different parts of the PDMS fiber, extracted, and analyzed prior to deployment (see section 7.3.5).
- 8.2. Blanks
 - 8.2.1. Solvent Blanks: Solvent blanks will be analyzed at the time of filling the inserts with designated solvent. If these contain significant levels of contamination, new vials with inserts will be filled with a separate source and the process will be repeated.

10. REFERENCES

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Appendix 1. Suggested Performance Reference Compounds (PRCs) and Surrogate Compounds for ESTCP ER-201735 project.

Candidate PRCs and surrogate compounds suitable for polycyclic aromatic hydrocarbon (PAH) and polychlorinated biphenyl (PCB) determinations when GCMS or GC-MS/MS is the method of detection.

Table 1. PRCs used for loading PDMS in ESTCP ER-201735.

Method 8270		Method 1668
PRCs		PRCs
PCBs #	PAHs	PCBs #
Low Sensitivity	Low Sensitivity	High Sensitivity
C13-37	C13-PHENANTHRENE	C13-28
C13-47	C13-FLUORANTHENE	C13-47
C13-54	C13-CHRYSENE	C13-70
C13-111	C13-INDENO(123-cd)PYRENE	C13-80
C13-138		C13-111
C13-178		C13-141
		C13-182
Example surrogates		Example surrogates
	d10-anthracene	C13-52
	d10-fluoranthene	C13-101
	d12-benz(a)anthracene	C13-138
		C13-153
		C13-180
		C13-209

Appendix 2. 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 30 ng per mL of extract (high resolution) and 150 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 30 ng/mL and approximately 80% of the compound is lost from the PDMS within the exposure timeframe (28 days), the expected concentration in the extract will be 6 ng/mL after 28 d.

Step 2: Indicate the length of PDMS per sample (extract). Here, we have chosen **10 cm** per sample extract and six replications. Therefore, the total amount of PDMS needed for the loading and sampling exercise is **12** pieces of **5 cm** segments resulting in a total fiber length of **60 cm**. Choose a vessel to accommodate the PDMS and water-methanol (80:20) inside without much headspace (here 120 mL amber glass bottle is used). For the PDMS length (**10 cm**) and extract volume (**250 μ L**), calculate the concentration in PDMS. Here, the calculated concentration in PDMS is **1184 ng/mL**. Use the PDMS-water partition coefficients (Ghosh et al., 2014) to calculate the concentration in water (only) at equilibrium ($C_{w,eq}$).

Step 3. Solve for initial solution concentration of PRCs ($C_{initial\ solution}$, ng/mL) that result in the PRC loadings in the PDMS:

$$C_{initial\ solution} = \frac{C_{PDMS} \times L_{fiber} \times V_{PDMS} + C_{w,eq} \times V_W}{V_W} \quad (1)$$

where, C_{PDMS} is the concentration of PRC in PDMS (1184 ng/mL), L_{fiber} is the fiber length (60 cm), V_{PDMS} is the volume of PDMS coating (0.633 μ L/cm). $C_{w,eq}$ [0.00526 ng/mL (C13-28)] is the concentration of PRCs in water at equilibrium and V_W is the volume of water:MeOH (100 mL).

Step 4. Solve for volume of working standard ($V_{working\ stand}$, μ L), that must be added to the water:methanol solution (W:M) (100 ml) for PRC loading on PDMS.

$$V_{working\ stand.} = \frac{C_{initial\ solution} \times V_{W:M}}{C_{Working\ stand.}} \quad (2)$$

The calculated volume of working standard is **18 μ L**. The $C_{initial\ solution}$ concentration of PRCs is 0.455 ng/mL and $C_{working\ stand.}$ is the concentration of PRCs in working standard (2500 ng/ml) in **acetone**. The working standard (2500 ng/ml) is prepared by diluting the stock solution (40000 ng/ml). Here we used 125 μ L of stock solution and diluted with acetone to a final volume of 2000 μ L. Nonane is miscible in acetone. The fraction of nonane in the prepared working standard is 0.06. **Caution should be taken in preparing working standards because of the potential for solvent incompatibility. The solvent ratios employed here lead to homogeneous solutions. Use of different solvents or different solvent amounts may lead to phase separation in the preparation of the working standard or the loading solution which can lead to an inability to achieve targeted PRC concentrations.**

Fiber Parameters															
575	core diameter with PDMS coating (μm)					Water:MeOH (80:20) volume:	100	ml		fiber	5	cm			
500	core diameter without PDMS coating (μm)					extract solvent (μl):	250	μl			12	No of 5 cm segments			
0.001806416	area (m2)					Total fiber spiked:	60	cm			60	total fiber spiked cm			
6.33227E-08	volume (m3)					PDMS volume (μL/cm):	0.633	μL/cm							
3.50543E-05	length (m) i.e. coating thickness					Fiber length per sample extract:	10	cm							
35.05	length (μm) i.e. coating thickness														
CALCULATIONS FOR PRC LOADING --> individual compound spiking															
log K _{PDMS-W} = 0.947*logK _{ow} -0.017 (PCB) ; log K _{PDMS-W} =0.725*logK _{ow} +0.479 (PAH)										Color Legends					
										Volume of solvent for extract					
										Fiber length per sample					
log K _{ow} - Hawker and Connell, 1988 (PCB) and log K _{ow} (SPARC estimates) PAH															
	logK _{ow} (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 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	stock solution in nonane ng/mL	volume of stock solution ml	volume of stock solution μl	
High Res PCBs															
C13-28	5.67	5.35	30	0.0075	1184	0.00526	0.9884	0.455	0.02	18.2	2500	40000	0.125	125	
C13-47	5.85	5.52	30	0.0075	1184	0.00355	0.9922	0.454	0.02	18.1	2500	40000	0.125	125	
C13-70	6.2	5.85	30	0.0075	1184	0.00166	0.9963	0.452	0.02	18.1	2500	40000	0.125	125	
C13-80	6.48	6.12	30	0.0075	1184	0.00090	0.9980	0.451	0.02	18.0	2500	40000	0.125	125	
C13-111	6.76	6.38	30	0.0075	1184	0.00049	0.9989	0.450	0.02	18.0	2500	40000	0.125	125	
C13-141	6.82	6.44	30	0.0075	1184	0.00043	0.9990	0.450	0.02	18.0	2500	40000	0.125	125	
C13-182	7.2	6.80	30	0.0075	1184	0.00019	0.9996	0.450	0.02	18.0	2500	40000	0.125	125	
										total volume of working standard in acetone =		2000 μl			
										fraction of nonane in working std =		0.06 (-)			
										fraction of nonane in water:MeOH spiking solution=		0.00125 (-)			
										Target extract concentration					
										Target concentration on PDMS					
										Volume of working standard					
										Concentration of working standard					

Standard Operating Procedure for the Preparation of Polyethylene (PE) Used for Passive Sampling

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Standard Operating Procedure for the Preparation of Polyethylene (PE)

Used for Passive and Active Sampling of HOCs

SCOPE AND APPLICATION

- 1.1 This method describes a procedure for preparing and handling polyethylene (PE) films that will be cut into strips and deployed to sample hydrophobic organic compounds (HOCs) in environmental media.
- 1.2 This method generates PE that can be deployed for passive or active (i.e., using mixing) sampling of HOCs in atmospheric, aqueous, or sediment-porewater systems.
- 1.3 PE that is prepared by this method is suitable for *ex situ* laboratory or *in situ* field deployment.

SUMMARY OF METHOD

- 2.1 A known mass of low density polyethylene (LDPE) sheet, usually gram quantities, is cleaned by sequentially extracting with methylene chloride, methanol, and ultrapure water in a closed glass vessel.
- 2.2 Clean PE is equilibrated with performance reference compounds (PRCs) dissolved in water or methanol-water (see Appendix 1 for possible PRCs).
- 2.3 PRC-impregnated PE is stored in water or aqueous PRC loading solution in glass vessels until use.
- 2.4 Shortly before deployment, the PE is cut into suitably sized strips and prepared for deployment.
- 2.5 During deployment, the PE is exposed to the environmental medium of concern. HOCs in the medium diffuse into the PE, while PRCs diffuse out.

INTERFERENCES

- 3.1 PE is susceptible to contamination from atmospheric vapors and contact with surfaces (e.g., worker hands), so it must remain in clean sealed vessels until deployment.

APPARATUS AND MATERIALS

- 4.1 Extraction vessels: 1-L glass bottles or screw capped jars (foil-lined lids).
- 4.2 Storage vessels: bottles with glass stoppers or amber jars (foil-lined lids).
- 4.3 Bottle/jar tumbler, shaker table, bottle roller, or equivalent.
- 4.4 Low density polyethylene (LDPE): commercial grade, large sheet at 25 μ m (1 mil) or 51 μ m (2 mil) thickness. The thickness is chosen to be strong enough to withstand stresses during deployment (e.g., insertion into sediment), but thin enough to exchange a significant fraction (e.g., >20%) of its PRCs during the deployment time to be used.
- 4.5 Food grade aluminum foil (solvent cleaned and/or combusted to remove any organic residue from foil production)

- 4.6 Stainless steel forceps
- 4.7 Teflon (or similar non-contaminating material) cutting board

REAGENTS

- 5.1 Methylene chloride, CH_2Cl_2 , pesticide grade or equivalent
- 5.2 Methanol, CH_3OH , pesticide grade or equivalent
- 5.3 Organic-free reagent water (as defined in SW-846 Chapter 1)
- 5.4 Research grade PRCs certified >98+% pure.

Note: Specific standard materials, concentrations, solvents, and solvent purity requirements must be determined based upon the target HOCs of concern and their likely concentrations in any particular application.

PRESERVATION AND HANDLING

- 6.1 Clean PE should be stored in clean, sealed, glass vessels.
- 6.2 PE loaded with PRCs should be stored in sealed glass containers that contain either:
 - (a) a few mL of organic-free reagent water added to maintain 100% relative humidity within the storage vessels (minimizing sorptive losses of PRCs to glass vessel walls),
 - (b) completely filled with organic-free reagent water (common after loading from aqueous methanol solutions), or
 - (c) still filled with the aqueous PRC-loading solution (preferred, but may lead to shipping concerns).
- 6.3 Laboratory and field personnel should wear nitrile or latex gloves whenever handling clean PE.
- 6.4 Methylene chloride-rinsed, stainless steel forceps and scissors are used when manipulation of clean PE is required.
- 6.5 Methylene chloride-rinsed, aluminum foil is used to cover any surface that clean PE may encounter.

PROCEDURE

- 7.1 Polyethylene Cleaning Procedure: LDPE is purchased from hardware/painting stores in large sheets ('dropcloth or plastic tarp' material) with thickness of 25 μm (1 mil) or 51 μm (2 mil), depending on the user's need for strength (choose thicker) and desire to use short deployment times (use thinner). The sheet is cut into strips sized for the environment and deployment apparatus to be used. An organic solvent cleaning sequence is then used to prepare the PE. This process ensures that extractable oligomers, plasticizers, and contaminating organic chemicals are removed from the PE prior to use. All extractions are performed sequentially in the same container.
 - 7.1.1 Methylene chloride is placed into the extraction vessel, and the PE strips are immersed in the container for 24 hours to enable time for diffusive transfers

out of the PE. The initial methylene chloride extract is discarded and a second methylene chloride extraction is performed for 24 hours. The second methylene chloride extract is discarded and replaced by methanol to remove methylene chloride from the PE. Methanol immersion is also done for 24 hours. The initial methanol extract is discarded and followed by a second methanol soak for 24 hours. Finally, the second methanol extract is discarded and the PE undergoes three 24-hour soaks with organic-free reagent water (within the same extraction vessel) to remove residual methanol from the PE.

7.1.2 The cleaned PE is stored in organic-free reagent water in the extraction vessel until further processing.

7.2 Polyethylene Preparation with Performance Recovery Compounds (PRCs): PRCs are loaded into the clean PE, prior to its field deployment, by utilizing either aqueous (Fernandez et al. 2009) or 80:20 methanol:water equilibrations (Booij et al., 2002). Depending on the hydrophobic organic compounds of interest, PRCs should be chosen to mimic mass transfer phenomena governing exchanges during field deployments. It is important to avoid adding PRCs that the analytical laboratory already uses as surrogate recovery, cleanup, or injection standards. PRC loading is performed by placing the PE in pre-cleaned glass vessels containing known PRC solutions made up in organic-free reagent water with or without pesticide-grade methanol. (The methanol swells the PE, enabling faster PRC uptake; but use of methanol also requires post PRC-impregnation removal of the methanol from the PE by soaking in water.) The PE user should load the PE with levels of PRCs that are a little greater than the concentrations of target HOCs that are expected to be accumulated from the environment, thereby facilitating the eventual chemical analyses. The PRC concentrations loaded in the PE can be found using each PRC's PE-water partition coefficient (e.g., Burgess et al. 2017) and the ratio of the PE mass to the aqueous solution volume of the loading solution. For example, one may set out to load 1 g of PE using an aqueous solution containing 10 ug of a PRC in a liter of water, so the ratio of PE to water, r_{PEw} , is 1/1000. If that PRC's K_{PEw} is 10^5 (ug/g_{PE})/(ug/mL_w), then one finds the fraction of that PRC that ends up in the 1 g of PE as:

$$\begin{aligned} f_{PE} &= (r_{PEw})(K_{PEw}) / (1 + r_{PEw}K_{PEw}) \\ &= (1 \text{ g}_{PE} / 1000 \text{ mL}_w)(10^5 \text{ mL}_w / \text{g}_{PE}) / [1 + (1 \text{ g}_{PE} / 1000 \text{ mL}_w)(10^5 \text{ mL}_w / \text{g}_{PE})] \\ &= 0.99 \end{aligned}$$

or 9.9 ug of the PRC is in the PE at equilibrium (i.e., 9.9 ug_{PRC}/g_{PE})

and the water concentration has dropped to 0.1 ug_{PRC} / L_w.

7.3 Sufficient PRC equilibration time during this PE preparation step is necessary to

ensure uniform PE loading across the entire PE thickness; hence thicker PE sheet is more robust for field use, but takes longer to load with PRCs. If previously untested PRCs are used, a time course study should be used to confirm PE-solution equilibration of the PRCs (e.g., Booij et al. 2002).

7.3.1 Isotopically labeled compounds are useful PRCs, surrogate recovery standards, and injection standards when Gas Chromatography-Mass Spectrometry (GCMS) is the method of separation and detection. For example, deuterated and C13-labeled polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) are effective methodological standards for PE passive sampling. If PAHs are the target contaminants, one subset of compounds, distributed across the range of PAHs to be assessed (e.g., d10-phenanthrene, d10-pyrene, and d12-chrysene), should be used as PRCs, while another set (e.g., d10-anthracene, d10-fluoranthene, and d12-benz(a)anthracene) is used as surrogate (recovery) compounds during later analysis of laboratory or field-deployed PE. Finally, still another set of compounds (e.g., d10-acenaphthene, d14-*m*-terphenyl, and d12-perylene) should be used as injection standards. Similar sets of labeled compounds should be used for other compound classes (see Appendix 1). Note: if PE samples are eventually to be analyzed at a contract laboratory, PRC choices must be made so as not to conflict with recovery and injection standards used by that laboratory.

7.3.2 As subsequent analysis (e.g., GCMS) is best achieved with both PRCs and target HOCs present at like concentrations in the PE extracts, the optimal concentration level of the PRC loaded into the PE is dependent on the environment in which the PE is to be deployed. For example, if a target HOC is expected to occur in the water or pore water near 1 ng/L levels, one can use that compound's LDPE-water partition coefficient (e.g., Fernandez et al., 2009; Lohmann, 2012; Burgess et al. 2017) to estimate the expected levels in the PE after deployment:

$$\text{Concentration in PE (ng/kg)} \sim K_{PE-water} * \text{concentration in (pore)water (ng/L)}$$

For example, if the $K_{PE-water}$ for the target HOC of interest is 10^5 (L/kg), then the concentration of the target HOC in the PE will approach 100 ug/kg as it equilibrates with water at 1 ng/L. Based on this estimate, the PRCs are loaded into the PE at slightly higher (e.g., factor of 2) concentrations since some fraction of these will be lost from the PE during deployment. Appendix 2 shows a typical calculation used to design a PRC-containing MeOH:H₂O solution of PCBs suited to loading an 0.82 g mass of PE (i.e., one or more PE pieces summing to 0.82 g) to achieve about 100 ug of each PRC per kg of PE.

7.3.3 Aqueous PRC Loading: A solvent-cleaned and dried glass container is filled with ultrapure water that has been spiked with known concentrations of PRCs (e.g., based on calculations like those shown in Appendix 2). A known mass of pre-cleaned PE is then added and weighted to insure complete PE submersion

and full exposure of PE surfaces to the solution. The vessel is agitated to remove any air pockets/bubbles adhering to the submerged PE. Equilibration times vary for different PRC/PE thickness combinations and the PE-water phase ratio. For PAHs and PCBs, one should use at least 30 days to insure homogeneous distributions of the PRCs throughout the entire thickness of the PE film unless faster equilibration has been confirmed with PRC/PE specific time-course testing of PRC concentrations in the PE or by showing that concentrations of PRCs are the same for films of different thicknesses, but the same masses. Generally, PE is stored in the aqueous PRC solution until that PE is to be deployed.

- 7.3.4 **Methanol-Aided PRC Loading:** A solvent-cleaned and dried glass container is filled with a mixture of pesticide grade methanol and ultrapure water (e.g., Booij et al. 2002) that has been spiked with known concentrations of PRCs (e.g., see calculations in Appendix 2).

Commonly, ^{13}C -labelled PRCs are obtained dissolved in solvents like nonane. If one adds too much of a solvent like nonane to 80:20 methanol:water (e.g., >10 mL/L), then one will see nonane floating on the PRC loading solution or a cloudy solution if shaking is employed. When PE strips are added to such a multiphase loading solution, the immiscible solvent is likely to (a) accumulate in the PE and change the polymer's affinity for the PRCs and/or (b) remain as a separate phase competing for the PRCs (note that even 1 mL of separate phase nonane is virtually the same volume as 1 g of PE strips, perhaps causing comparable partitioning of the PRCs into this solvent and the LDPE strips.) Consequently, one should be sure to look for the occurrence of a separate solvent phase when spiking the PRC loading solution. For the particular case of nonane, adding about 2 mL nonane per liter of the methanol:water loading solution appears to be acceptable. Spiking volumes of other solvents (e.g., hexane) should be tested for their miscibility with the PRC loading solution before use.

After preparing the loading solution, a known mass of pre-cleaned PE is then added and weighted down to insure complete submersion and full exposure of the PE surfaces to the solution. The vessel should be agitated to remove any bubbles/air pockets adhering to the submerged PE. Equilibration times vary for different PRC/PE thickness combinations and the PE-solvent phase ratio, but typically this step is completed within 7 days since methanol swells the PE and thereby speeds PRC diffusion into the polymer sheet (Booij et al., 2002). Generally, the PE is stored in the PRC solution until shortly before it is to be deployed. Before deployment, the PRC-loaded PE is rinsed with ultrapure water, and then it is soaked in ultrapure water for 24 h to remove most of the methanol from the PE, while leaving the more hydrophobic PRCs almost completely in the PE. This methanol leaching step is repeated twice to insure complete methanol removal.

QUALITY CONTROL

- 8.1 **PRC Loading Validation:** At least six representative samples of prepared PE should be collected from different parts of the PRC-loaded PE (e.g., 1 cm x 10 cm x 25 μm pieces weighing about 25 mg each), extracted, and analyzed prior to field deployment

to validate that the PRC concentrations are consistent with their intended loadings and these PRCs have uniform concentrations in a batch of PE.

- 8.2 Target HOC Blanks: Subsamples of prepared PE, commensurate in size with the planned environmental PE samples (e.g., 10 cm wide by 5 cm long by 25 μ m thick and therefore weighing about 120 mg), should be collected, extracted, and analyzed prior to field deployment to demonstrate that other substances have not contaminated the PE which would contribute to interfering background for the target HOCs analysis using the intended target analyte detection approach.

METHOD PERFORMANCE

- 9.1 PRC data, obtained from PE samples collected from >six pieces of the prepared PE, should be consistent within about $\pm 10\%$ (i.e., $100 \times \text{standard deviation} / \text{mean}$).
- 9.2 Target HOC concentrations should be undetectable in the prepared PE at the levels of interest. For example, assuming a target HOC with a level of interest at $10 \text{ pg/L} = 10^{-5} \text{ ng/mL}_{\text{water}}$ and having $K_{PE \text{ water}} = 10^5 \text{ mL}_{\text{water}}/\text{g PE}$, requires background below:

$$(\text{level of interest}) \times K_{LDPE \text{ water}} = 1 \text{ ng HOC /g PE.}$$

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Appendix 1. Suggested Performance Reference Compounds (PRCs), Surrogate Compounds (Recovery Standards), and Injection Standards.

A. PRCs, suitable for polycyclic aromatic hydrocarbon (PAH) determinations when Gas Chromatography-Mass Spectrometry (GCMS) is the preferred method of detection, include, but are not restricted to, deuterated PAH compounds. One subset should be used as PRCs, while reserving others for use as surrogate (recovery) compounds. Still other compounds such as terphenyl can be used as injection standards.

Targets: PAHs Method: EPA 8270d with GCMS-SIM				
PRCs	13C6-phenanthrene	13C6-fluoranthene	13C6-chrysene	13C6-indeno(1,2,3-cd)pyrene
Surrogates	d10-anthracene	d10-fluoranthene	d12-benz(a)anthracene	d12-perylene
Injection Standards	d10-acenaphthene	d14- <i>m</i> -terphenyl		

B. PRCs and surrogate compounds suitable for polychlorinated biphenyl (PCB) determinations when GCMS is the preferred method of detection include, but are not restricted to, ¹³C-labeled or deuterated PCB congeners. One subset, for example including a tri-, tetra-, penta-, hexa-, and heptachloro-biphenyl, can be used as PRCs while reserving different tri-, tetra-, penta-, hexa-, and heptachloro-biphenyl congeners to serve as surrogate compounds (see below) and injection standards.

Targets: PCBs Method: EPA 8270d with GCMS-SIM						
PRCs	¹³ C PCB-37	¹³ C PCB-47	¹³ C PCB-54	¹³ C PCB-111	¹³ C PCB-138	¹³ C PCB-178
log <i>K_{ow}</i>	5.68	5.87	5.32	6.49	6.71	6.98
number Cl's	3	4	4	5	6	7
Surrogates	¹³ C PCB-3	¹³ C PCB-15	¹³ C PCB-28	¹³ C PCB-52	¹³ C PCB-118	¹³ C PCB-153
number Cl's	1	2	3	4	5	6
Surrogates		¹³ C PCB-180	¹³ C PCB-194	¹³ C PCB-208	¹³ C PCB-209	
number Cl's		7	8	9	10	
Injection Standards	¹³ C PCB-19	¹³ C PCB-105	¹³ C PCB-170			

C. When analyzing for organochlorine pesticides such as DDT using GCMS, ¹³C labeled compounds can serve as PRCs and surrogate standards. Since DDT has been shown to degrade to form DDE or DDD in certain situations, one should use the 4,4'- isomer of DDT and the 2,4'- isomers of DDE and DDD as PRCs to allow appearance of ¹³C-labelled 4,4'-DDE or 4,4'-DDD to be interpreted as arising from reaction of the DDT PRC during the deployment. Deuterated or ¹³C labeled PCBs can be used as surrogate (recovery) and injection standards.

Targets: DDTs Method: GCMS Detection Limit ~ 200 pg / 100 mg PE			
PRCs	¹³ C 2,4'-DDE	¹³ C 2,4'-DDD	¹³ C 4,4'-DDT
Surrogates	¹³ C-PCB111	¹³ C-PCB153	¹³ C 2,4'-DDT
Injection Standards	d6 PCB 77	¹³ C PCB 105	¹³ C PCB 167

Appendix 2. Example of spreadsheet used to design a PRC solution needed to impregnate PE for PCB sampling.

Step 1: Find/estimate PE-spiking solvent partition coefficients for PRCs in solvents of interest (see spreadsheet below). Here 80:20 MeOH:H₂O values from Booiij et al. (2002) are used to develop a correlation with K_{ow} values from the literature (Hawker and Connell, 1988); this relation is then used to estimate K_{PE-(80:20)m:w} values for other PCB congeners partitioning between PE and an 80:20 MeOH:water solution.

Step 2: Choose the size of PE needed for the sampling exercise (here a single 1 mil-thick strip of 5 cm width and 68 cm length) and solve for the PE mass (here 0.82 g). Choose a vessel which is large enough to fit the PE inside without extensive PE-PE surface contact, but small enough so that unacceptably expensive masses of the labeled PRCs are not used (here 125 mL ground glass stopped flask). For this PE mass and solution volume, use the PE-solution partition coefficients from step 1 to solve for the fractions of each PRC that will be in the PE at equilibrium using:

$$\text{fraction in PE} = 1 - (1 / (1 + \text{Mass}_{\text{PE}} * K_{\text{PE-solution}} / \text{Volume}_{\text{solution}})) \quad \text{Eq. 1}$$

(e.g., 5.8% for congener #52)

Step 3. Solve for spiking solution concentrations of PRCs that result in desired PRC loadings in the PE (here 100 ng/g_{PE}) using:

$$C_{\text{initial spiking solution}} = C_{\text{desired in PE}} * \text{Mass}_{\text{PE}} / \text{fraction in PE} / \text{Volume}_{\text{solution}} \quad \text{Eq. 2}$$

(e.g., here we find we need about 11.3 ng congener #52 per mL to achieve 100 ng/g PE; this is concentration of the spiking solution that the investigator must make up to prepare PE for subsequent sampling at sites where it is expected that the (pore)water will cause the PE to accumulate about 10 to 100 ng of target PCBs/g_{PE}). Note that the values vary from PRC to PRC, so one might choose to load from a mean solution concentration (*ca.* 5 ng/mL) if the PRCs are supplied at the same concentrations in a stock solution.

PE is stored in the PRC loading solution until shortly before passive sampling use.

Step 4. If spiking solutions contain organic co-solvents like MeOH, this MeOH must be leached out of the PE before the polymer film can be used for passive sampling. To insure that MeOH leaching will not substantially change PRC loading, one may calculate whether substantial fractions of the PRCs will be lost in subsequent steps required to leach the MeOH from the PE. Since the leaching steps involve use of H₂O (with only a little MeOH from the PE), use the PE-water partition coefficients. For PCBs, these coefficients are derived from a linear free energy relationship (LFER) found in the review by Lohmann (2012). With these values, we can solve for the fractional losses of individual PRCs to each batch of the leachate contained in 1000 mL ground glass stoppered flasks, using:

$$\text{fraction of each PRC remaining in PE after a single leach step} = 1 - (1 / (1 + K_{\text{PE-H}_2\text{O}} * \text{Mass}_{\text{PE}} / \text{Volume}_{\text{H}_2\text{O}})) \quad \text{Eq. 3}$$

For example, in the case of congener #52, one finds 99.66% of the PRC remains in the PE after the first leach (see below). Two additional leaches lower this to 99.32% and 98.98%, respectively. More hydrophobic congeners are leached even less in this case.

Example spreadsheet calculation for spiking PCB PRCs into LDPE from a 80:20 methanol-water solution.														
step 1						step 2		step 3		step 4				
								Solution concentration		fraction of PRC left in PE after				
						for PE mass (g) 0.82		(ng/mL) in in order to get		each water soak to remove MeOH				
	Training data for estimation of $K_{PE-(80:20)m:w}$		potential 13C-labelled PCBs to use as PRCs		use correlation to estimate partition coeff'	Volume of MeOH:water (mL) 125		100 ng/g PE			estim log K_{PE-w}	1st leach (Eq. 3)	2nd leach (Eq. 3)	3rd leach (Eq. 3)
PCB congener	log KPE- MeOH:water (ref 1)	log Kow (ref 2)	congener	log Kow (ref 2)	log K_{PE-} (80:20)m:w	fraction of each PRC in PE at equilib' (Eq. 1)		ng/mL MeOH:H2O (Eq. 2)		log Kpew = 1.14*log Kow-1.14 (ref 3)	1000 mL water	1000	1000 mL water	
4	0.20	4.65	52	5.84	0.97	5.8%		11.3		5.52	0.997	0.993	0.990	
29	1.05	5.6	101	6.38	1.26	10.7%		6.1		6.13	minimal leaching back into water			
155	1.29	6.41	153	6.92	1.55	18.8%		3.5		6.75	1.000			
204	1.67	7.3	180	7.36	1.78	28.4%		2.3		7.25	1.000			
			28	5.67	0.88	4.8%		13.8		5.32	0.995	0.990	0.985	
			47	5.85	0.98	5.9%		11.2		5.53	minimal leaching back into water			
			111	6.76	1.46	16.0%		4.1		6.57	1.000			
			153	6.92	1.55	18.8%		3.5		6.75	1.000			
			178	7.14	1.66	23.3%		2.8		7.00	1.000			
use to find following correlation:														
log $K_{PE-(80:20)m:w}$ = 0.532 (± 0.094) * log K_{ow} (Hawker) - 2.133 (± 0.57)						PE mass		5.3		geom ave				
N = 4, R2 = 0.94, S.E. 0.18						number of strips		1						
						PE density (g/cm3)		0.95						
1. Booij, K, Smedes, F., van Weerlee, E.M., Chemosphere 2002, 46, 1157-1161.						PE thickenss (cm)		0.00254		for 1 mil sheet				
2. Hawker DW and Connell DW. 1988. Environ. Sci. Technol. 22: 382-387.						PE length (cm)		68						
3. Lohmann, R. Environ. Sci. & Technol.; 2012, 46, 606–618.						PE width (cm)		5						
						length*width*thickness *number of strips*density								
						mass of PE (g) 0.82								

Standard Operating Procedure for the Extraction and Analysis of Polyethylene (PE) Used in Polyethylene Devices (PEDs)

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Standard Operating Procedure for the Extraction and Analysis of Polyethylene (PE) Used in Polyethylene Devices (PEDs)

SCOPE AND APPLICATION

- 1.4 This method describes procedures for chemical analysis of contaminants contained in polyethylene (PE) that has been deployed in passive samplers used to assess hydrophobic organic compounds (HOCs) in environmental media.
- 1.5 This procedure generates extracts suitable for High Resolution Gas Chromatography/Mass Spectrometry (GCMS) analysis.
- 1.6 This extraction procedure is applicable to PE used in laboratory (ex situ) - or field (in situ)-exposed usage.
- 1.4 Procedures for loading PE with PRCs are discussed in a companion SOP, “Standard Operating Procedure for the Preparation of Polyethylene (PE) Used for Passive Sampling”

SUMMARY OF METHOD

- 2.1 Upon recovery from the field, the PE, while still in the deployment device (e.g., stainless steel mesh or aluminum frame), should be carefully cleaned (e.g., remove adhering sediment) and then cut into appropriate lengths (e.g., to obtain replicates or to acquire sections exposed to varying depths into a sediment bed). The PE pieces, usually 10 to 100 milligram quantities, are placed in pre-cleaned, amber, glass vials with a few drops of water for shipping. Once received by the analytical laboratory, each sample is spiked with Surrogate standards (to assess analyte recoveries) and submerged in a suitable solvent (e.g., methylene chloride) for at least 12 hours. The extract is quantitatively transferred to a large vessel suited for solvent evaporation, and then the PE is re-extracted two more times with methylene chloride, with the extracts combined for evaporative concentration and eventual GCMS (or suitable) instrumental analysis. After extraction, the PE is air-dried and weighed.
- 2.2 A shaker table or other suitable system is recommended for the extractions to facilitate PE-solvent contact.

INTERFERENCES

- 3.1 PE is susceptible to contamination from atmospheric and surficial sources, and so it must be handled using clean techniques.
- 3.2 While the sediment solids, biofilms, and inorganic precipitates on PE surfaces does not prevent HOC accumulation in the PE during in situ deployment, these coatings can substantially complicate subsequent chemical analysis. Careful removal of adhering sediment or surface growths via wiping with a water-wetted Kimwipe® may be necessary. Surface coatings of organic films on PE (e.g., oil or tar residues) can be

removed without compromising the sample by using solvent-saturated wipes (<minute contact times) followed by immediate Surrogate standard addition and solvent extraction.

APPARATUS AND MATERIALS

- 4.1 Extraction vessels: amber glass vials (foil-lined lids)
- 4.2 Concentrating vessels: 100 mL glass, pear-shaped flask with glass stopper; 250 mL glass, round-bottom flask with glass stopper or equivalent
- 4.3 Bottle/jar tumbler, shaker table, bottle roller or equivalent
- 4.4 Analytical balance - capable of weighing to 0.1 mg (i.e., small value relative to samplers weights that are typically between 10 and 100 mg).
- 4.5 Food-grade aluminum foil
- 4.6 Stainless steel forceps
- 4.7 Single-edge razor blades
- 4.8 Teflon (or similar non-contaminating material) cutting board
- 4.9 Glass transfer pipettes
- 4.10 Kimberly-Clark Kimwipe® or equivalent

REAGENTS

- 5.1 Methylene chloride, CH₂Cl₂, pesticide grade or equivalent (other solvent suited to analytes of interest).
- 5.2 Hexane, C₆H₁₄, pesticide grade or equivalent
- 5.3 Organic-free reagent water (as defined in SW-846 Chapter One)
- 5.4 Research grade surrogate and injection standard compounds certified >98+% pure or equivalent.

PREPARATION AND HANDLING

- 6.1 Upon recovery and return to a clean working environment, the PE should be surface cleaned prior to any cutting or extraction. The PE surface should be wiped and rinsed free of surface particles and coatings as much as possible. This may include briefly (< minute) wiping with a hexane-soaked Kimwipe® (or equivalent) to remove oily or tarry exterior staining. If water wet, the PE surface should be blotted dry with a clean wipe.
- 6.2 Laboratory and field personnel should wear nitrile or latex gloves whenever handling PE to avoid cross-contaminating the PE.
- 6.3 Methylene chloride (pesticide grade) rinsed, stainless steel forceps and scissors are used when manipulation of PE is required.
- 6.4 Clean aluminum foil is used to cover any surface that PE may encounter.

PROCEDURE

- 7.1 Solvent Extraction: Laboratory and/or field blank and field-exposed PE is spiked with known quantities of surrogate compounds to assess analytical recoveries and extracted using organic solvents prior to analysis by GC/MS.
- 7.2 The PE is inspected for surface biofilms, particles, mud, or oily coatings. Biofilm mass should be removed as much as possible by using a clean wipe followed by a rinse with organic-free reagent water. Particles and sedimentary debris are removed by rinsing with organic-free reagent water and careful surface scraping if necessary to remove adhered/imbedded material. Oily coatings (e.g., coal tar staining or hydrocarbon slicks) are removed by soaking clean wipes in hexane and using forceps to hold and wipe both PE surfaces. This is not an exhaustive extraction and should be done quickly (<minute) and immediately prior to immersion in solvent. PE surfaces are blotted dry if water wet.
- 7.3 The PE is transferred to a pre-cleaned amber vial (size determined by dimensions of PE, typically 15-40 mL). Vial must be large enough for complete immersion of PE without excessive PE folding.
- 7.4 Known masses of surrogate compounds (Appendix 1) in a methylene chloride- compatible solvent are added to the vial. Typical additions are: 2.5-20 ng for aqueous samples; 50-250 ng for sediment samples, depending on target HOCs and their expected concentrations in the PE.
- 7.5 Methylene chloride is added to the vial to completely submerge the PE for a period of at least 12 hours.
- 7.6 The extract is transferred to a pre-cleaned glass concentration vessel. A second aliquot of methylene chloride is added to the extraction vial and agitated for >10 minutes. This step is repeated two more times.
- 7.7 After the final extract transfer, the PE is dried in air dry in the extraction vial and then weighed on an analytical balance until a consistent PE mass is obtained. This result is used to calculate the final target HOC concentrations measured in the PE sampler in units of HOC mass per PE mass.
- 7.8 Extracts are concentrated using rotary evaporation (or equivalent) down to suitable volumes for GCMS analysis; the resultant concentrated extracts are transferred to smaller vials (e.g., for autosamplers) according to standard laboratory practices. Before analysis, appropriate injection standards are added to the final extracts to allow for evaluation of the total volume of extract analyzed (Appendix 1).
 - a. Typical final extract volumes are:
 - b. 50-250 μ L for water column-exposed PE
 - c. 1-4 mL for contaminated sediment bed-exposed PE

QUALITY CONTROL

- 8.1 Method blanks, field blanks, matrix spikes, and/or replicate samples should be subjected to exactly the same analytical procedures as those used on field/lab-exposed PE samples.

8.2 QA/QC metrics, that are specific to the type of target HOCs of interest and the analytical methods used to quantify them, should be applied. Typical values for targets, like PAHs and PCBs, that are analyzed by capillary gas chromatography-low resolution mass spectrometry, in which picogram/uL detection is common, are:

8.2.1 Freshly prepared polyethylene and trip blanks: <0.1 ng HOC / g PE

Freshly cleaned PE samples, and samples of PE that traveled to and from the field site ("trip blank"), should have no significant peaks where PRCs, surrogate standards, injection standards, and target analytes elute.

8.2.2 PRC-loaded polyethylene reproducibility ($\pm 1\sigma/\text{mean}$, N=6): <10%

Individual batches of PE loaded with PRCs should exhibit reproducible PRC concentrations in the PE before deployment.

:

8.2.3 Recoveries of Surrogate Standards: >70% to < 120%

Surrogate standards should be recovered from PE samples at nearly 100%, plus or minus analytical precision. An exception may be relatively volatile compounds (e.g., mono-, di-chlorobiphenyls, naphthalene) that may be significantly lost when extracts are evaporated (e.g., recovery down to 60%).

8.2.4 Precision of replicate PE extract analyses (N $\geq$ 3): <25%.

The reproducibility of all analytes (injection standards, surrogate standards, PRCs, and target compounds) determined with multiple instrumental analyses of the same PE sample extract, even run on different dates, should fall within suitably narrow bounds.

8.2.5 Detection limits using PE samples: ≤ 1 ng / g PE

Assuming 100 mg PE samples and 100 uL final extract volumes, target analytes, such as PAHs and PCBs, analyzed by GCMS (or methods with like sensitivity) should have <ppb detection limits.

METHOD PERFORMANCE

- 9.1 The method performance is assessed by determining the recovery and reproducibility in analyzing surrogate compounds (Appendix 1). All other lab-specific QA/QC metrics should be adhered to.
- 9.2 Successful PE deployment is achieved when significant (>method precision) losses of PRCs occurred, allowing one to use their behavior to adjust target compound levels in the PE up to equilibrium concentrations (Fernandez et al. 2009; Tcaciuc et al. 2014).

REFERENCES

- Fernandez L.A., Harvey, C.F., and Gschwend, P.M. Using performance reference compounds in polyethylene passive samplers to deduce sediment pore water concentrations for numerous target chemicals. *Environ. Sci. Technol.*, 43, 8888-8894, 2009.
- Tcaciuc, AP, JN Apell, and PM Gschwend. " Passive Sampler PRC Calculation Software and User's Guide". Available at <https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Sediments/ER-200915>. July 2014.

Appendix 1 Suggested Performance Reference Compounds (PRCs), Surrogate Compounds (Recovery Standards), and Injection Standards. The laboratory preparing the PE must coordinate PRC choices with the laboratory doing the PE analyses to avoid conflicting uses.

A. PRCs, suitable for polycyclic aromatic hydrocarbon (PAH) determinations when Capillary Gas Chromatography-Mass Spectrometry (GCMS) is used for analysis include, but are not restricted to, deuterated PAHs. One subset should be used as PRCs, while reserving others for use as surrogate (recovery) and injection standards. Unlabeled compounds such as terphenyl can be used as injection standards if they are readily resolved from the other analytes.

Targets: PAHs Method: GCMS Detection Limit ~ 100 pg / 100 mg PE			
PRCs	¹³ C6-phenanthrene, ¹³ C6-fluoranthene, ¹³ C6-chrysene, ¹³ C6-indeno(1,2,3-cd)pyrene		
Surrogates	d10-anthracene	d10-fluoranthene	d12-benz(a)anthracene
Injection Standards	d10-acenaphthene	d14- <i>m</i> -terphenyl	d12-perylene

B. PRCs and surrogate compounds suitable for polychlorinated biphenyl (PCB) determinations when GCMS is the method separation and detection include, but are not restricted to, ¹³C-labeled or deuterated PCB congeners. One subset, for example including tri-, tetra-, penta-, hexa-, and heptachloro-biphenyls, can be used as PRCs while reserving different tri-, tetra-, penta-, hexa-, and heptachloro-biphenyl congeners to serve as surrogate compounds. Still other compounds such as deuterated PAHs or rare PCBs (not contained in Aroclor/Clophan mixtures such as: PCB-39, PCB-55, PCB-104, PCB-150 and PCB-188) can be used as injection standards.

Targets: PCBs Method: GCMS Detection Limit ~ 100 pg / 100 mg PE	
PRCs	¹³ C labelled PCB congeners: 37, 47, 54, 111, 138, 178
Surrogates	¹³ C labelled PCB congeners: 3, 15, 28, 52, 118, 153, 180, 194, 208, 209
Injection Standards	¹³ C labelled PCB congeners: 19, 105, 170

C. When analyzing for organochlorine pesticides such as DDT using GCMS, ¹³C labeled compounds can serve as PRCs. However, since DDT has been seen to degrade to form DDE or DDD in certain situations, one should use the 4,4'- isomer of DDT and the 2,4'-isomers of DDE and DDD as PRCs to allow appearance of ¹³C-labelled 4,4'-DDE or 4,4'-DDD to be interpreted as arising from reaction the DDT PRC during the deployment. Deuterated or ¹³C labeled PCBs can be used as surrogate (recovery) and injection standards.

Targets: DDTs Method: GCMS Detection Limit ~ 200 pg / 100 mg PE			
PRCs	¹³ C 2,4'-DDE	¹³ C 2,4'-DDD	¹³ C 4,4'-DDT
Surrogates	¹³ C-PCB111	¹³ C-PCB153	¹³ C PCB 178
Injection Standards	d6 PCB 77	¹³ C PCB 105	¹³ C PCB 167

SOP QUESTIONS FROM COMMERCIAL LABORATORIES AND ANSWERS FROM THE POLYMERIC SAMPLER EXPERTS

Question 1: Am I correct in assuming that the sections of the SOP that refer to surrogates or injection standards are not applicable? Each lab is free to use their current SOP listed compounds to support these needs correct?

Response: Yes. Each lab is free to adapt the SOP to the analytical method being used provided the modifications do not interfere with use of the Performance Reference Compounds (PRCs) specified. All labs must correct the polymeric sampler extract concentrations using surrogate recoveries. Use of standardized PRCs and consistent correction for surrogate recoveries is required to ensure different labs that utilize these SOPs produce comparable data.

Question 2: Are the QA and method performance sections applicable? Aren't these SOPs supposed to prescribe sampler loading and extraction procedures – giving the laboratories flexibility to use different analytical methods?

Response: Yes, subject to restrictions noted in response to Question 1 above.

Question 3: Is there flexibility in the methods for labs to make minor changes? For example, in section 7.3.2 of the SPME SOP a volume of 200mL is specified for the spiking solution. Could other volumes be used so long as the 80:20 water/methanol ratio specified in the method is maintained?

Response: Flexibility is allowed within acceptable ranges specified in the EPA method being used. Certainly larger volumes can be used. Here an example with 200 mL is given for a small PDMS segment i.e. 5 cm and small sampling efforts. For PDMS segments of 30 cm a large vessel volume is recommended.

Question 4: Section 7.3.3 of the SPME SOP mentions agitating the PDMS rod at a rate of 130 strokes per minute, which seems high. I would be concerned about the fiber being physically affected by this robust rate. What if my agitating equipment only goes up to 60 strokes per minute?

Response: The vessel should be filled with PRC solution with minimal headspace; in such conditions the movement of PDMS during 1D agitation is very limited, even at high mixing rates (e.g 120 strokes per minute). With an overhead tumbler the risk of PDMS breakage is high so this approach is not recommended.

If fewer than 130 strokes is used, longer PDMS exposure to PRC solution is required. For example, 130 strokes agitation could achieve acceptable loading in 4 weeks but 60 strokes agitation may require 6 weeks.

Question 5: Section 7.3.3 of the SPME SOP states a minimum of 21 days is required for the loading of PCB PRCs. I'm not that familiar with SPME loading but the time frame seems long to me given 7 days is specified for PE?

Response: A key reason the loading time for PE is shorter is because the SOP calls for more solvent in the PRC loading solution, which effectively "opens up" the PE polymer for faster diffusive loading. The PE SOP calls for a 80/20 methanol/water solution whereas the PDMS SOP calls for a 20/80 solvent/water solution. It may be possible to increase the solvent ratio to achieve faster PDMS PRC loading; however, a 21 day loading and 20/80 solvent/water mix is

recommended based on experience. A secondary reason for slower PDMS loading with PRCs is that the PRCs enter the polymer from one side only (diffusion from outside of the PDMS cylinder inward toward the glass core) whereas diffusion into the PE strip occurs from both sides.

Question 6: Section 5.3 of the PE Preparation and Analysis SOP states that surrogates and injection standards must be >98% pure. While we strive to use the purest standards available (within reasonable cost constraints) our corporate QA policy allows us to use >96% purity reagents in this area.

Response: Standards >98% purity are recommended. If standards of lesser purity are used, blanks must be carefully monitored and impurities must be accounted in data reporting and interpretation.

Question 7: Regarding “SOP PE (prep)- 4.1 Extraction vessels:” – are clear or amber jars preferred?

Response: Amber.

Question 8: Regarding “SOP PE (prep) - 7.1 Polyethylene Cleaning Procedures:” - should a differential weight be determined on uncleaned vs. cleaned PE to determine density?

Response: We recommend weighing the polymer after all of the following steps have been completed.

- Sampler retrieval from the sediment exposure
- Gentle sampler cleaning to remove any biofilms etc. (see response to 16 below)
- Sampler extraction in solvent
- Sampler drying to remove solvent

When the sampler is extracted, it “soaks up” solvent and therefore is heavier immediately after extraction than it is normally. We often set the extracted samplers to evaporate in a fume hood for a day or so, periodically weighing the sampler to ensure the weight has stabilized and all solvent has evaporated. We use the final stabilized weight in subsequent computations.

Question 9: Regarding “SOP PE (prep) - 8.1 PRC Loading Validation:” - what should be done with the remaining parts of the strip? Can this be used in another application?

Response: Strips can be stored in the PRC loading solution. It’s critical to collect a portion of the strip for analysis to obtain the PRC concentration at time zero – this must be done for each sampling event.

Question 10: Regarding “SOP PE (extract/analyze) - 2.1 Summary of Method:” - who is responsible for QCing these vessels?

Response: We recommend including a method blank (i.e. an “unloaded” sampler using standard glassware from lab during extraction) to ensure there are no contamination due to laboratory equipment etc. If contamination is encountered, additional diagnostic tests specific to the lab and method would be required.

Question 11: Regarding “SOP PE (extract/analyze) - 2.1 Summary of Method: What is the desired precision?”

Response: Precision in the 5-10% range is desired.

Question 12: Regarding “SOP PE (extractanalyze) - 2.2 Summary of Method:” - when the PRCs are loaded, are they rolled or shaken? Should the same mechanism be used for the extraction?

Response: Either can work. There is no need to be consistent with the loading vs. extraction mechanism. Regarding PE PRC loading, the critical detail is that the polymer is fully submerged. Problems can arise if polymer strips are on top of one another in the loading solution.

Question 13: Regarding “SOP PE (extractanalyze) - 7.1.6 Procedure:” If the initial weight is taken and we are able to determine a differential weight, should we not use desiccators before and after to negate humidity difference?

Response: No. See response to question 8.

Question 14: Regarding “SOP PE (extractanalyze) - 8.1 Quality Control:” - I am not sure of the order of clean, cut and load with PRCs. There is some inconsistency in sections 2.4 and 7.1. We prefer cut, clean and load with PRCs to minimize exposure of the prepared PE.

Response: You can do it in the order you prefer. Cut, clean, and load is fine.

Question 15: Regarding “SOP PE (prep): Section 6.1.” Is cleaned PE stored dry? Or in water? Or ?

Response: It is recommended that the cleaned PE be stored in the bottle and solution used to clean it, with as little air as possible.

Question 16: Regarding “SOP PE (extractanalyze):” Can a soft toothbrush be used to remove biofilm? Section 6.1 and 7.1.1. How far should we go with cleaning?

Response: Yes! It’s critical to remove all of the debris (including any biofilm) such that only the polymer (not polymer + biofilm) is extracted, which permits use of polymer- and contaminant-specific partitioning constant use to convert polymer extract concentrations into sediment porewater concentrations. Cleaning should be done *gently* using a soft bristled toothbrush so as to not damage the sampler. Note that it will not be possible to remove staining and that is OK.

Question 17: Regarding “SOP PE (extractanalyze): section 7.1.3” – it says to add surrogate compounds to the jar. Should this not say pipet onto the PE strip in the jar, and make sure to add before the solvent.

Response: Add surrogate then immediately add the solvent.

Question 18: Regarding “SOP PE (extractanalyze):” Can some allowance be added for cleanup of extracts before GC/MS analysis?

Response: Certainly. It is not typical to require cleanup for PAHs and PCBs using these methods. If using polymeric samplers to measure other organic contaminants (e.g. dioxins), cleanup may be required.

ATTACHMENT 4

***Task 2 Loading and Analysis of Polydimethylsiloxane
(PDMS) Solid-Phase Microextraction (SPME) and Low-
Density Polyethylene (LDPE) Polymetric Samplers:
Data Comparability Memo***

DATA COMPARABILITY ANALYSIS MEMORANDUM

Task 2 Loading and Analysis of Solid-Phase Microextraction (SPME) and Low-Density Polyethylene (LDPE) Polymetric Samplers

1. INTRODUCTION

This memo presents and discusses data comparability of the loading and analysis of polycyclic aromatic hydrocarbon (PAH) and polychlorinated biphenyl (PCB) performance reference compounds (PRCs) performed by participating laboratories. The PAH and PCB PRCs loaded and analyzed here were isotopically-labeled performance reference compounds (PRCs), which were loaded into polydimethylsiloxane (PDMS) and low-density polyethylene (LDPE) polymer segments by the laboratories. Danny Reible's group at Texas Tech University (TTU) and Phil Gschwend's group at the Massachusetts Institute of Technology (MIT), respective subject matter experts for use of PDMS and LDPE samplers, prepared the pre-cleaned samplers in six replicates (plus one sampler as a method blank) for all participating laboratories. Laboratories loaded PRCs into the samplers following the standard operating procedures (SOPs) provided by TTU (TTU 2018) and MIT (MIT 2017) respectively for SPME and LDPE. Once the PRC loading was completed, loaded samplers (and the method blank samplers) were extracted per the standardized polymeric sampler SOPs and quantified using standard EPA methods.

The PAH PRCs are independent of the analytical method the laboratories use; thus, there is only one suite of PRCs for each method. PCB PRCs vary by analytical method and as such there are two suites of PCB PRCs: one for regular sensitivity (low resolution mass spectrometry) and one for high sensitivity (high resolution mass spectrometry) methods.

- PAH PRCs: $^{13}\text{C}_6$ -phenanthrene, $^{13}\text{C}_6$ -fluoranthene, $^{13}\text{C}_6$ -chrysene, $^{13}\text{C}_6$ -indeno(1,2,3-cd)pyrene
- PCBs PRCs (Low-Sensitivity Methods): ^{13}C -labeled PCB congeners 37, 47, 54, 111, 138, and 178
- PCBs PRCs (High-Sensitivity Methods): ^{13}C -labeled PCB congeners 28, 47, 70, 80, 111, 141, 182

Four commercial laboratories and three university research laboratories participated in Task 2. Per the final Demonstration Plan, each laboratory quantified PAHs using a low sensitivity analytical method (EPA Method 8270D-SIM) and PCBs using a high or low sensitivity analytical method (EPA Method 1668C or EPA Method 8270D-SIM, respectively). To obscure laboratory identity, participating laboratories are identified by randomly-assigned numbers. See Table 1 for a list of which laboratories performed each analysis.

Resulting data submitted by participating commercial laboratories were subject to a Stage 4 (full) data validation. Data Validation Reports (DVR, Pyron 2019) for SPME and LDPE sample analysis were prepared separately (Attachments 2, 3) to document the scope and findings of the validation. The DVRs found no notable procedural or quality control issues that deviated from the analytical methods and the laboratories' SOPs. This data comparability memo for the analytical data (Demonstration Task 2) thus confidently assumes that analytical results submitted by participating commercial laboratories herein are representative analytical results generated by each laboratory's standard practices under optimal conditions of their instrumentation.

Data submitted by university laboratories were not subject to an independent data validation. Analytical methodologies used by university laboratories have been consistently applied to their research relevant to the passive sampling studies and results published over the years. However, it should be noted that university laboratory methodologies may not closely follow EPA published methods and may differ from EPA method requirements. In particular, quality control components such as the frequencies and acceptance criteria for instrument tuning, initial calibration, calibration verification, and analyte quantitation (e.g., surrogate spike recovery corrections on sample results) can be different from protocols used by commercial laboratories. University laboratory data were included in this analysis to document its comparability with data generated via EPA methods produced by commercial laboratories. The "target" concentrations of PRCs were established by back-calculating the laboratory-specific PRC loaded concentrations that would be achieved from the PRC amounts and concentrations each laboratory used during the loading procedures per SOPs provided by TTU and MIT. The target concentrations were used to assess the accuracy of each laboratory's results, as described in more detail below.

Note that the analytical results for PDMS were reported as nanogram per milliliter of PDMS (ng/mL-PDMS), where results for LDPE samplers were reported as nanogram per gram of LDPE (ng/g-LDPE). Conversion conventions for these reporting units were provided by TTU and MIT, respectively.

2. DATA COMPARABILITY ASSESSMENT METHODS

Data comparability was evaluated based on accuracy, precision, and sensitivity.

2.1 Accuracy

Accuracy was determined by comparing the analytical results to the target concentrations determined for each participating laboratories by back-calculating from the amounts and concentrations of their spiking solutions, following SOPs provided by TTU and MIT (Attachments 1, 2). As established in the Demonstration Plan (USACE *et al.*, 2018), a criterion of $\pm 50\%$ for PRCs; a PRC value outside 50-150% of the respective target concentration is considered as an outlier. According to EPA Method 1668C, labeled compounds such as PRCs must meet this standard, whereas target unlabeled congeners are

held to a $\pm 30\%$ standard. Because only isotopically-labeled PRCs were quantified under Task 2, only the $\pm 50\%$ accuracy criterion applies.

2.2 Precision

Precision was determined by the relative percent difference (RPD) if only two measurements performed by a laboratory are subjected for comparison. RPD is the difference divided by the average of two values that indicated the level of difference between the two values. In cases where more than two measurements were compared, the percent relative standard deviation (%RSD) was applied to evaluate the level of variation with the group of data. %RSD is percent of the standard deviation divided by the mean of a group of data. According to EPA Method 1668C, Method 8270D, and Method 1625C, replicate analysis precision within a laboratory is evaluated by comparing the %RSD value for replicate analyses to the $\leq 20\%$ criterion. Inter-laboratory precision was not applicable for Task 2 because laboratory-specific target loaded concentrations varied.

2.3 Sensitivity

Method sensitivity is evaluated with the method reporting limits (MRLs) or Practical Quantitation Limits (PQLs) that a laboratory can achieve given a sample matrix under the laboratory's standard operation. In some cases where the commercial laboratories did not report sample-specific MRLs (*i.e.* MRLs that are specific determined for the PRCs), the lowest-point of the initial calibration standard was used for this comparison.

3. ASSESSMENT FINDINGS FOR SPME SAMPLER ANALYSIS

The findings of individual laboratory replicate analysis accuracy, and inter-method data comparability for the loading, extraction and analysis of PAH and PCB PRCs in SPME samplers with low- and high-sensitivity GC/MS are discussed in the following sections.

3.1 PAH PRCs by Low-Sensitivity GC/MS

Four commercial laboratories (19, 48, 83, and 98) and two university laboratories (9 and 64) analyzed the PAH PRCs loaded in PDMS with low-sensitivity GC/MS. As shown in Table 2, results reported by commercial and university laboratories met the accuracy criteria of 50-150% target concentrations with the following exceptions:

- Commercial laboratory 48: $^{13}\text{C}_6$ -Phenanthrene,
- Commercial laboratory 83: $^{13}\text{C}_6$ -Phenanthrene and $^{13}\text{C}_6$ -Indeno[1,2,3-cd]pyrene,
- Commercial laboratory 98: $^{13}\text{C}_6$ -Phenanthrene, and
- University laboratory 9: $^{13}\text{C}_6$ -Fluoranthene.

These results were less than 50% of the target concentrations. The lower recovery of PAH PRCs reported by laboratory 83 may have resulted from the use of poor solvent choice in spiking standard, leading to bias in the loading condition. The significantly altered loading condition might have altered the loading efficiency (actual vs. calculated loaded concentration) from that of other participating laboratories. Low recovery of phenanthrene

by multiple labs may have been due to volatile losses. Low recovery of fluoranthene by lab 9 was unexplained.

All laboratory replicate analysis %RSD values were well less than the criterion of $\leq 20\%$, which demonstrated acceptable precision within each laboratory.

MRLs reported by the commercial laboratories indicated sufficient sensitivity to detect and quantitate the expected levels of target analytes in this analysis.

Based on the accuracy and precision analyses, methodologies used by the four commercial laboratories (using standardized methodology) and three university laboratories (using in-house research methods) showed satisfactory comparability in analyzing PAH PRCs in PDMS with low-sensitivity GC/MS methodologies.

Note that commercial laboratories 19 and 83 and university laboratories 9 and 64 used internal standard technique, where commercial laboratories 48 and 98 used isotope dilution technique for analyte quantitation.

3.2 PCB PRCs by Low-Sensitivity GC/MS

Two commercial laboratories (14 and 17) and two university laboratories (4 and 55) analyzed the PCB PRCs loaded in PDMS with low-sensitivity GC/MS methods. As shown in Table 3, results reported by commercial and university laboratories met the accuracy criteria of 50-150% target concentrations with the following exceptions:

- Commercial laboratory 14: ^{13}C -PCB 37
- Commercial laboratory 17: ^{13}C -PCBs 54, 111, 138, and 178, and
- University laboratory 4: ^{13}C -PCB 54.

The lower recovery of PCB PRCs reported by laboratory 17 may have resulted from the poor solvent choice (methanol/ethanol) and lower PRC concentrations in the loading solution. Low recovery of PCB 54 by lab 4 and PCB 37 by lab 14 was unexplained.

All laboratory replicate analysis %RSD values were well less than the criterion of $\leq 20\%$, which demonstrated acceptable precision within each of the participating laboratories.

MRLs reported by the commercial laboratories indicated sufficient sensitivity to detect and quantitate the expected levels of target analytes in this analysis.

Based on the accuracy and precision analyses, methodologies used by the two commercial laboratories (using standardized methodology) and the two university laboratories (using in-house research methods) showed satisfactory comparability in analyzing PCB PRCs in SPME fibers with low-sensitivity GC/MS methodologies.

Note that all commercial and university laboratories herein analyzed the PCB PRCs loaded in PDMS with low-sensitivity GC/MS methods used internal standard technique (as opposed to isotope dilution) for analyte quantitation.

3.3 PCB PRCs by High-Sensitivity GC/MS

Two commercial laboratories (37 and 95) and one university laboratory (2) analyzed the PCB PRCs loaded in PDMS with high-sensitivity GC/MS. As shown in Table 4, all results reported by commercial and university laboratories met the accuracy criteria of 50-150% target concentrations, indicating satisfactory accuracy.

All laboratory replicate analysis %RSD values were well less than the criterion of $\leq 20\%$, which demonstrated acceptable precision within each of the participating laboratories.

MRLs reported by the commercial laboratories indicated sufficient sensitivity to detect and quantitate the expected levels of target analytes in this analysis.

Based on the accuracy and precision analyses, methodologies used by the two commercial laboratories (using standardized methodology) and one university laboratory (using in-house research methods) showed satisfactory comparability in loading and analyzing PCB PRCs in SPME fibers with high-sensitivity GC/MS methodologies.

4. ASSESSMENT FINDINGS FOR LDPE SAMPLER ANALYSIS

The findings of individual laboratory replicate analysis accuracy, and inter-method data comparability for the loading, extraction and analysis of PAH and PCB PRCs in LDPE samplers with low- and high-sensitivity GC/MS are discussed in the following sections.

4.1 PAH PRCs by Low-Sensitivity GC/MS

Four commercial laboratories (34, 52, 58, and 84) and two university laboratories (15 and 50) loaded and analyzed the PAH PRCs in LDPE samplers with low-sensitivity GC/MS. As shown in Table 5, results reported by commercial and university laboratories met the accuracy criteria of 50-150% target concentration, with the following exceptions:

- Commercial laboratory 34: $^{13}\text{C}_6$ -Phenanthrene ($<50\%$ of target concentration),
- Commercial laboratory 52: $^{13}\text{C}_6$ -indeno[1,2,3cd]pyrene ($>150\%$ of target concentration),
- Commercial laboratory 84: $^{13}\text{C}_6$ -Phenanthrene $^{13}\text{C}_6$ -Fluoranthene, $^{13}\text{C}_6$ -Chrysene ($<50\%$ of target concentration) and $^{13}\text{C}_6$ -indeno[1,2,3cd]pyrene ($>150\%$ of target concentration)
- University laboratory 15: $^{13}\text{C}_6$ -Phenanthrene $^{13}\text{C}_6$ -Fluoranthene, and $^{13}\text{C}_6$ -indeno[1,2,3cd]pyrene ($>150\%$ of target concentration).

An in-depth investigation of analytical results and loading conditions were conducted by the laboratory's chemists to identify possible causes of the overall outlying recovery of PAH PRCs reported by laboratory 84. No significant anomalies were identified. However, the loading condition (amount and concentration of loading solution and loading time)

applied by laboratory 84 was significantly different from that of commercial laboratory 52, which used the same extraction and analytical methods as laboratory 84. The target concentration for laboratory 84 was approximately 1000 ng/g-LDPE, twice as that of laboratory 52.

For the overall high-bias recovery of PAH PRCs reported by university laboratory 15, the laboratory indicated that the addition of approximately 1.4 mL of nonane into the loading solution may have been enhanced loading of the PRCs into the LDPE polymer.

All laboratory replicate analysis %RSD values were well less than the criterion of $\leq 20\%$, which demonstrated acceptable precision within each of the participating laboratories.

Notable deviations of accuracy criteria were observed on results reported by commercial laboratory 84 and university laboratory 15, most likely due to the variations occurred during LDPE sampler loading. SOPs were revised to address this issue.

Note that commercial laboratories 34 and 58 and university laboratories 15 and 50 used internal standard technique, where commercial laboratories 52 and 84 used isotope dilution technique for analyte quantitation. University laboratory 15 normalized their results with surrogate spike recovery.

4.2 PCB PRCs by Low-Sensitivity GC/MS

Two commercial laboratories (11 and 91) and two university laboratories (5 and 52) loaded and analyzed the PCB PRCs in LDPE samplers with low-sensitivity GC/MS methods. As shown in Table 6, results reported by commercial and university laboratories met the accuracy criteria of 50-150% target concentrations, except for the following:

- Commercial laboratory 11: ^{13}C -PCB 47 and ^{13}C -PCB 111 ($>150\%$ of the target concentration),
- Commercial laboratory 91: All PCB PRCs except ^{13}C -PCB 54 ($>150\%$ of the target concentration),
- University laboratory 5: All PCB PRCs except ^{13}C -PCB 138 and ^{13}C -PCB 178 ($>150\%$ of the target concentration), and
- University laboratory 52: All PCB PRCs except ^{13}C -PCB 54 ($>150\%$ of the target concentration).

As shown above, an overall biased-high recovery of PCB PRCs using the low-sensitivity methods was observed on all participating laboratories. The proportion of nonane present in the loading solution have caused changes in the LDPE polymer, resulting in higher loaded concentrations than anticipated based on equilibrium partitioning. LDPE SOPs were updated to prevent this issue during future method applications.

All laboratory replicate analysis %RSD values were well less than the criterion of $\leq 20\%$, which demonstrated acceptable precision within each of the participating laboratories.

Note that all commercial and university laboratories herein analyzed the PCB PRCs loaded in LDPE with low-sensitivity GC/MS methods used internal standard technique (as

opposed to isotope dilution) for analyte quantitation. University laboratory 52 normalized their results with surrogate spike recovery.

Based on the accuracy and precision analyses, data comparability for the analysis of PCB PRCs in LDPE samplers was not conclusive.

4.3 PCB PRCs by High-Sensitivity GC/MS

Two commercial laboratories (86 and 93) and one university laboratory (69) loaded and analyzed the PCB PRCs in LDPE samplers with high-sensitivity GC/MS methods. As shown in Table 7, most PCB PRC recovery exceeded the upper limit of the accuracy criteria of 50-150% target concentrations, as follows:

- Commercial laboratory 86: ^{13}C -PCB 80 and ^{13}C -PCB 111 (>150% of the target concentration),
- Commercial laboratory 93: ^{13}C -PCB 28 and ^{13}C -PCB 80 (>150% of the target concentration)
- University laboratory 69: All PCB PRCs (>>150% of the target concentration)

As indicated above, notable deviations of accuracy criteria were observed on results reported university laboratory 69. The proportion of nonane present in the loading solution lab 69 used may have caused changes in the LDPE polymer, resulting in higher loaded concentrations than anticipated based on equilibrium partitioning. LDPE SOPs were updated to prevent this issue during future method applications.

All laboratory replicate analysis %RSD values were well less than the criterion of $\leq 20\%$. The overall low %RSD values demonstrated an excellent precision within each of the participating laboratories.

Note that university laboratory 69 normalized their results with surrogate spike recovery.

Table 1. Tests Performed by Laboratories

PRCs	Method Sensitivity	Target Concentration Range ^(A)		SPME Laboratory ^(B)		LDPE Laboratory ^(B)	
		SPME	LDPE	Commercial	University	Commercial	University
PAHs	Low	1184, 5922 ^(C)	500, 1000 ^(D)	19, 48, 83, 98	9, 64	34, 52, 58, 84	15, 50
PCBs	Low	1184, 5922 ^(C)	500, 1000 ^(E)	14, 17	4, 55	11, 91	5, 52
	High	1184, 1000 ^(D)	500, 1000 ^(F)	37, 95	2	86, 93	69

Notes:

SPME sampler results were reported in ng/mL-SPME; LDPE results were reported in ng/g-LDPE

^(A) – Target concentrations were determined by back-calculating from the volumes and concentrations of loading solutions; concentration for each PRC varies and may differ between laboratories, and thus presented as approximate concentration ranges herein.

^(B) – Each laboratory was randomly assigned a number in each type of analysis.

^(C) – For laboratories 17 and 83 only

^(D) – For laboratory 84 only

^(E) – For laboratory 11

^(F) – For laboratory 86

Table 2. PAH PRCs in PDMS by Low-Sensitivity Methods

PRCs	Target Concentrations		Commercial Laboratory								University Laboratory			
			19		48		83		98		9 ^(A)		64	
	Labs 64, 48, 98, 19, 9	Lab 83	Avg	RSD	Avg	RSD	Avg	RSD	Avg	RSD	Avg	RSD	Avg	RSD
¹³ C ₆ -Phenanthrene	1180	5920	1030	16%	419	19%	2510	1%	418	3%	1400	3%	1090	1%
¹³ C ₆ -Fluoranthene	1180	5920	1250	16%	581	15%	3450	2%	905	2%	449	3%	1180	9%
¹³ C ₆ -Chrysene	1180	5920	1480	10%	923	17%	3950	2%	823	7%	789	2%	1180	5%
¹³ C ₆ -Indeno[1,2,3-cd]pyrene	1180	5920	833	6%	926	16%	2080	4%	1090	11%	1130	2%	1140	8%

Notes:

Unit: Nanogram per milliliter of polydimethylsiloxane (ng/mL-PDMS)

Shaded number indicated that the value did not meet the accuracy evaluation criterion.

^(A): Only submitted results for three replicates.

Avg: Average value; based on six replicates analyzed/reported by each laboratory, except laboratory 9.

PAH: Polycyclic aromatic hydrocarbon

PRCs: Performance reference compounds

RSD: Relative standard deviation; criterion was set at ≤20% as guideline for precision evaluation

Table 3. PCB PRCs in PDMS by Low-Sensitivity Methods

PRCs	Target Concentrations		Commercial Laboratory				University Laboratory			
			14		17		4 ^(A)		55	
	Labs 4, 14, 55	Lab17	Avg	RSD	Avg	RSD	Avg	RSD	Avg	RSD
¹³ C-PCB 37	1180	5920	540	20%	3590	8%	923	3%	1210	5%
¹³ C-PCB 47	1180	5920	1510	2%	3930	9%	874	3%	1150	5%
¹³ C-PCB 54	1180	5920	1580	2%	2370	9%	414	4%	1050	4%
¹³ C-PCB 111	1180	5920	1160	6%	2720	11%	1220	6%	1100	3%
¹³ C-PCB 138	1180	5920	1240	4%	2300	12%	1060	8%	1350	4%
¹³ C-PCB 178	1180	5920	1290	5%	2090	10%	1050	12%	1220	7%

Notes:

Unit: Nanogram per milliliter of polydimethylsiloxane (ng/mL-PDMS)

Shaded number indicated that the value did not meet the accuracy evaluation criterion.

Avg: Average value; based on six replicates analyzed/reported by each laboratory, except laboratory 4.

^(A): Only submitted results for three replicates.

PCB: Polychlorinated biphenyl

PRCs: Performance reference compounds

RPD: Relative percent difference

RSD: Relative standard deviation; criterion was set at $\leq 20\%$ as guideline for precision evaluation

Table 4. PCB PRCs in PDMS by High-Sensitivity Methods

PRCs	Target Concentrations	Commercial Laboratory				University Laboratory	
		37		95		2	
		Avg	RSD	Avg	RSD	Avg	RSD
¹³ C-PCB 28	1180	923	3%	708	2%	1030	5%
¹³ C-PCB 47	1180	953	2%	750	2%	1140	4%
¹³ C-PCB 70	1180	953	2%	957	1%	1100	9%
¹³ C-PCB 80	1180	908	2%	963	5%	1120	6%
¹³ C-PCB 111	1180	977	2%	1010	2%	1050	4%
¹³ C-PCB 141	1180	1100	0%	1160	4%	1110	4%
¹³ C-PCB 182	1180	1080	4%	1180	6%	1080	3%

Notes:

Unit: Nanogram per milliliter of polydimethylsiloxane (ng/mL-PDMS)

Avg: Average value; based on six replicates analyzed/reported by each laboratory.

PCB: Polychlorinated biphenyl

PRCs: Performance reference compounds

RPD – Relative percent difference

RSD: Relative standard deviation; criterion was set at ≤20% as guideline for precision evaluation

Table 5. PAH PRCs in LDPE by Low-Sensitivity Methods

PRCs	Target Concentrations			Commercial Laboratory								University Laboratory			
				34		52		58		84		15 ^(A)		50	
	All Labs Except 15, 84	Lab 15	Lab 84	Avg	RSD	Avg	RSD	Avg	RSD	Avg	RSD	Avg	RSD	Avg	RSD
¹³ C ₆ -Phenanthrene	500	498	990	227	7%	526	2%	333	12%	342	6%	962	8%	409	11%
¹³ C ₆ -Fluoranthene	500	521	1000	624	6%	493	2%	332	8%	358	7%	869	10%	319	6%
¹³ C ₆ -Chrysene	500	510	990	456	6%	494	6%	362	7%	313	5%	708	11%	324	7%
¹³ C ₆ -Indeno[1,2,3-cd]pyrene	500	517	950	460	16%	920	2%	664	18%	922	7%	902	10%	523	3%

Notes:

Unit: Nanogram per gram of low-density polyethylene (ng/g-LDPE)

Shaded number indicated that the value did not meet the evaluation criterion.

^(A): Results were corrected with surrogate spike recovery.

Avg: Average value; based on six replicates reported by each laboratory; Laboratory 15 reported results for 10 replicates.

PAH: Polycyclic aromatic hydrocarbon

PRCs: Performance reference compounds

RSD: Relative standard deviation; criterion was set at ≤20% as guideline for precision evaluation

Table 6. PCB PRCs in LDPE by Low-Sensitivity Methods

PRCs	Commercial Laboratory						University Laboratory					
	11			91			5			52 ^(A)		
	Target	Avg	RSD	Target	Avg	RSD	Target	Avg	RSD	Target	Avg	RSD
¹³ C-PCB 37	1000	1210	20%	500	1120	8%	500	1530	9%	522	1550	11%
¹³ C-PCB 47	1000	1690	17%	500	1410	9%	500	2030	9%	532	1860	16%
¹³ C-PCB 54	1000	687	17%	500	489	9%	500	1380	9%	423	644	13%
¹³ C-PCB 111	1000	2230	14%	500	1630	11%	500	1120	9%	488	1700	18%
¹³ C-PCB 138	1000	1100	16%	500	971	12%	500	742	10%	531	1190	18%
¹³ C-PCB 178	1000	1190	14%	500	915	10%	500	622	11%	571	1150	20%

Notes:

Unit: Nanogram per gram of low-density polyethylene (ng/g-LDPE)

Shaded number indicated that the value did not meet the evaluation criterion.

^(A): Results were corrected with surrogate spike recovery.

Avg: Average value; based on six replicates reported by each laboratory; Laboratory 52 reported results for 10 replicates.

ng/g-PE: nanogram per gram of polyethylene sampler

PCB: Polychlorinated biphenyl

PRCs: Performance reference compounds

RPD – Relative percent difference

RSD: Relative standard deviation; criterion was set at $\leq 20\%$ as guideline for precision evaluation

Table 7. PCBs in LDPE by High-Sensitivity Methods

PRCs	Commercial Laboratory						University Laboratory		
	86			93			69 ^(A)		
	Target	Avg	RSD	Target	Avg	RSD	Target	Avg	RSD
¹³ C-PCB 28	1000	1350	14%	500	796	8%	502	1990	5%
¹³ C-PCB 47	1000	1250	15%	500	510	3%	532	1860	4%
¹³ C-PCB 70	1000	912	15%	500	408	5%	544	1590	9%
¹³ C-PCB 80	1000	1730	16%	500	813	4%	516	2050	6%
¹³ C-PCB 111	1000	1620	15%	500	619	2%	488	1700	4%
¹³ C-PCB 141	1000	1060	16%	500	390	2%	517	1290	4%
¹³ C-PCB 182	1000	1170	16%	500	425	3%	913	2150	3%

Notes:

Unit: Nanogram per gram of low-density polyethylene (ng/g-LDPE)

Shaded number indicated that the value did not meet the evaluation criterion.

^(A): Results were corrected with surrogate spike recovery.

Avg: Average value; based on six replicates reported by each laboratory; Laboratory 69 reported results for 10 replicates.

ng/g-PE: nanogram per gram of polyethylene sampler

PCB: Polychlorinated biphenyl

PRCs: Performance reference compounds

RPD – Relative percent difference

RSD: Relative standard deviation; criterion was set at ≤20% as guideline for precision evaluation

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APPENDIX F
Quality control criteria for analytical methods

Table 1 – PCB Congeners Analysis Quality Control Evaluation Criteria Summary

QC Parameters and Performance Frequency	Laboratory and Referenced Analytical Method					
	ALS (EPA 8270D)	ARI (EPA 8270D)	AXYS-SGS (EPA 1668C)	Battelle (EPA 8270D)	TestAmerica (EPA 1668C)	Vista (EPA 1668C)
Tuning (Resolution Check) At the beginning and the end of each 12-hour period of analysis.	Same as Method	Same as Method	Same as Method		Same as Method	• Same as Method. • An appropriate lock mass will be monitored for each descriptor and shall not vary by more than $\pm 20\%$ throughout the respective retention time window.
GC Column Performance Check Prior to ICAL or calibration verification.	N/A	N/A	Same as Method		Same as Method	Same as Method
Initial Calibration (ICAL) Prior to sample analysis; as needed if failure of calibration verification; or a new lot is used as standard source.	• Same as Method • Minimum Average Response Factor is ≥ 0.2	Same as Method	• Same as Method • Standards' result values are within 15% of true values.		Same as Method	• Same as Method • The signal to noise ratio (S/N) must exceed 10:1 for all ions monitored (except Di-CBs are at or above 2.5:1). • In-house limits of 60-140% as the acceptance criteria for second source standard.
Calibration Verification (CCV), Ongoing Precision Recovery (OPR), or Verification (VER) At the beginning of each 12-hour period.	Same as Method	Same as Method	• Same as Methods. • SOP Tables 4a and 4b.		Same as Method	• Same as Method • The relative retention times of the peak for a native and labeled PCB should be within 0.5% of the retention time windows established from the initial calibration curve.

QC Parameters and Performance Frequency	Laboratory and Referenced Analytical Method					
	ALS (EPA 8270D)	ARI (EPA 8270D)	AXYs-SGS (EPA 1668C)	Battelle (EPA 8270D)	TestAmerica (EPA 1668C)	Vista (EPA 1668C)
Method Blank One per preparatory batch, run after calibration standards and before samples.	Target analytes must be less than reporting limit.	No analytes detected $\geq \frac{1}{2}$ limit of quantitation or $\geq 5\%$ of the associated regulatory limit for the analyte or $\geq 10\%$ of the sample result for the analyte, whichever is greater, per method.	Analyte amounts in blank samples for PCB congeners 77, 81, 114, 123, 126 and 169 must be ≤ 2 pg/congener/sample, amounts of PCB congeners 156, 157, 167 and 189 must be ≤ 10 pg/congener/sample, and the maximal amount of PCB 11 must be ≤ 150 pg/sample. Amounts of all other individual PCB congeners or coelutions must be ≤ 50 pg/congener/sample in blank samples. The sum of all 209 congeners should be ≤ 300 pg/sample. Higher levels are acceptable where sample concentrations exceed 10 times the blank levels.		Target analytes must be less than estimated maximum levels (EMLs) in SOP Table 4	$\leq$ Minimum level or one-third of the regulatory compliance limit, whichever is greater.
Instrument Blank At the beginning of each 12-hour period.	Same as Method Blank.	Same as Method Blank.	Same as Method Blank.		Target analytes must be less than EMLs in SOP Table 4	$\leq$ Minimum level or one-third of the regulatory compliance limit, whichever is greater.
Laboratory Control Sample (LCS) One per preparatory batch.	%R value should be within 70-130% of the true value	%R value should be within 70-130% of the true value	SOP Tables 4a and 4b.		Within control limits for OPR (SOP Tables 10A and 10B).	Within control limits for OPR
Matrix Spike (MS) (OPTIONAL)	%R value should be within 70-130% of the true value - RPD $\leq 30\%$	%R value should be within 70-130% of the true value	N/A		NA	Within control limits for OPR
Sample Duplicate or MS Duplicate (MSD) (OPTIONAL)	RPD $\leq 30\%$	RPD $\leq 30\%$	RPD $\leq 20\%$ (applicable to concentrations ≥ 10 times the DL)		N/A	RPD $\leq 25\%$
Extraction Standards and Cleanup Standards Every field sample, standard, and QC sample.	- Same as Method for Internal standard recovery - Surrogate Spike recovery is	- Same as Method for Internal standard recovery - Surrogate Spike recovery is within 70-130%.	- Same as Method - SOP Tables 4a and 4b.		Same as Method	- Same as Method - The absolute retention times of the internal standards shall be within ± 15 seconds of the retention times obtained during calibration.

QC Parameters and Performance Frequency	Laboratory and Referenced Analytical Method					
	ALS (EPA 8270D)	ARI (EPA 8270D)	AXYs-SGS (EPA 1668C)	Battelle (EPA 8270D)	TestAmerica (EPA 1668C)	Vista (EPA 1668C)
	within 70 - 130%.					
Compound Identification	Same as Method	Same as Method)	Same as Method		Same as Method	Same as Method

Notes:

N/A: Not applicable

EPA 8270D - USEPA. 1998. Test Methods for Evaluating Solid Waste (SW 846). Third Edition and Revised Update IIIA. Method 8000 and Method 8270D. Office of Solid Waste and Emergency Response, Washington, D.C. April 1998 and Updates.

EPA 1668C - USEPA Method 1668C - Chlorinated Biphenyl Congeners in Water, Soil, Sediment, Biosolids, and Tissue by HRGC/HRMS. April 2010.

Table 2 – PAHs Analysis Quality Control Evaluation Criteria Summary

QC Parameter & Performance Frequency	Laboratory and Referenced Method					
	ALS EPA 8270D-SIM	ARI EPA 8270D-SIM	AXYS-SGS EPA 8270C-SIM EPA 1625 (HRGC/MS)	Battelle EPA 8270D-SIM	TestAmerica EPA 8270C-SIM EPA 1625 (GC/MS)	Vista EPA 8270C-SIM EPA 1625 (HRGC/MS)
Tuning Prior to calibration and every 12 hours during sample analysis	Same as Method. SOP Tables 4 and 4A	Same as Method.	- Calibration gas PFTBA (FC43) unit mass resolution at m/e 69/70 and 219/220. Unit mass resolution is demonstrated by the presence of a resolved peak at m/z 70 and m/e 220. - Instrument sensitivity: S/N 3:1 for 10 pg of acenaphthene and dibenzo(a,h)anthracene. - Prior to the analysis of samples, the sensitivity of the GC/MS is checked by running a low-level calibration solution (Table 6a, Level A), which is less concentrated than the corresponding lowest level calibration solution used in the initial calibration. - The GC resolution is checked with every bracket of samples by monitoring the valley height (expressed in terms of the smaller peak in the pair) between benzo(b)fluoranthene and benzo(k)fluoranthene pair and the valley height between phenanthrene and anthracene in the calibration solution.		Tune the mass spectrometer as needed using perfluorotributylamine (PFTBA) and the instrument data system auto-tune program. Select the DFTPP tune optimization profile for the auto-tune program. Criteria not specified in SOP.	- Tune the instrument using PFK to meet the minimum required resolution power of 8000. - The peakwidth at 6°/11 of the peak height must not exceed 125 ppm in mass for 8000 resolutions at 192.9888 or any other PFK reference signal close to 128.0626.
DDT Breakdown Check Daily prior to analysis of samples	N/A	Degradation < 20% for DDT	N/A		N/A	N/A

QC Parameter & Performance Frequency	Laboratory and Referenced Method					
	ALS EPA 8270D-SIM	ARI EPA 8270D-SIM	AXYs-SGS EPA 8720C-SIM EPA 1625 (HRGC/MS)	Battelle EPA 8270D-SIM	TestAmerica EPA 8270C-SIM EPA 1625 (GC/MS)	Vista EPA 8270C-SIM EPA 1625 (HRGC/MS)
Relative Retention Time (RRT) Evaluation Each Sample	RRT of each target analyte in each calibration standard within ± 0.05 RRT units.	RRT of each target analyte in each calibration standard within ± 0.05 RRT units.	- RT within ± 3 seconds of the predicted retention time determined from the calibration standard and adjusted relative to the peak retention time reference (i.e. labelled surrogate). - A second requirement is that an authentic elute after its labelled analog.		N/A	The RRT of the analyte compared to the RRT of the labeled standard must be within ± 0.008 RRT units of the RRTs from the continuing calibration.
Initial Calibration (ICAL)	- A minimum of five points. - Analytes' RRFs must meet method limits across calibration range. - Analytes %RSDs must be less than or equal to 20%, or the analyte must employ a linear or non-linear calibration model with a coefficient of determination (r^2) greater than 0.99. - Verify ICAL with one second-source standard at mid-point concentration. Value for all analytes within $\pm 30\%$ of expected value.	- A minimum of five points. - Analytes' RRFs must meet method limits across calibration range. - Analytes %RSDs must be less than or equal to 20%, or the analyte must employ a linear or non-linear calibration model with a coefficient of determination (r^2) greater than 0.99. - Up to 10% of the total analytes may fail 1 and 2 above. - Verify ICAL with one second-source standard at mid-point concentration. Value for all analytes within $\pm 30\%$ of expected value.	- Calibration standard solutions are presented in SOP Table 6. - Linearity is demonstrated by a 5-point calibration over the working concentration range with a relative standard deviation of the RRFs $\leq 20\%$ for targets with a labelled analog present and all labelled compounds, $\leq 35\%$ for targets with no labelled analog present.		- SOP Table 3 lists ICAL concentrations. %RSD must be $\leq 30\%$ for analytes and internal standards. - Verify ICAL with one second-source standard at mid-point (CS4) concentration. Value for all analytes within $\pm 30\%$ of expected value.	- Calibration standard solutions are presented in SOP Table 2. - The signal to noise ratio (S/N) must be $\geq 10:1$ for all ions monitored. - The percent relative standard deviation for the mean relative response factors must be no greater than 30% for the unlabeled analytes and for the internal standards. - A resolution of 8,000 must be achieved. - The ions listed in SOP Table 5 must be monitored with a total cycle time of 1 second or less.

QC Parameter & Performance Frequency	Laboratory and Referenced Method					
	ALS EPA 8270D-SIM	ARI EPA 8270D-SIM	AXYs-SGS EPA 8720C-SIM EPA 1625 (HRGC/MS)	Battelle EPA 8270D-SIM	TestAmerica EPA 8270C-SIM EPA 1625 (GC/MS)	Vista EPA 8270C-SIM EPA 1625 (HRGC/MS)
Calibration verification (CCV) Before sample analysis, and every 12 hours of analysis time	- Average RRFs for analytes must meet the method defined limits. %Difference/Drift for analytes $\leq 20\%$ - If no more than 20% of the compounds, included in the initial calibration, differ from their true concentration by 40%, the initial calibration is valid and no corrective action is necessary.	- Average RRFs for analytes must meet the method defined limits. %Difference/Drift for analytes $\leq 20\%$ - Up to 20% of the target analytes may fail the criteria in 1 and 2 so long as the sample analyses associated with the CCV are J flagged.	- Opening Cal Ver: Concentrations of native compounds and labelled surrogates must be within $\pm 25\%$ of expected values for all targets. - Closing Cal Ver: Concentrations of native compounds must be within $\pm 25\%$ of expected values. - Concentrations of labelled surrogates must be within $\pm 25\%$ of expected values, with any two (2) values allowed to be within $\pm 40\%$. - Ion ratios for authentic and labelled dibenz[ah]anthracene, indeno[1,2,3-cd]pyrene and benzo[ghi]perylene must be within $\pm 35\%$ of the mid-point of the I-CAL. - All other native analytes and labelled surrogates must be within $\pm 20\%$ of the mid-point of the I-CAL.		%Difference/Drift for analytes must be $\leq 30\%$ (SOP Table 7). - The recovery standard response must be within 50-200% of the response in the corresponding CS4 calibration level of the initial calibration. - New ICAL is needed if this criterion is not met.	A verification (VER) standard from the initial calibration curve (CS3), tune check, and column performance check is injected at the beginning of an analytical 12-hour sequence. The following criteria must be met: - The signal to noise ratio (S/N) must be $\geq 10:1$ for all ions monitored. - The percent relative standard deviation for the mean relative response factors must be no greater than 30% for the unlabeled analytes and 35% for the internal standards. - If the criteria cannot be met, recalibrate.
Internal Standards Every field sample, standard, and QC sample	- Retention time ± 30 seconds from retention time of the midpoint standard in the ICAL or CCV. - EICP area within -50% to +100% of ICAL midpoint standard	- Retention time ± 30 seconds from retention time of the midpoint standard in the ICAL or CCV. - EICP area within -50% to +100% of ICAL midpoint standard	Within -50% to +100% of ICAL midpoint standard.		The recovery standard response must be within 50-200% of the response in the corresponding CS4 calibration level of the initial calibration.	- Recovery of the internal standards must be within 50-150% recovery. - If outside of this criterion, the SIN must be $\geq 10:1$. An "H" qualifier will denote a recovery that is less than 50%. - Samples with internal standard recoveries less than 20% may be diluted

Table 1 – PCB Congeners Analysis Quality Control Evaluation Criteria Summary

QC Parameters and Performance Frequency	Laboratory and Referenced Analytical Method					
	ALS (EPA 8270D)	ARI (EPA 8270D)	AXYS-SGS (EPA 1668C)	Battelle (EPA 8270D)	TestAmerica (EPA 1668C)	Vista (EPA 1668C)
Tuning (Resolution Check) At the beginning and the end of each 12-hour period of analysis.	Same as Method	Same as Method	Same as Method		Same as Method	• Same as Method. • An appropriate lock mass will be monitored for each descriptor and shall not vary by more than $\pm 20\%$ throughout the respective retention time window.
GC Column Performance Check Prior to ICAL or calibration verification.	N/A	N/A	Same as Method		Same as Method	Same as Method
Initial Calibration (ICAL) Prior to sample analysis; as needed if failure of calibration verification; or a new lot is used as standard source.	• Same as Method • Minimum Average Response Factor is ≥ 0.2	Same as Method	• Same as Method • Standards' result values are within 15% of true values.		Same as Method	• Same as Method • The signal to noise ratio (S/N) must exceed 10:1 for all ions monitored (except Di-CBs are at or above 2.5:1). • In-house limits of 60-140% as the acceptance criteria for second source standard.
Calibration Verification (CCV), Ongoing Precision Recovery (OPR), or Verification (VER) At the beginning of each 12-hour period.	Same as Method	Same as Method	• Same as Methods. • SOP Tables 4a and 4b.		Same as Method	• Same as Method • The relative retention times of the peak for a native and labeled PCB should be within 0.5% of the retention time windows established from the initial calibration curve.

QC Parameters and Performance Frequency	Laboratory and Referenced Analytical Method					
	ALS (EPA 8270D)	ARI (EPA 8270D)	AXYs-SGS (EPA 1668C)	Battelle (EPA 8270D)	TestAmerica (EPA 1668C)	Vista (EPA 1668C)
Method Blank One per preparatory batch, run after calibration standards and before samples.	Target analytes must be less than reporting limit.	No analytes detected $\geq \frac{1}{2}$ limit of quantitation or $\geq 5\%$ of the associated regulatory limit for the analyte or $\geq 10\%$ of the sample result for the analyte, whichever is greater, per method.	Analyte amounts in blank samples for PCB congeners 77, 81, 114, 123, 126 and 169 must be ≤ 2 pg/congener/sample, amounts of PCB congeners 156, 157, 167 and 189 must be ≤ 10 pg/congener/sample, and the maximal amount of PCB 11 must be ≤ 150 pg/sample. Amounts of all other individual PCB congeners or coelutions must be ≤ 50 pg/congener/sample in blank samples. The sum of all 209 congeners should be ≤ 300 pg/sample. Higher levels are acceptable where sample concentrations exceed 10 times the blank levels.		Target analytes must be less than estimated maximum levels (EMLs) in SOP Table 4	$\leq$ Minimum level or one-third of the regulatory compliance limit, whichever is greater.
Instrument Blank At the beginning of each 12-hour period.	Same as Method Blank.	Same as Method Blank.	Same as Method Blank.		Target analytes must be less than EMLs in SOP Table 4	$\leq$ Minimum level or one-third of the regulatory compliance limit, whichever is greater.
Laboratory Control Sample (LCS) One per preparatory batch.	%R value should be within 70-130% of the true value	%R value should be within 70-130% of the true value	SOP Tables 4a and 4b.		Within control limits for OPR (SOP Tables 10A and 10B).	Within control limits for OPR
Matrix Spike (MS) (OPTIONAL)	%R value should be within 70-130% of the true value - RPD $\leq 30\%$	%R value should be within 70-130% of the true value	N/A		NA	Within control limits for OPR
Sample Duplicate or MS Duplicate (MSD) (OPTIONAL)	RPD $\leq 30\%$	RPD $\leq 30\%$	RPD $\leq 20\%$ (applicable to concentrations ≥ 10 times the DL)		N/A	RPD $\leq 25\%$
Extraction Standards and Cleanup Standards Every field sample, standard, and QC sample.	- Same as Method for Internal standard recovery - Surrogate Spike recovery is	- Same as Method for Internal standard recovery - Surrogate Spike recovery is within 70-130%.	- Same as Method - SOP Tables 4a and 4b.		Same as Method	- Same as Method - The absolute retention times of the internal standards shall be within ± 15 seconds of the retention times obtained during calibration.

QC Parameters and Performance Frequency	Laboratory and Referenced Analytical Method					
	ALS (EPA 8270D)	ARI (EPA 8270D)	AXYs-SGS (EPA 1668C)	Battelle (EPA 8270D)	TestAmerica (EPA 1668C)	Vista (EPA 1668C)
	within 70 - 130%.					
Compound Identification	Same as Method	Same as Method)	Same as Method		Same as Method	Same as Method

Notes:

N/A: Not applicable

EPA 8270D - USEPA. 1998. Test Methods for Evaluating Solid Waste (SW 846). Third Edition and Revised Update IIIA. Method 8000 and Method 8270D. Office of Solid Waste and Emergency Response, Washington, D.C. April 1998 and Updates.

EPA 1668C - USEPA Method 1668C - Chlorinated Biphenyl Congeners in Water, Soil, Sediment, Biosolids, and Tissue by HRGC/HRMS. April 2010.

Table 2 – PAHs Analysis Quality Control Evaluation Criteria Summary

QC Parameter & Performance Frequency	Laboratory and Referenced Method					
	ALS EPA 8270D-SIM	ARI EPA 8270D-SIM	AXYS-SGS EPA 8270C-SIM EPA 1625 (HRGC/MS)	Battelle EPA 8270D-SIM	TestAmerica EPA 8270C-SIM EPA 1625 (GC/MS)	Vista EPA 8270C-SIM EPA 1625 (HRGC/MS)
Tuning Prior to calibration and every 12 hours during sample analysis	Same as Method. SOP Tables 4 and 4A	Same as Method.	- Calibration gas PFTBA (FC43) unit mass resolution at m/e 69/70 and 219/220. Unit mass resolution is demonstrated by the presence of a resolved peak at m/z 70 and m/e 220. - Instrument sensitivity: S/N 3:1 for 10 pg of acenaphthene and dibenzo(a,h)anthracene. - Prior to the analysis of samples, the sensitivity of the GC/MS is checked by running a low-level calibration solution (Table 6a, Level A), which is less concentrated than the corresponding lowest level calibration solution used in the initial calibration. - The GC resolution is checked with every bracket of samples by monitoring the valley height (expressed in terms of the smaller peak in the pair) between benzo(b)fluoranthene and benzo(k)fluoranthene pair and the valley height between phenanthrene and anthracene in the calibration solution.		Tune the mass spectrometer as needed using perfluorotributylamine (PFTBA) and the instrument data system auto-tune program. Select the DFTPP tune optimization profile for the auto-tune program. Criteria not specified in SOP.	- Tune the instrument using PFK to meet the minimum required resolution power of 8000. - The peakwidth at 6°/11 of the peak height must not exceed 125 ppm in mass for 8000 resolutions at 192.9888 or any other PFK reference signal close to 128.0626.
DDT Breakdown Check Daily prior to analysis of samples	N/A	Degradation < 20% for DDT	N/A		N/A	N/A

QC Parameter & Performance Frequency	Laboratory and Referenced Method					
	ALS EPA 8270D-SIM	ARI EPA 8270D-SIM	AXYs-SGS EPA 8720C-SIM EPA 1625 (HRGC/MS)	Battelle EPA 8270D-SIM	TestAmerica EPA 8270C-SIM EPA 1625 (GC/MS)	Vista EPA 8270C-SIM EPA 1625 (HRGC/MS)
Relative Retention Time (RRT) Evaluation Each Sample	RRT of each target analyte in each calibration standard within ± 0.05 RRT units.	RRT of each target analyte in each calibration standard within ± 0.05 RRT units.	- RT within ± 3 seconds of the predicted retention time determined from the calibration standard and adjusted relative to the peak retention time reference (i.e. labelled surrogate). - A second requirement is that an authentic elute after its labelled analog.		N/A	The RRT of the analyte compared to the RRT of the labeled standard must be within ± 0.008 RRT units of the RRTs from the continuing calibration.
Initial Calibration (ICAL)	- A minimum of five points. - Analytes' RRFs must meet method limits across calibration range. - Analytes %RSDs must be less than or equal to 20%, or the analyte must employ a linear or non-linear calibration model with a coefficient of determination (r^2) greater than 0.99. - Verify ICAL with one second-source standard at mid-point concentration. Value for all analytes within $\pm 30\%$ of expected value.	- A minimum of five points. - Analytes' RRFs must meet method limits across calibration range. - Analytes %RSDs must be less than or equal to 20%, or the analyte must employ a linear or non-linear calibration model with a coefficient of determination (r^2) greater than 0.99. - Up to 10% of the total analytes may fail 1 and 2 above. - Verify ICAL with one second-source standard at mid-point concentration. Value for all analytes within $\pm 30\%$ of expected value.	- Calibration standard solutions are presented in SOP Table 6. - Linearity is demonstrated by a 5-point calibration over the working concentration range with a relative standard deviation of the RRFs $\leq 20\%$ for targets with a labelled analog present and all labelled compounds, $\leq 35\%$ for targets with no labelled analog present.		- SOP Table 3 lists ICAL concentrations. %RSD must be $\leq 30\%$ for analytes and internal standards. - Verify ICAL with one second-source standard at mid-point (CS4) concentration. Value for all analytes within $\pm 30\%$ of expected value.	- Calibration standard solutions are presented in SOP Table 2. - The signal to noise ratio (S/N) must be $\geq 10:1$ for all ions monitored. - The percent relative standard deviation for the mean relative response factors must be no greater than 30% for the unlabeled analytes and for the internal standards. - A resolution of 8,000 must be achieved. - The ions listed in SOP Table 5 must be monitored with a total cycle time of 1 second or less.

QC Parameter & Performance Frequency	Laboratory and Referenced Method					
	ALS EPA 8270D-SIM	ARI EPA 8270D-SIM	AXYs-SGS EPA 8720C-SIM EPA 1625 (HRGC/MS)	Battelle EPA 8270D-SIM	TestAmerica EPA 8270C-SIM EPA 1625 (GC/MS)	Vista EPA 8270C-SIM EPA 1625 (HRGC/MS)
Calibration verification (CCV) Before sample analysis, and every 12 hours of analysis time	- Average RRFs for analytes must meet the method defined limits. %Difference/Drift for analytes $\leq 20\%$ - If no more than 20% of the compounds, included in the initial calibration, differ from their true concentration by 40%, the initial calibration is valid and no corrective action is necessary.	- Average RRFs for analytes must meet the method defined limits. %Difference/Drift for analytes $\leq 20\%$ - Up to 20% of the target analytes may fail the criteria in 1 and 2 so long as the sample analyses associated with the CCV are J flagged.	- Opening Cal Ver: Concentrations of native compounds and labelled surrogates must be within $\pm 25\%$ of expected values for all targets. - Closing Cal Ver: Concentrations of native compounds must be within $\pm 25\%$ of expected values. - Concentrations of labelled surrogates must be within $\pm 25\%$ of expected values, with any two (2) values allowed to be within $\pm 40\%$. - Ion ratios for authentic and labelled dibenz[ah]anthracene, indeno[1,2,3-cd]pyrene and benzo[ghi]perylene must be within $\pm 35\%$ of the mid-point of the I-CAL. - All other native analytes and labelled surrogates must be within $\pm 20\%$ of the mid-point of the I-CAL.		%Difference/Drift for analytes must be $\leq 30\%$ (SOP Table 7). - The recovery standard response must be within 50-200% of the response in the corresponding CS4 calibration level of the initial calibration. - New ICAL is needed if this criterion is not met.	A verification (VER) standard from the initial calibration curve (CS3), tune check, and column performance check is injected at the beginning of an analytical 12-hour sequence. The following criteria must be met: - The signal to noise ratio (S/N) must be $\geq 10:1$ for all ions monitored. - The percent relative standard deviation for the mean relative response factors must be no greater than 30% for the unlabeled analytes and 35% for the internal standards. - If the criteria cannot be met, recalibrate.
Internal Standards Every field sample, standard, and QC sample	- Retention time ± 30 seconds from retention time of the midpoint standard in the ICAL or CCV. - EICP area within -50% to +100% of ICAL midpoint standard	- Retention time ± 30 seconds from retention time of the midpoint standard in the ICAL or CCV. - EICP area within -50% to +100% of ICAL midpoint standard	Within -50% to +100% of ICAL midpoint standard.		The recovery standard response must be within 50-200% of the response in the corresponding CS4 calibration level of the initial calibration.	- Recovery of the internal standards must be within 50-150% recovery. - If outside of this criterion, the SIN must be $\geq 10:1$. An "H" qualifier will denote a recovery that is less than 50%. - Samples with internal standard recoveries less than 20% may be diluted

QC Parameter & Performance Frequency	Laboratory and Referenced Method					
	ALS EPA 8270D-SIM	ARI EPA 8270D-SIM	AXYS-SGS EPA 8720C-SIM EPA 1625 (HRGC/MS)	Battelle EPA 8270D-SIM	TestAmerica EPA 8270C-SIM EPA 1625 (GC/MS)	Vista EPA 8270C-SIM EPA 1625 (HRGC/MS)
						and re-injected.
Method blank One per preparation batch of 20 or less samples	No analytes detected > RL (½ RL for DoD projects).	No analytes detected > ½ RL. For common laboratory contaminants, no analytes detected ≥ RL.	SOP Table 8.		No analytes detected > RL (½ RL for DoD projects).	• Levels of native isomers measured in the method blank must be less than the method minimum level or one-third the regulatory compliance level, whichever is greater or ten times lower than the concentration found in any sample within the analytical batch. • If the levels are greater, then the data must be evaluated to determine whether the batch shall be re-extracted or the data is qualified appropriately.
Laboratory control sample (LCS)	See Laboratory QA Plan (LQAP). Reported along with LCS results.	See Laboratory QA Plan (LQAP). Reported along with LCS results.	SOP Table 8.		SOP Table 7	Ongoing Precision and Recovery Samples (OPR); SOP Table 3.

QC Parameter & Performance Frequency	Laboratory and Referenced Method					
	ALS EPA 8270D-SIM	ARI EPA 8270D-SIM	AXYS-SGS EPA 8720C-SIM EPA 1625 (HRGC/MS)	Battelle EPA 8270D-SIM	TestAmerica EPA 8270C-SIM EPA 1625 (GC/MS)	Vista EPA 8270C-SIM EPA 1625 (HRGC/MS)
						and re-injected.
Method blank One per preparation batch of 20 or less samples	No analytes detected > RL (½ RL for DoD projects).	No analytes detected > ½ RL. For common laboratory contaminants, no analytes detected ≥ RL.	SOP Table 8.		No analytes detected > RL (½ RL for DoD projects).	- Levels of native isomers measured in the method blank must be less than the method minimum level or one-third the regulatory compliance level, whichever is greater or ten times lower than the concentration found in any sample within the analytical batch. - If the levels are greater, then the data must be evaluated to determine whether the batch shall be re-extracted or the data is qualified appropriately.
Laboratory control sample (LCS)	See Laboratory QA Plan (LQAP). Reported along with LCS results.	See Laboratory QA Plan (LQAP). Reported along with LCS results.	SOP Table 8.		SOP Table 7	Ongoing Precision and Recovery Samples (OPR); SOP Table 3.

QC Parameter & Performance Frequency	Laboratory and Referenced Method					
	ALS EPA 8270D-SIM	ARI EPA 8270D-SIM	AXYs-SGS EPA 8720C-SIM EPA 1625 (HRGC/MS)	Battelle EPA 8270D-SIM	TestAmerica EPA 8270C-SIM EPA 1625 (GC/MS)	Vista EPA 8270C-SIM EPA 1625 (HRGC/MS)
One per preparation batch of 20 or less samples						
Matrix Spike (MS) and MS Duplicate (MSD)	- For matrix evaluation, see LQAP. MS recovery is advisory. - RPD $\leq$ 30% (MS/MSD or sample duplicate). Limits are advisory.	- For matrix evaluation, see LQAP. MS recovery is advisory. - RPD $\leq$ 30% (MS/MSD or sample duplicate). Limits are advisory.	SOP Table 8.		N/A	N/A
Surrogate Spikes Every field and QC sample	See LQAP. Criteria reported along with surrogate results.	QC acceptance criteria for LCS specified by DoD, if available; otherwise method-specified criteria or laboratory's own in-house criteria (No more than 1 acid surrogate or 1 base surrogate is allowed out of control, all surrogate recoveries must be > 10%.)	SOP Table 8 for SPMD samples, including criteria for PRCs.		SOP Table 7	N/A
Laboratory Duplicates (Optional)	N/A	N/A	Duplicates must fall within $\pm 20\%$ of the mean (applicable to concentrations ≥ 10 times the DL). (Note that $\pm 20\%$ of the mean is equivalent to 40 relative percent difference)		N/A	N/A

QC Parameter & Performance Frequency	Laboratory and Referenced Method					
	ALS EPA 8270D-SIM	ARI EPA 8270D-SIM	AXYS-SGS EPA 8270C-SIM EPA 1625 (HRGC/MS)	Battelle EPA 8270D-SIM	TestAmerica EPA 8270C-SIM EPA 1625 (GC/MS)	Vista EPA 8270C-SIM EPA 1625 (HRGC/MS)
Compound Identification	Same as Method.	Same as Method	- Peak responses must be at least three times the background noise level. - The retention time (RT) must be within three seconds of that predicted from the calibration run and the sample retention time reference (labelled compound). - Peak maxima for the quantification and confirmation ions must coincide within two seconds. - The relative ion abundance ratios must be within 20% of the opening calibration values.		- The quantitation ion must be present. - The internal standard quantitation ions must be present. - The relative intensities of confirmation ions should agree to within $\pm 30\%$ between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 20% and 80%). The absence of confirmation ions should be considered carefully when making decisions regarding qualitative identification. Confirmation ions may have lower response than quantitation ions and may not always be present at lower concentrations. Their absence in this case may not be cause for determining that the analyte is not present. The absence of confirmation ions at higher levels where they should have been detectable may be cause for determination that an analyte is not present. - The sample component retention time must compare to within ± 0.2 min. of the retention time of the internal standard component. For reference, the standard must be run within the same 12-hour period as the sample. - If a compound cannot be verified by all the above criteria, but in the technical judgment of the analyst the identification is correct, the analyst shall report that identification and proceed with quantitation.	- For a peak to be considered real, the signal to noise ratio must be 2.5 to 1 or greater. If these criteria are not met, establish the reporting limit. - The RRT of the analyte compared to the RRT of the labeled standard must be within ± 0.008 RRT units of the RRT's from the continuing calibration. - Recovery of the internal standards must be within 50-150% recovery. If outside of this criteria, the SIN must be greater than 10:1. An "H" qualifier will denote a recovery that is less than 50%. Samples with internal standard recoveries less than 20% may be diluted and re-injected. - If broad background interference restricts the sensitivity of the analysis, the analyst must employ additional cleanup on the archive sample (if available) and reanalyze. If no archive is available, samples are qualified and narrated appropriately.

Notes:

N/A - Not applicable.; DoD – U.S. Department of Defense

EPA 8270D - USEPA. 1998. Test Methods for Evaluating Solid Waste (SW 846). Third Edition and Revised Update IIIA. Method 8000 and Method 8270D. Office of Solid Waste and Emergency Response, Washington, D.C. April 1998 and Updates.

EPA 1625 – 40CFR, Appendix A to Part 136, Method 1625 Revision B, Semivolatile Organic Compounds by Isotope Dilution GC/MS

HRGC/MS – High resolution gas chromatography coping with mass spectrometry; GC/MS – Gas chromatography coping with mass spectrometry; RL – Reporting Limit

APPENDIX G
Task 3 Supporting Information

APPENDIX G-1
Summary of Exposure Conditions by Laboratory

Exposure Conditions

Lab ID	Sampling Type	Sample ID	Out from Fridge Date	Time Mixed	Date Sampled	Time Sampled	Temperature	Date Retrieved	Time Retrieved	Temperature	Sediment Comment	Sampler comment	Note	Laboratory General Notes
Lab 50	Active	17	3/2/2020	10:20	3/4/2020	14:00	71F	4/2/2020	11:15	71F	well mixed sediment with oily phase	all covered by sediment	2+2.2cm PAH PDMS sample extracted	Note 1: sampling and retrieval time for different PE/PDMS samples may vary, but the differences are within 5 minutes.
Lab 50	Active	19	3/2/2020	10:30	3/4/2020	14:20	71F	4/2/2020	12:20	71F	well mixed sediment with oily phase	all covered by sediment		Note 2: temperature listed are the room temperature.
Lab 50	Active	22	3/2/2020	10:40	3/4/2020	14:40	71F	4/2/2020	13:25	71F	well mixed sediment with oily phase	all covered by sediment		Note 3: the sevens jar (#10) was also sampled with PE/PDMS passive samplers for passive exposure and can be used as an extra replicate.
Lab 50	Active	23	3/2/2020	10:50	3/4/2020	15:00	71F	4/2/2020	15:10	71F	well mixed sediment with oily phase	all covered by sediment	9.6cm PCB PDMS sample extracted, red robust on inner wall	
Lab 50	Active	24	3/2/2020	11:00	3/4/2020	15:20	71F	4/2/2020	14:35	71F	well mixed sediment with oily phase	all covered by sediment		
Lab 50	Active	26	3/2/2020	11:10	3/4/2020	15:40	71F	4/2/2020	14:00	71F	well mixed sediment with oily phase	all covered by sediment		
Lab 50	Passive	11	3/2/2020	11:20	3/4/2020	16:00	71F	4/2/2020	17:45	71F	native sediment with oily phase	all covered by sediment		
Lab 50	Passive	12	3/2/2020	11:30	3/4/2020	16:20	71F	4/2/2020	18:25	71F	native sediment with oily phase	all covered by sediment	surface water may slightly leak	
Lab 50	Passive	13	3/2/2020	11:40	3/4/2020	16:40	71F	4/2/2020	19:00	71F	native sediment with oily phase	all covered by sediment	sediment is more dense than other jars	
Lab 50	Passive	14	3/2/2020	11:50	3/4/2020	17:00	71F	4/2/2020	19:37	71F	native sediment with oily phase	all covered by sediment		
Lab 50	Passive	15	3/2/2020	12:00	3/4/2020	17:20	71F	4/2/2020	16:36	71F	native sediment with oily phase	all covered by sediment	surface water may slightly leak	
Lab 50	Passive	16	3/2/2020	12:20	3/4/2020	17:40	71F	4/2/2020	16:00	71F	native sediment with oily phase	all covered by sediment		
Lab 50	Passive	10	3/2/2020	12:10	3/4/2020	18:00	71F	4/2/2020	17:10	71F	native sediment with oily phase	all covered by sediment		
Lab 58	Active	17	3/2/2020	ABOUT 8AM	3/5/2020	8:15	21.8C	4/2/2020	10:30	71F	well mixed sediment with oily/water phase	all covered by sediment	5cm PAH PDMS sample extracted,using 2cm only	Note 1: sampling and retrieval time for different PE/PDMS samples may vary, but the differences are within 5 minutes.
Lab 58	Active	19	3/2/2020		3/5/2020	8:15	21.8C	4/2/2020	10:30	71F	well mixed sediment with oily/water phase	all covered by sediment	10cm PCB PDMS sample extracted	Note 2: temperature listed is temp of sample jar
Lab 58	Active	22	3/2/2020		3/5/2020	8:15	21.8C	4/2/2020	10:30	71F	well mixed sediment with oily/water phase	all covered by sediment	2cmx1cm PE PAH sample extracted	Note 3: active samples sediment settled(compacted). During shaking process samples where shaken to homogenize every couple days
Lab 58	Active	23	3/2/2020		3/5/2020	8:15	21.8C	4/2/2020	10:30	71F	well mixed sediment with oily/water phase	all covered by sediment	5cmx2cm PCB sample extracted	
Lab 58	Active	24	3/2/2020		3/5/2020	8:15	21.8C	4/2/2020	10:30	71F	well mixed sediment with oily/water phase	all covered by sediment		
Lab 58	Active	26	3/2/2020		3/5/2020	8:15	21.8C	4/2/2020	10:30	71F	well mixed sediment with oily/water phase	all covered by sediment		
Lab 58	Passive	11	3/2/2020		3/5/2020	8:15	21.8C	4/2/2020	10:30	71F	well mixed at start only	all covered by sediment		
Lab 58	Passive	12	3/2/2020		3/5/2020	8:15	21.8C	4/2/2020	10:30	71F	well mixed at start only	all covered by sediment		
Lab 58	Passive	13	3/2/2020		3/5/2020	8:15	21.8C	4/2/2020	10:30	71F	well mixed at start only	all covered by sediment		
Lab 58	Passive	14	3/2/2020		3/5/2020	8:15	21.8C	4/2/2020	10:30	71F	well mixed at start only	all covered by sediment		
Lab 58	Passive	15	3/2/2020		3/5/2020	8:15	21.8C	4/2/2020	10:30	71F	well mixed at start only	all covered by sediment		
Lab 58	Passive	16	3/2/2020		3/5/2020	8:15	21.8C	4/2/2020	10:30	71F	well mixed at start only	all covered by sediment		
Lab 34	Active	A1	3/4/2020	NA	3/6/2020	NA	72F	6/4/2020	NA	72F	well mixed sediment with oily phase	all covered by sediment; sar		Notes:
Lab 34	Active	A2	3/4/2020	NA	3/6/2020	NA	72F	6/4/2020	NA	72F	some settling at the bottom; oily phase on top	all covered by sediment; sar		All jars were stirred on 3/4 to homogenize. The static jars were then placed on the countnertop to start settling. The active jars were placed on the orbital shaker.
Lab 34	Active	A3	3/4/2020	NA	3/6/2020	NA	72F	6/4/2020	NA	72F	some settling at the bottom; oily phase on top	all covered by sediment; sar		"Sample ID" - jar ID; in the EDD reported in field
Lab 34	Active	A4	3/4/2020	NA	3/6/2020	NA	72F	6/4/2020	NA	72F	well mixed sediment with oily phase	all covered by sediment; sar		"Study_Specific_Location_ID"
Lab 34	Active	A5	3/4/2020	NA	3/6/2020	NA	72F	6/4/2020	NA	72F	well mixed sediment with oily phase	all covered by sediment; sar		"Date sampled" - date passive samplers added
Lab 34	Active													Extract volumes were 1000 uL for all PE samplers; 250 uL for PAH PDMS; 100 uL for PCB PDMS

Lab 34	Active	A6	3/4/2020	NA	3/6/2020	NA	72F	6/4/2020	NA	72F	well mixed sediment with oily phase	all covered by sediment; samplers look much cleaner than from active exposures with not much stain	For PE, used hexane-damp Kimwipe to clean the surface. For PDMS only used Milli-Q water and Kimwipes. All active and static jars were wrapped with Teflon tape around the lids to ensure tight seal. Static jars were kept upright; active jars were on the orbital shaker on the side at 140 rpm and were also manually mixed once a week by shaking in various directions by hand (without opening the jars). 2 cm PDMS extracted for PAHs, 10 cm for PCBs, and the entire size of PE for both PAHs and PCBs	The results in the EDD are reported in ng/g for PE samplers and in ng/mL-PDMS for PDMS samplers	
Lab 34	Passive	S1	3/4/2020	NA	3/6/2020	NA	72F	6/4/2020	NA	72F	about 1 inch of water on top, cottage cheese texture sediment, bubbly	all covered by sediment; samplers look much cleaner than from active exposures with not much stain			
Lab 34	Passive	S2	3/4/2020	NA	3/6/2020	NA	72F	6/4/2020	NA	72F	about 1 inch of water on top, cottage cheese texture sediment, bubbly	all covered by sediment; samplers look much cleaner than from active exposures with not much stain			
Lab 34	Passive	S3	3/4/2020	NA	3/6/2020	NA	72F	6/4/2020	NA	72F	about 1 inch of water on top covered with a rusty looking floating later, cottage cheese texture sediment	all covered by sediment; samplers look much cleaner than from active exposures with not much stain			
Lab 34	Passive	S4	3/4/2020	NA	3/6/2020	NA	72F	6/4/2020	NA	72F	about 1 inch of water on top covered with a rusty looking floating later, cottage cheese texture sediment	all covered by sediment; samplers look much cleaner than from active exposures with not much stain			
Lab 34	Passive	S5	3/4/2020	NA	3/6/2020	NA	72F	6/4/2020	NA	72F	about 1 inch of water on top covered with a rusty looking floating later, cottage cheese texture sediment	all covered by sediment; samplers look much cleaner than from active exposures with not much stain			
Lab 34	Passive	S6	3/4/2020	NA	3/6/2020	NA	72F	6/4/2020	NA	72F	about 1 inch of water on top covered with a rusty looking floating later, cottage cheese texture sediment	all covered by sediment; samplers look much cleaner than from active exposures with not much stain			
Lab 84	Active	1,7	3/2/2020	11:00	3/5/2020	16:00	(not recorded)	4/3/2020	15:00	(not recorded)	Samples were dark colored	Strong smell of PAH's		Note 1: sampling and retrieval time for different PE/PDMS samples may vary, but the differences are within 5 minutes.	
Lab 84	Active	2,8	3/2/2020	11:00	3/5/2020	16:00		4/3/2020	15:00		Samples were dark colored	Strong smell of PAH's		Note 2: temperature listed are the room temperature. Temperature in the lab was between 20 and 22 degrees C.	
Lab 84	Active	3,9	3/2/2020	11:00	3/5/2020	16:00		4/3/2020	15:00		Samples were dark colored	Strong smell of PAH's			
Lab 84	Active	4,10	3/2/2020	11:00	3/5/2020	16:00		4/3/2020	15:00		Samples were dark colored	Strong smell of PAH's			
Lab 84	Active	5,11	3/2/2020	11:00	3/5/2020	16:00		4/3/2020	15:00		Samples were dark colored	Strong smell of PAH's			
Lab 84	Active	6,12	3/2/2020	11:00	3/5/2020	16:00		4/3/2020	15:00		Samples were dark colored	Strong smell of PAH's			
Lab 84	Passive	13,19	3/2/2020	11:00	3/5/2020	16:00	(not recorded)	4/3/2020	15:00	(not recorded)	Samples were dark colored	Strong smell of PAH's			
Lab 84	Passive	14,20	3/2/2020	11:00	3/5/2020	16:00		4/3/2020	15:00		Samples were dark colored	Strong smell of PAH's			
Lab 84	Passive	15,21	3/2/2020	11:00	3/5/2020	16:00		4/3/2020	15:00		Samples were dark colored	Strong smell of PAH's			
Lab 84	Passive	16,22	3/2/2020	11:00	3/5/2020	16:00		4/3/2020	15:00		Samples were dark colored	Strong smell of PAH's			
Lab 84	Passive	17,23	3/2/2020	11:00	3/5/2020	16:00		4/3/2020	15:00		Samples were dark colored	Strong smell of PAH's			
Lab 84	Passive	18,24	3/2/2020	11:00	3/5/2020	16:00		4/3/2020	15:00		Samples were dark colored	Strong smell of PAH's			
Lab 52	Most details not available				3/3/2020		4/3/2020								
Lab 15	Details not available														
Lab 9	Active	17	3/2/2020	10:20	3/4/2020	14:00	71F	4/2/2020	11:15	71F	well mixed sediment with oily phase	all covered by sediment	2+2.2cm PAH PDMS sample extracted	Note 1: sampling and retrieval time for different PE/PDMS samples may vary, but the differences are within 5 minutes.	
Lab 9	Active	19	3/2/2020	10:30	3/4/2020	14:20	71F	4/2/2020	12:20	71F	well mixed sediment with oily phase	all covered by sediment		Note 2: temperature listed are the room temperature.	

Lab 9	Active	22	3/2/2020 10:40	3/4/2020 14:40 71F	4/2/2020 13:25 71F	well mixed sediment with oily phase	all covered by sediment		Note 3: the sevens jar (#10) was also sampled with PE/PDMS passive samplers for passive exposure and can be used as an extra replicate.
Lab 9	Active	23	3/2/2020 10:50	3/4/2020 15:00 71F	4/2/2020 15:10 71F	well mixed sediment with oily phase	all covered by sediment	9.6cm PCB PDMS sample extracted, red robust on inner wall	
Lab 9	Active	24	3/2/2020 11:00	3/4/2020 15:20 71F	4/2/2020 14:35 71F	well mixed sediment with oily phase	all covered by sediment		
Lab 9	Active	26	3/2/2020 11:10	3/4/2020 15:40 71F	4/2/2020 14:00 71F	well mixed sediment with oily phase	all covered by sediment		
Lab 9	Passive	11	3/2/2020 11:20	3/4/2020 16:00 71F	4/2/2020 17:45 71F	native sediment with oily phase	all covered by sediment		
Lab 9	Passive	12	3/2/2020 11:30	3/4/2020 16:20 71F	4/2/2020 18:25 71F	native sediment with oily phase	all covered by sediment	surface water may slightly leak	
Lab 9	Passive	13	3/2/2020 11:40	3/4/2020 16:40 71F	4/2/2020 19:00 71F	native sediment with oily phase	all covered by sediment	sediment is more dense than other jars	
Lab 9	Passive	14	3/2/2020 11:50	3/4/2020 17:00 71F	4/2/2020 19:37 71F	native sediment with oily phase	all covered by sediment		
Lab 9	Passive	15	3/2/2020 12:00	3/4/2020 17:20 71F	4/2/2020 16:36 71F	native sediment with oily phase	all covered by sediment	surface water may slightly leak	
Lab 9	Passive	16	3/2/2020 12:20	3/4/2020 17:40 71F	4/2/2020 16:00 71F	native sediment with oily phase	all covered by sediment		
Lab 9	Passive	10	3/2/2020 12:10	3/4/2020 18:00 71F	4/2/2020 17:10 71F	native sediment with oily phase	all covered by sediment		
Lab 19	Active	17	3/2/2020 ABOUT 8AM	3/5/2020 8:15 21.8C	4/2/2020 10:30 71F	well mixed sediment with oily/water phase	all covered by sediment	5cm PAH PDMS sample extracted,using 2cm only	Note 1: sampling and retrieval time for different PE/PDMS samples may vary, but the differences are within 5 minutes.
Lab 19	Active	19	3/2/2020	3/5/2020 8:15 21.8C	4/2/2020 10:30 71F	well mixed sediment with oily/water phase	all covered by sediment	10cm PCB PDMS sample extracted	Note 2: temperature listed is temp of sample jar
Lab 19	Active	22	3/2/2020	3/5/2020 8:15 21.8C	4/2/2020 10:30 71F	well mixed sediment with oily/water phase	all covered by sediment	2cmx1cm PE PAH sample extracted	Note 3: active samples sediment settled(compacted). During shaking process samples where shaken to homogenize every couple days
Lab 19	Active	23	3/2/2020	3/5/2020 8:15 21.8C	4/2/2020 10:30 71F	well mixed sediment with oily/water phase	all covered by sediment	5cmx2cm PCB sample extracted	
Lab 19	Active	24	3/2/2020	3/5/2020 8:15 21.8C	4/2/2020 10:30 71F	well mixed sediment with oily/water phase	all covered by sediment		
Lab 19	Active	26	3/2/2020	3/5/2020 8:15 21.8C	4/2/2020 10:30 71F	well mixed sediment with oily/water phase	all covered by sediment		
Lab 19	Passive	11	3/2/2020	3/5/2020 8:15 21.8C	4/2/2020 10:30 71F	well mixed at start only	all covered by sediment		
Lab 19	Passive	12	3/2/2020	3/5/2020 8:15 21.8C	4/2/2020 10:30 71F	well mixed at start only	all covered by sediment		
Lab 19	Passive	13	3/2/2020	3/5/2020 8:15 21.8C	4/2/2020 10:30 71F	well mixed at start only	all covered by sediment		
Lab 19	Passive	14	3/2/2020	3/5/2020 8:15 21.8C	4/2/2020 10:30 71F	well mixed at start only	all covered by sediment		
Lab 19	Passive	15	3/2/2020	3/5/2020 8:15 21.8C	4/2/2020 10:30 71F	well mixed at start only	all covered by sediment		
Lab 19	Passive	16	3/2/2020	3/5/2020 8:15 21.8C	4/2/2020 10:30 71F	well mixed at start only	all covered by sediment		
Lab 83	Active	A1	3/4/2020 NA	3/6/2020 NA 72F	6/4/2020 NA 72F	well mixed sediment with oily phase	all covered by sediment; sar	For PE, used hexane-damp Kimwipe to clean the surface. For PDMS only used Milli-Q water and Kimwipes. All active and static jars were wrapped with Teflon tape around the lids to ensure tight seal. Static jars were kept upright; active jars were on the orbital	Notes:
Lab 83	Active	A2	3/4/2020 NA	3/6/2020 NA 72F	6/4/2020 NA 72F	some settling at the bottom; oily phase on top	all covered by sediment; sar		All jars were stirred on 3/4 to homogenize. The static jars were then placed on the coutnertop to start settling. The active jars were placed on the orbital shaker.
Lab 83	Active	A3	3/4/2020 NA	3/6/2020 NA 72F	6/4/2020 NA 72F	some settling at the bottom; oily phase on top	all covered by sediment; sar		"Sample ID" - jar ID; in the EDD reported in field
Lab 83	Active	A4	3/4/2020 NA	3/6/2020 NA 72F	6/4/2020 NA 72F	well mixed sediment with oily phase	all covered by sediment; sar		"Study_Specific_Location_ID"
Lab 83	Active	A5	3/4/2020 NA	3/6/2020 NA 72F	6/4/2020 NA 72F	well mixed sediment with oily phase	all covered by sediment; sar		"Date sampled" - date passive samplers added
Lab 83	Active	A6	3/4/2020 NA	3/6/2020 NA 72F	6/4/2020 NA 72F	well mixed sediment with oily phase	all covered by sediment; sar		Extract volumes were 1000 uL for all PE samplers; 250 uL for PAH PDMS; 100 uL for PCB PDMS
Lab 83	Active	A6	3/4/2020 NA	3/6/2020 NA 72F	6/4/2020 NA 72F	well mixed sediment with oily phase	all covered by sediment; sar		The results in the EDD are reported in ng/g for PE samplers and in ng/mL-PDMS for PDMS samplers
Lab 83	Passive	S1	3/4/2020 NA	3/6/2020 NA 72F	6/4/2020 NA 72F	about 1 inch of water on top, cottage cheese texture sediment, bubbly	all covered by sediment; samplers look much cleaner than from active exposures with not much stain		

Lab 83	Passive	S2	3/4/2020	NA	3/6/2020	NA	72F	6/4/2020	NA	72F	about 1 inch of water on top, cottage cheese texture sediment, bubbly	all covered by sediment; samplers look much cleaner than from active exposures with not much stain	active jars were on the orbital shaker on the side at 140 rpm and were also manually mixed once a week by shaking in various directions by hand (without opening the jars). 2 cm PDMS extracted for PAHs, 10 cm for PCBs, and the entire size of PE for both PAHs and PCBs		
Lab 83	Passive	S3	3/4/2020	NA	3/6/2020	NA	72F	6/4/2020	NA	72F	about 1 inch of water on top covered with a rusty looking floating later, cottage cheese texture sediment	all covered by sediment; samplers look much cleaner than from active exposures with not much stain			
Lab 83	Passive	S4	3/4/2020	NA	3/6/2020	NA	72F	6/4/2020	NA	72F	about 1 inch of water on top covered with a rusty looking floating later, cottage cheese texture sediment	all covered by sediment; samplers look much cleaner than from active exposures with not much stain			
Lab 83	Passive	S5	3/4/2020	NA	3/6/2020	NA	72F	6/4/2020	NA	72F	about 1 inch of water on top covered with a rusty looking floating later, cottage cheese texture sediment	all covered by sediment; samplers look much cleaner than from active exposures with not much stain			
Lab 83	Passive	S6	3/4/2020	NA	3/6/2020	NA	72F	6/4/2020	NA	72F	about 1 inch of water on top covered with a rusty looking floating later, cottage cheese texture sediment	all covered by sediment; samplers look much cleaner than from active exposures with not much stain			
Lab 98	Active	1,7	3/2/2020	11:00	3/5/2020	16:00	(not recorded)	4/3/2020	15:00	(not recorded)	Samples were dark colored	Strong smell of PAH's		Note 1: sampling and retrieval time for different PE/PDMS samples may vary, but the differences are within 5 minutes.	
Lab 98	Active	2,8	3/2/2020	11:00	3/5/2020	16:00		4/3/2020	15:00		Samples were dark colored	Strong smell of PAH's		Note 2: temperature listed are the room temperature. Temperature in the lab was between 20 and 22 degrees C.	
Lab 98	Active	3,9	3/2/2020	11:00	3/5/2020	16:00		4/3/2020	15:00		Samples were dark colored	Strong smell of PAH's			
Lab 98	Active	4,10	3/2/2020	11:00	3/5/2020	16:00		4/3/2020	15:00		Samples were dark colored	Strong smell of PAH's			
Lab 98	Active	5,11	3/2/2020	11:00	3/5/2020	16:00		4/3/2020	15:00		Samples were dark colored	Strong smell of PAH's			
Lab 98	Active	6,12	3/2/2020	11:00	3/5/2020	16:00		4/3/2020	15:00		Samples were dark colored	Strong smell of PAH's			
Lab 98	Passive	13,19	3/2/2020	11:00	3/5/2020	16:00	(not recorded)	4/3/2020	15:00	(not recorded)	Samples were dark colored	Strong smell of PAH's			
Lab 98	Passive	14,20	3/2/2020	11:00	3/5/2020	16:00		4/3/2020	15:00		Samples were dark colored	Strong smell of PAH's			
Lab 98	Passive	15,21	3/2/2020	11:00	3/5/2020	16:00		4/3/2020	15:00		Samples were dark colored	Strong smell of PAH's			
Lab 98	Passive	16,22	3/2/2020	11:00	3/5/2020	16:00		4/3/2020	15:00		Samples were dark colored	Strong smell of PAH's			
Lab 98	Passive	17,23	3/2/2020	11:00	3/5/2020	16:00		4/3/2020	15:00		Samples were dark colored	Strong smell of PAH's			
Lab 98	Passive	18,24	3/2/2020	11:00	3/5/2020	16:00		4/3/2020	15:00		Samples were dark colored	Strong smell of PAH's			
Lab 38	Active	S1	3/5/2020	AM	3/6/2020	ND	71F	4/13/2020	11:30	69F	well mixed sediment with oily phase	all covered by sediment	Sediment sample was on a 1D-Shaker throughout the period of deployment	Note 1: AM means morning period	
Lab 38	Active	S2	3/5/2020	AM	3/6/2020	ND	71F	4/13/2020	-	69F	well mixed sediment with oily phase	all covered by sediment			Note 2: sampling and retrieval time for all PDMS samples lasted for about 2 hours for all sampling.
Lab 38	Active	S3	3/5/2020	AM	3/6/2020	ND	71F	4/13/2020	-	69F	well mixed sediment with oily phase	all covered by sediment			Note 3: temperature listed are the room temperature.
Lab 38	Passive	S1	3/5/2020	AM	3/6/2020	ND	71F	4/13/2020	-	69F	mixed sediment with overlying water-oily phase	all covered by sediment	Static throughout the period of deployment		
Lab 38	Passive	S2	3/5/2020	AM	3/6/2020	ND	71F	4/13/2020	-	69F	mixed sediment with overlying water-oily phase	all covered by sediment			
Lab 38	Passive	S3	3/5/2020	AM	3/6/2020	ND	71F	4/13/2020	1:45PM	69F	mixed sediment with overlying water-oily phase	all covered by sediment			
Lab 48	Most details not available				3/3/2020		4/3/2020								

PRC Loading #1

Lab ID	Sampler Type	PRCs	Sample ID	Loading Solution	Loading Solution Volume (mL)	Estimate Sampler Mass/ Length	Designed Loaded Concentration	Designed Extract Solvent Volume (uL)	PRCs Spiked Date	PRCs Spiked Time	Temperature (F)	Extracted C0 Sampler Mass/ Length	C0 Retrieved Date	Retrieved Time	Temperature (F)	Note
Lab 50	PE	PAH	1	water only	960	5 mg	500 ug/g	1000	8/19/2019	10:20	71	4.6 mg	9/23/2019	13:00	71	For PE PAH samplers, the 4 PRCs were spiked seperately, while other PRCs were spiked together into the other three vessels.
Lab 50	PE	PAH	2	water only	960	5 mg	500 ug/g	1000	8/19/2019	10:20	71	5.7 mg	9/23/2019	13:05	71	
Lab 50	PE	PAH	3	water only	960	5 mg	500 ug/g	1000	8/19/2019	10:20	71	4.8 mg	9/23/2019	13:10	71	
Lab 50	PE	PAH	4	water only	960	5 mg	500 ug/g	1000	8/19/2019	10:20	71	5.2 mg	9/23/2019	13:15	71	
Lab 50	PE	PAH	5	water only	960	5 mg	500 ug/g	1000	8/19/2019	10:20	71	4.5 mg	9/23/2019	13:20	71	
Lab 50	PE	PAH	6	water only	960	5 mg	500 ug/g	1000	8/19/2019	10:20	71	5.5 mg	9/23/2019	13:25	71	The actual number and mass of passive samplers and the round volume of spiked PRCs are the reason for the difference between designed loaded PRC concentrations and the target loaded concentration.
Lab 50	PE	PCB	1	water only	2000	25 mg	10 ug/g	1000	8/19/2019	10:30	71	26 mg	9/23/2019	13:30	71	
Lab 50	PE	PCB	2	water only	2000	25 mg	10 ug/g	1000	8/19/2019	10:30	71	24.9 mg	9/23/2019	13:35	71	
Lab 50	PE	PCB	3	water only	2000	25 mg	10 ug/g	1000	8/19/2019	10:30	71	27.8 mg	9/23/2019	13:40	71	
Lab 50	PE	PCB	4	water only	2000	25 mg	10 ug/g	1000	8/19/2019	10:30	71	26.5 mg	9/23/2019	13:45	71	
Lab 50	PE	PCB	5	water only	2000	25 mg	10 ug/g	1000	8/19/2019	10:30	71	26.7 mg	9/23/2019	13:50	71	
Lab 50	PE	PCB	6	water only	2000	25 mg	10 ug/g	1000	8/19/2019	10:30	71	27.8 mg	9/23/2019	13:55	71	
Lab 9	PDMS	PAH	1	80:20 water:methonal	100	5 cm	15792 ng/mL	200	10/10/2019	14:30	71	2 cm	11/8/2019	15:00	71	PAH PDMS samplers were observed to have declamination in the first batch.
Lab 9	PDMS	PAH	2	80:20 water:methonal	100	5 cm	15792 ng/mL	200	10/10/2019	14:30	71	2 cm	11/8/2019	15:03	71	
Lab 9	PDMS	PAH	3	80:20 water:methonal	100	5 cm	15792 ng/mL	200	10/10/2019	14:30	71	2 cm	11/8/2019	15:06	71	A new batch of PAH PDMS samplers were spiked on October 2019.
Lab 9	PDMS	PAH	4	80:20 water:methonal	100	5 cm	15792 ng/mL	200	10/10/2019	14:30	71	2 cm	11/8/2019	15:09	71	
Lab 9	PDMS	PAH	5	80:20 water:methonal	100	5 cm	15792 ng/mL	200	10/10/2019	14:30	71	2 cm	11/8/2019	15:12	71	
Lab 9	PDMS	PAH	6	80:20 water:methonal	100	5 cm	15792 ng/mL	200	10/10/2019	14:30	71	2 cm	11/8/2019	15:15	71	
Lab 9	PDMS	PCB	1	80:20 water:methonal	100	10 cm	790 ng/mL	50	8/19/2019	10:45	71	10 cm	9/23/2019	14:18	71	
Lab 9	PDMS	PCB	2	80:20 water:methonal	100	10 cm	790 ng/mL	50	8/19/2019	10:45	71	10 cm	9/23/2019	14:21	71	
Lab 9	PDMS	PCB	3	80:20 water:methonal	100	10 cm	790 ng/mL	50	8/19/2019	10:45	71	10 cm	9/23/2019	14:24	71	
Lab 9	PDMS	PCB	4	80:20 water:methonal	100	10 cm	790 ng/mL	50	8/19/2019	10:45	71	10 cm	9/23/2019	14:27	71	
Lab 9	PDMS	PCB	5	80:20 water:methonal	100	10 cm	790 ng/mL	50	8/19/2019	10:45	71	10 cm	9/23/2019	14:30	71	
Lab 9	PDMS	PCB	6	80:20 water:methonal	100	10 cm	790 ng/mL	50	8/19/2019	10:45	71	10 cm	9/23/2019	14:33	71	
Lab 58	PE	PAH	7	water only	1000	5 mg	500 ug/g	250	8/30/2019	19:30	Room Temp	4.4 mg	10/1/2019	18:24	71	
Lab 58	PE	PAH	8	water only	1000	5 mg	500 ug/g	250	8/30/2019	19:30	71	4.1 mg	10/1/2019	18:24	71	
Lab 58	PE	PAH	9	water only	1000	5 mg	500 ug/g	1000	8/30/2019	19:30	71	4.6 mg	10/1/2019	18:24	71	
Lab 58	PE	PAH	10	water only	1000	5 mg	500 ug/g	1000	8/30/2019	19:30	71	4.3 mg	10/1/2019	18:24	71	
Lab 58	PE	PAH	11	water only	1000	5 mg	500 ug/g	1000	8/30/2019	19:30	71	4.4 mg	10/1/2019	18:24	71	
Lab 58	PE	PAH	12	water only	1000	5 mg	500 ug/g	1000	8/30/2019	19:30	71	4 mg	10/1/2019	18:24	71	
Lab 58	PE	PCB	7	water only	2000	25 mg	10 ug/g	1000	8/30/2019	19:28	71	23.9 mg	10/1/2019	18:24	71	
Lab 58	PE	PCB	8	water only	2000	25 mg	10 ug/g	1000	8/30/2019	19:28	71	23.8 mg	10/1/2019	18:24	71	
Lab 58	PE	PCB	9	water only	2000	25 mg	10 ug/g	1000	8/30/2019	19:28	71	23.4 mg	10/1/2019	18:24	71	
Lab 58	PE	PCB	10	water only	2000	25 mg	10 ug/g	1000	8/30/2019	19:28	71	24.9 mg	10/1/2019	18:24	71	
Lab 58	PE	PCB	11	water only	2000	25 mg	10 ug/g	1000	8/30/2019	19:28	71	23.8 mg	10/1/2019	18:24	71	
Lab 58	PE	PCB	12	water only	2000	25 mg	10 ug/g	250	8/30/2019	19:28	71	23.5 mg	10/1/2019	18:24	71	
Lab 19	PDMS	PAH	1	80:20 water:methonal	100	5 cm	15792 ng/mL	125	8/30/2019	18:59	Room Temp	5 cm	10/1/2019	18:24	71	
Lab 19	PDMS	PAH	2	80:20 water:methonal	100	5 cm	15792 ng/mL	275	8/30/2019	18:59	71	5 cm	10/1/2019	18:24	71	
Lab 19	PDMS	PAH	3	80:20 water:methonal	100	5 cm	15792 ng/mL	275	8/30/2019	18:59	71	5 cm	10/1/2019	18:24	71	
Lab 19	PDMS	PAH	4	80:20 water:methonal	100	5 cm	15792 ng/mL	275	8/30/2019	18:59	71	5 cm	10/1/2019	18:24	71	
Lab 19	PDMS	PAH	5	80:20 water:methonal	100	5 cm	15792 ng/mL	275	8/30/2019	18:59	71	5 cm	10/1/2019	18:24	71	
Lab 19	PDMS	PAH	6	80:20 water:methonal	100	5 cm	15792 ng/mL	125	8/30/2019	18:59	71	5 cm	10/1/2019	18:24	71	
Lab 19	PDMS	PCB	1	80:20 water:methonal	100	10 cm	790 ng/mL	50	8/30/2019	18:55	71	10 cm	10/1/2019	18:24	71	
Lab 19	PDMS	PCB	2	80:20 water:methonal	100	10 cm	790 ng/mL	300	8/30/2019	18:55	71	10 cm	10/1/2019	18:24	71	
Lab 19	PDMS	PCB	3	80:20 water:methonal	100	10 cm	790 ng/mL	300	8/30/2019	18:55	71	10 cm	10/1/2019	18:24	71	

Lab 19	PDMS	PCB	4	80:20 water:methonal	100	10	cm	790 ng/mL	300	8/30/2019	18:55	71	10	cm	10/1/2019	18:24	71	
Lab 19	PDMS	PCB	5	80:20 water:methonal	100	10	cm	790 ng/mL	300	8/30/2019	18:55	71	10	cm	10/1/2019	18:24	71	
Lab 19	PDMS	PCB	6	80:20 water:methonal	100	10	cm	790 ng/mL	50	8/30/2019	18:55	71	10	cm	10/1/2019	18:24	71	
Lab 34	PE	PAH	PAH PED 1	water only	800	5	mg	666.7 ug/g	1000	9/24/2019	NA	72	5.33	mg	11/8/2019	13:00	72	Used "french press method" which resulted in all PEDs floating toward the top of the dome and clumping together. Jars were kept upright and rotation fo the orbital shaker was low due to leaky lids (aluminum foil didn' t allow proper seal). 1-L amber jars were used. PRCs were exchanged from nonane to methanol by evaporating down to ~100 uL and then adding methanol to reconstitute.
Lab 34	PE	PAH	PAH PED 2	water only	800	5	mg	666.7 ug/g	1000	9/24/2019	NA	72	5.24	mg	11/8/2019	13:05	72	
Lab 34	PE	PAH	PAH PED 3	water only	800	5	mg	666.7 ug/g	1000	9/24/2019	NA	72	5.22	mg	11/8/2019	13:10	72	
Lab 34	PE	PAH	PAH PED 4	water only	800	5	mg	666.7 ug/g	1000	9/24/2019	NA	72	4.61	mg	11/8/2019	13:15	72	
Lab 34	PE	PAH	PAH PED 5	water only	800	5	mg	666.7 ug/g	1000	9/24/2019	NA	72	5.03	mg	11/8/2019	13:20	72	
Lab 34	PE	PAH	PAH PED 6	water only	800	5	mg	666.7 ug/g	1000	9/24/2019	NA	72	5.49	mg	11/8/2019	13:25	72	
Lab 34	PE	PCB	PCB PED 1	water only	800	25	mg	8.3 ug/g	1000	9/24/2019	NA	72	27.44	mg	11/8/2019	13:30	72	
Lab 34	PE	PCB	PCB PED 2	water only	800	25	mg	8.3 ug/g	1000	9/24/2019	NA	72	25.07	mg	11/8/2019	13:35	72	
Lab 34	PE	PCB	PCB PED 3	water only	800	25	mg	8.3 ug/g	1000	9/24/2019	NA	72	24.22	mg	11/8/2019	13:40	72	
Lab 34	PE	PCB	PCB PED 4	water only	800	25	mg	8.3 ug/g	1000	9/24/2019	NA	72	26.07	mg	11/8/2019	13:45	72	
Lab 34	PE	PCB	PCB PED 5	water only	800	25	mg	8.3 ug/g	1000	9/24/2019	NA	72	24.71	mg	11/8/2019	13:50	72	Used 120 mL clear narrow neck bottles which were wrapped in aluminum foil for darkness. PRC spikes were in acetone. * For extraction of time zero PCB SPMEs 250 uL volume was used, however the spiking level was designe based on 100 uL volume plannned for sediment SPME
Lab 34	PE	PCB	PCB PED 6	water only	800	25	mg	8.3 ug/g	1000	9/24/2019	NA	72	24.95	mg	11/8/2019	13:55	72	
Lab 83	PDMS	PAH	PAH SPME 1	80:20 water:methonal	120	5	cm	39480 ng/mL	250	9/24/2019	NA	72	2	cm	11/8/2019	15:00	72	
Lab 83	PDMS	PAH	PAH SPME 2	80:20 water:methonal	120	5	cm	39480 ng/mL	250	9/24/2019	NA	72	2	cm	11/8/2019	15:03	72	
Lab 83	PDMS	PAH	PAH SPME 3	80:20 water:methonal	120	5	cm	39480 ng/mL	250	9/24/2019	NA	72	2	cm	11/8/2019	15:06	72	
Lab 83	PDMS	PAH	PAH SPME 4	80:20 water:methonal	120	5	cm	39480 ng/mL	250	9/24/2019	NA	72	2	cm	11/8/2019	15:09	72	
Lab 83	PDMS	PAH	PAH SPME 5	80:20 water:methonal	120	5	cm	39480 ng/mL	250	9/24/2019	NA	72	2	cm	11/8/2019	15:12	72	
Lab 83	PDMS	PAH	PAH SPME 6	80:20 water:methonal	120	5	cm	39480 ng/mL	250	9/24/2019	NA	72	2	cm	11/8/2019	15:15	72	
Lab 83	PDMS	PCB	PCB SPME 1	80:20 water:methonal	120	10	cm	1579 ng/mL	250 *	9/24/2019	NA	72	10	cm	11/8/2019	14:18	72	
Lab 83	PDMS	PCB	PCB SPME 2	80:20 water:methonal	120	10	cm	1579 ng/mL	250 *	9/24/2019	NA	72	10	cm	11/8/2019	14:21	72	
Lab 83	PDMS	PCB	PCB SPME 3	80:20 water:methonal	120	10	cm	1579 ng/mL	250 *	9/24/2019	NA	72	10	cm	11/8/2019	14:24	72	fluoranthene 574 chrysene 513 indeno(1,2,3-cd)pyrene 501
Lab 83	PDMS	PCB	PCB SPME 4	80:20 water:methonal	120	10	cm	1579 ng/mL	250 *	9/24/2019	NA	72	10	cm	11/8/2019	14:27	72	
Lab 83	PDMS	PCB	PCB SPME 5	80:20 water:methonal	120	10	cm	1579 ng/mL	250 *	9/24/2019	NA	72	10	cm	11/8/2019	14:30	72	
Lab 83	PDMS	PCB	PCB SPME 6	80:20 water:methonal	120	10	cm	1579 ng/mL	250 *	9/24/2019	NA	72	10	cm	11/8/2019	14:33	72	
Lab 84	PE	PAH	8	water only	1000	5	mg	500 ug/g	500	9/20/2019	14:00		5	mg	10/29/2019			
Lab 84	PE	PAH	9	water only	1000	5	mg	500 ug/g	500	9/20/2019	14:00		5	mg	10/29/2019			
Lab 84	PE	PAH	10	water only	1000	5	mg	500 ug/g	500	9/20/2019	14:00		5	mg	10/29/2019			
Lab 84	PE	PAH	11	water only	1000	5	mg	500 ug/g	500	9/20/2019	14:00		4	mg	10/29/2019			
Lab 84	PE	PAH	12	water only	1000	5	mg	500 ug/g	500	9/20/2019	14:00		5	mg	10/29/2019			
Lab 84	PE	PCB	1	water only	2000	25	mg	10 ug/g	100	9/20/2019	14:00		25	mg	10/29/2019			all polyethylene sheets were submerged by piercing w/pipette
Lab 84	PE	PCB	2	water only	2000	25	mg	10 ug/g	100	9/20/2019	14:00		25	mg	10/29/2019			
Lab 84	PE	PCB	3	water only	2000	25	mg	10 ug/g	100	9/20/2019	14:00		24	mg	10/29/2019			Temperature in the lab during this time ranged from 20 to 22 degrees C.
Lab 84	PE	PCB	4	water only	2000	25	mg	10 ug/g	100	9/20/2019	14:00		24	mg	10/29/2019			
Lab 84	PE	PCB	5	water only	2000	25	mg	10 ug/g	100	9/20/2019	14:00		25	mg	10/29/2019			
Lab 84	PE	PCB	6	water only	2000	25	mg	10 ug/g	100	9/20/2019	14:00		24	mg	10/29/2019			
Lab 98	PDMS	PAH	19	80:20 water:methanol	100	5	cm	39480 ng/mL	500	9/22/2019	15:30	(not recorded)	2	cm	10/30/2019	(not recorded)	(not recorded)	
Lab 98	PDMS	PAH	20	80:20 water:methanol	100	5	cm	39480 ng/mL	500	9/22/2019	15:30		2	cm	10/30/2019			
Lab 98	PDMS	PAH	21	80:20 water:methanol	100	5	cm	39480 ng/mL	500	9/22/2019	15:30		2	cm	10/30/2019			
Lab 98	PDMS	PAH	22	80:20 water:methanol	100	5	cm	39480 ng/mL	500	9/22/2019	15:30		2	cm	10/30/2019			
Lab 98	PDMS	PAH	23	80:20 water:methanol	100	5	cm	39480 ng/mL	500	9/22/2019	15:30		2	cm	10/30/2019			
Lab 98	PDMS	PAH	24	80:20 water:methanol	100	5	cm	39480 ng/mL	500	9/22/2019	15:30		2	cm	10/30/2019			
Lab 98	PDMS	PCB	13	80:20 water:methanol	100	10	cm	474 ng/mL	100	9/22/2019	15:30		10	cm	10/30/2019			
Lab 98	PDMS	PCB	14	80:20 water:methanol	100	10	cm	474 ng/mL	100	9/22/2019	15:30		10	cm	10/30/2019			
Lab 98	PDMS	PCB	15	80:20 water:methanol	100	10	cm	474 ng/mL	100	9/22/2019	15:30		10	cm	10/30/2019			
Lab 98	PDMS	PCB	16	80:20 water:methanol	100	10	cm	474 ng/mL	100	9/22/2019	15:30		10	cm	10/30/2019			
Lab 98	PDMS	PCB	17	80:20 water:methanol	100	10	cm	474 ng/mL	100	9/22/2019	15:30		10	cm	10/30/2019			
Lab 98	PDMS	PCB	18	80:20 water:methanol	100	10	cm	474 ng/mL	100	9/22/2019	15:30		10	cm	10/30/2019			
Lab 52	Details Not Available																	
Lab 38	PDMS	PAH	1	80:20 water:methonal	100	5	cm	15792 ng/mL	200	9/2/2019	10:30	69	2	cm	10/3/2019	10:30	69	
Lab 38	PDMS	PAH	2	80:20 water:methonal	100	5	cm	15792 ng/mL	200	9/2/2019	-	69	2	cm	10/3/2019	-	69	
Lab 38	PDMS	PAH	3	80:20 water:methonal	100	5	cm	15792 ng/mL	200	9/2/2019	-	69	2	cm	10/3/2019	-	69	
Lab 38	PDMS	PAH	4	80:20 water:methonal	100	5	cm	15792 ng/mL	200	9/2/2019	-	69	2	cm	10/3/2019	-	69	
Lab 38	PDMS	PAH	5	80:20 water:methonal	100	5	cm	15792 ng/mL	200	9/2/2019	-	69	2	cm	10/3/2019	-	69	
Lab 38	PDMS	PAH	6	80:20 water:methonal	100	5	cm	15792 ng/mL	200	9/2/2019	-	69	2	cm	10/3/2019	-	69	

Lab 38	PDMS	PCB	1	80:20 water:methonal	100	10	cm	790 ng/mL	50	9/2/2019	-	69	10	cm	10/3/2019	-	69
Lab 38	PDMS	PCB	2	80:20 water:methonal	100	10	cm	790 ng/mL	50	9/2/2019	-	69	10	cm	10/3/2019	-	69
Lab 38	PDMS	PCB	3	80:20 water:methonal	100	10	cm	790 ng/mL	50	9/2/2019	-	69	10	cm	10/3/2019	-	69
Lab 38	PDMS	PCB	4	80:20 water:methonal	100	10	cm	790 ng/mL	50	9/2/2019	-	69	10	cm	10/3/2019	-	69
Lab 38	PDMS	PCB	5	80:20 water:methonal	100	10	cm	790 ng/mL	50	9/2/2019	-	69	10	cm	10/3/2019	-	69
Lab 38	PDMS	PCB	6	80:20 water:methonal	100	10	cm	790 ng/mL	50	9/2/2019	12:20	69	10	cm	10/3/2019	11:20	69
Lab 48	Details Not Available																
Lab 15	Details Not Available																

PRC Loading #2

Lab ID	Sampler Type	PRCs	Sample ID	Loading Solution	Loading Solution Volume (mL)	Estimate Sampler Mass/ Length	Designed Loaded Concentration	Designed Extract Solvent Volume (uL)	Original PRCs Spiked Date	PRCs Spiked Time	Temperature (F)	Modified Date	Extracted C0 Sampler Mass/ Length	C0 Retrieved Date	Retrieved Time	Temperature (F)	Note
Lab 50	PE	PAH	1	water only	960	1 mg	500 ug/g	1000	8/19/2019	10:20	71	12/20/2019	1.4 mg	1/22/2020	10:30	71	The PE stripes loaded with PAHs were sepreated by mesh metal bags and kept submerged.
Lab 50	PE	PAH	2	water only	960	1 mg	500 ug/g	1000	8/19/2019	10:20	71	12/20/2019	0.8 mg	1/22/2020	10:35	71	6 pieces of 1cm x 1cm PE were cutted from different PAH loaded PE for the second batch analysis.
Lab 50	PE	PAH	3	water only	960	1 mg	500 ug/g	1000	8/19/2019	10:20	71	12/20/2019	1.2 mg	1/22/2020	10:40	71	
Lab 50	PE	PAH	4	water only	960	1 mg	500 ug/g	1000	8/19/2019	10:20	71	12/20/2019	1.1 mg	1/22/2020	10:45	71	
Lab 50	PE	PAH	5	water only	960	1 mg	500 ug/g	1000	8/19/2019	10:20	71	12/20/2019	1.3 mg	1/22/2020	10:50	71	
Lab 50	PE	PAH	6	water only	960	1 mg	500 ug/g	1000	8/19/2019	10:20	71	12/20/2019	1.6 mg	1/22/2020	10:55	71	
Lab 50	PE	PCB	1	water only	2000	5 mg	10 ug/g	1000	8/19/2019	10:30	71	12/20/2019	5.7 mg	1/22/2020	11:00	71	Most of the PE stripes loaded with PCBs were put into mesh metal bags to keep seperated.
Lab 50	PE	PCB	2	water only	2000	5 mg	10 ug/g	1000	8/19/2019	10:30	71	12/20/2019	5.5 mg	1/22/2020	11:05	71	Several PE PCB sheets were seperated by a piercing metal line.
Lab 50	PE	PCB	3	water only	2000	5 mg	10 ug/g	1000	8/19/2019	10:30	71	12/20/2019	7 mg	1/22/2020	11:10	71	6 pieces of 1cm x 5cm PE were cutted from different PCB loaded PE for the second batch analysis.
Lab 50	PE	PCB	4	water only	2000	5 mg	10 ug/g	1000	8/19/2019	10:30	71	12/20/2019	6.5 mg	1/22/2020	11:15	71	
Lab 50	PE	PCB	5	water only	2000	5 mg	10 ug/g	1000	8/19/2019	10:30	71	12/20/2019	5.2 mg	1/22/2020	11:20	71	
Lab 50	PE	PCB	6	water only	2000	5 mg	10 ug/g	1000	8/19/2019	10:30	71	12/20/2019	7 mg	1/22/2020	11:25	71	
Lab 9	PDMS	PAH	1	80:20 water:methanol	100	5 cm	19740 ng/mL	250	10/10/2019	14:30	71	\	2 cm	1/30/2020	9:00	71	6x2cm PDMS PAH samples were taken at the second batch.
Lab 9	PDMS	PAH	2	80:20 water:methanol	100	5 cm	19740 ng/mL	250	10/10/2019	14:30	71	\	2 cm	1/30/2020	9:03	71	
Lab 9	PDMS	PAH	3	80:20 water:methanol	100	5 cm	19740 ng/mL	250	10/10/2019	14:30	71	\	2 cm	1/30/2020	9:06	71	
Lab 9	PDMS	PAH	4	80:20 water:methanol	100	5 cm	19740 ng/mL	250	10/10/2019	14:30	71	\	2 cm	1/30/2020	9:09	71	
Lab 9	PDMS	PAH	5	80:20 water:methanol	100	5 cm	19740 ng/mL	250	10/10/2019	14:30	71	\	2 cm	1/30/2020	9:12	71	
Lab 9	PDMS	PAH	6	80:20 water:methanol	100	5 cm	19740 ng/mL	250	10/10/2019	14:30	71	\	2 cm	1/30/2020	9:15	71	
Lab 9	PDMS	PCB	1	80:20 water:methanol	100	10 cm	790 ng/mL	50	8/19/2019	10:45	71	\	10 cm	9/23/2019	14:18	71	We don't have enough PDMS PCB samples for the second batch C0 analysis.
Lab 9	PDMS	PCB	2	80:20 water:methanol	100	10 cm	790 ng/mL	50	8/19/2019	10:45	71	\	10 cm	9/23/2019	14:21	71	
Lab 9	PDMS	PCB	3	80:20 water:methanol	100	10 cm	790 ng/mL	50	8/19/2019	10:45	71	\	10 cm	9/23/2019	14:24	71	
Lab 9	PDMS	PCB	4	80:20 water:methanol	100	10 cm	790 ng/mL	50	8/19/2019	10:45	71	\	10 cm	9/23/2019	14:27	71	
Lab 9	PDMS	PCB	5	80:20 water:methanol	100	10 cm	790 ng/mL	50	8/19/2019	10:45	71	\	10 cm	9/23/2019	14:30	71	
Lab 9	PDMS	PCB	6	80:20 water:methanol	100	10 cm	790 ng/mL	50	8/19/2019	10:45	71	\	10 cm	9/23/2019	14:33	71	
Lab 58	PE	PAH	7	water only	1000	1 mg	500 ug/g	100	8/30/2019	9:30	RoomTemp	12/20/2019	1.1 mg	1/30/2020	14:22	RoomTemp	
Lab 58	PE	PAH	8	water only	1000	1 mg	500 ug/g	100	8/30/2019	9:30	71	12/20/2019	1.5 mg	1/30/2020	14:22	71	6 pieces of 1cm x 0.5cm PE were cut from different PAH loaded PE for the second batch analysis.
Lab 58	PE	PAH	9	water only	1000	1 mg	500 ug/g	100	8/30/2019	9:30	71	12/20/2019	1.3 mg	1/30/2020	14:22	71	
Lab 58	PE	PAH	10	water only	1000	1 mg	500 ug/g	100	8/30/2019	9:30	71	12/20/2019	1.6 mg	1/30/2020	14:22	71	
Lab 58	PE	PAH	11	water only	1000	1 mg	500 ug/g	100	8/30/2019	9:30	71	12/20/2019	1.3 mg	1/30/2020	14:22	71	
Lab 58	PE	PAH	12	water only	1000	1 mg	500 ug/g	100	8/30/2019	9:30	71	12/20/2019	1.5 mg	1/30/2020	14:22	71	
Lab 58	PE	PCB	1	water only	2000	5 mg	10 ug/g	100	8/30/2019	9:28	71	12/20/2019	6.1 mg	1/30/2020	14:15	71	
Lab 58	PE	PCB	2	water only	2000	5 mg	10 ug/g	100	8/30/2019	9:28	71	12/20/2019	6.2 mg	1/30/2020	14:15	71	
Lab 58	PE	PCB	3	water only	2000	5 mg	10 ug/g	100	8/30/2019	9:28	71	12/20/2019	5 mg	1/30/2020	14:15	71	6 pieces of 1cm x 2cm PE were cut from different PCB loaded PE for the second batch analysis.
Lab 58	PE	PCB	4	water only	2000	5 mg	10 ug/g	100	8/30/2019	9:28	71	12/20/2019	5.2 mg	1/30/2020	14:15	71	
Lab 58	PE	PCB	5	water only	2000	5 mg	10 ug/g	100	8/30/2019	9:28	71	12/20/2019	5.4 mg	1/30/2020	14:15	71	
Lab 58	PE	PCB	6	water only	2000	5 mg	10 ug/g	100	8/30/2019	9:28	71	12/20/2019	5 mg	1/30/2020	14:15	71	
Lab 34	PE	PAH	PAH PED 7	water only	800	1.25 mg	666.7 ug/g	1000	9/24/2019	NA	72	12/20/2019	1.47 mg	1/28/2020	NA	72	For the second round, the PEs were pulled out of the spiking jars, then each PE piece was wrapped in pre-cleaned stainless-sleel mesh to prohibit clumping together. The samplers were then returned ot the original spiking jars. The aluminum foil was removed from the lids but the agitation was still kept low to avoid sorption of PRCs to the talfon lid liner
Lab 34	PE	PAH	PAH PED 8	water only	800	1.25 mg	666.7 ug/g	1000	9/24/2019	NA	72	12/20/2019	1.51 mg	1/28/2020	NA	72	
Lab 34	PE	PAH	PAH PED 9	water only	800	1.25 mg	666.7 ug/g	1000	9/24/2019	NA	72	12/20/2019	1.5 mg	1/28/2020	NA	72	
Lab 34	PE	PAH	PAH PED 10	water only	800	1.25 mg	666.7 ug/g	1000	9/24/2019	NA	72	12/20/2019	1.54 mg	1/28/2020	NA	72	
Lab 34	PE	PAH	PAH PED 11	water only	800	1.25 mg	666.7 ug/g	1000	9/24/2019	NA	72	12/20/2019	1.5 mg	1/28/2020	NA	72	
Lab 34	PE	PAH	PAH PED 12	water only	800	1.25 mg	666.7 ug/g	1000	9/24/2019	NA	72	12/20/2019	1.42 mg	1/28/2020	NA	72	
Lab 34	PE	PCB	PCB PED 7	water only	800	1.25 mg	8.3 ug/g	1000	9/24/2019	NA	72	12/20/2019	6.29 mg	1/28/2020	NA	72	
Lab 34	PE	PCB	PCB PED 8	water only	800	1.25 mg	8.3 ug/g	1000	9/24/2019	NA	72	12/20/2019	7.07 mg	1/28/2020	NA	72	
Lab 34	PE	PCB	PCB PED 9	water only	800	1.25 mg	8.3 ug/g	1000	9/24/2019	NA	72	12/20/2019	6.51 mg	1/28/2020	NA	72	

Lab 34	PE	PCB	PCB PED 10	water only	800	1.25 mg	8.3 ug/g	1000	9/24/2019	NA	72	12/20/2019	7.28 mg	1/28/2020	NA	72	the carbon number.	
Lab 34	PE	PCB	PCB PED 11	water only	800	1.25 mg	8.3 ug/g	1000	9/24/2019	NA	72	12/20/2019	6.55 mg	1/28/2020	NA	72		
Lab 34	PE	PCB	PCB PED 12	water only	800	1.25 mg	8.3 ug/g	1000	9/24/2019	NA	72	12/20/2019	5.58 mg	1/28/2020	NA	72		
Lab 83	PDMS	PAH	NA	80:20 water:methanol	120	5 cm	39480 ng/mL	250	9/24/2019	NA	72	NA	2 cm	NA	NA	72	Not analyzed for the second time; original results looked good.	
Lab 83	PDMS	PAH	NA	80:20 water:methanol	120	5 cm	39480 ng/mL	250	9/24/2019	NA	72	NA	2 cm	NA	NA	72		
Lab 83	PDMS	PAH	NA	80:20 water:methanol	120	5 cm	39480 ng/mL	250	9/24/2019	NA	72	NA	2 cm	NA	NA	72		
Lab 83	PDMS	PAH	NA	80:20 water:methanol	120	5 cm	39480 ng/mL	250	9/24/2019	NA	72	NA	2 cm	NA	NA	72		
Lab 83	PDMS	PAH	NA	80:20 water:methanol	120	5 cm	39480 ng/mL	250	9/24/2019	NA	72	NA	2 cm	NA	NA	72		
Lab 83	PDMS	PAH	NA	80:20 water:methanol	120	5 cm	39480 ng/mL	250	9/24/2019	NA	72	NA	2 cm	NA	NA	72		
Lab 83	PDMS	PCB	NA	80:20 water:methanol	120	10 cm	1579 ng/mL	250 *	9/24/2019	NA	72	NA	10 cm	NA	NA	72	* For extraction of time zero PCB SPMEs 250 uL volume was used, however the spiking level was designe based on 100 uL volume planned for sediment SPME	
Lab 83	PDMS	PCB	NA	80:20 water:methanol	120	10 cm	1579 ng/mL	250 *	9/24/2019	NA	72	NA	10 cm	NA	NA	72		
Lab 83	PDMS	PCB	NA	80:20 water:methanol	120	10 cm	1579 ng/mL	250 *	9/24/2019	NA	72	NA	10 cm	NA	NA	72		
Lab 83	PDMS	PCB	NA	80:20 water:methanol	120	10 cm	1579 ng/mL	250 *	9/24/2019	NA	72	NA	10 cm	NA	NA	72		
Lab 83	PDMS	PCB	NA	80:20 water:methanol	120	10 cm	1579 ng/mL	250 *	9/24/2019	NA	72	NA	10 cm	NA	NA	72		
Lab 83	PDMS	PCB	NA	80:20 water:methanol	120	10 cm	1579 ng/mL	250 *	9/24/2019	NA	72	NA	10 cm	NA	NA	72		
Lab 84	PE	PAH	7	water only	1000	1.25 mg	500 ug/g	500	9/20/2019	14:00 (not recorded)			1.49 mg	1/24/2020 (not recorded)	(not recorded)	actual PAH mass:	phenanthrene	880
Lab 84	PE	PAH	8	water only	1000	1.25 mg	500 ug/g	500	9/20/2019	14:00			1.25 mg	1/24/2020			fluoranthene	574
Lab 84	PE	PAH	9	water only	1000	1.25 mg	500 ug/g	500	9/20/2019	14:00			1.62 mg	1/24/2020			chrysene	513
Lab 84	PE	PAH	10	water only	1000	1.25 mg	500 ug/g	500	9/20/2019	14:00			1.71 mg	1/24/2020			indeno(1,2,3-cd)pyr	501
Lab 84	PE	PAH	11	water only	1000	1.25 mg	500 ug/g	500	9/20/2019	14:00			1.22 mg	1/24/2020				
Lab 84	PE	PAH	12	water only	1000	1.25 mg	500 ug/g	500	9/20/2019	14:00			1.74 mg	1/24/2020				
Lab 84	PE	PCB	1	water only	2000	5 mg	10 ug/g	100	9/20/2019	14:00			6 mg	1/24/2020			all polyethylene sheets were submerged by piercing w/pipette	
Lab 84	PE	PCB	2	water only	2000	5 mg	10 ug/g	100	9/20/2019	14:00			5 mg	1/24/2020				
Lab 84	PE	PCB	3	water only	2000	5 mg	10 ug/g	100	9/20/2019	14:00			6 mg	1/24/2020				
Lab 84	PE	PCB	4	water only	2000	5 mg	10 ug/g	100	9/20/2019	14:00			7 mg	1/24/2020				
Lab 84	PE	PCB	5	water only	2000	5 mg	10 ug/g	100	9/20/2019	14:00			5 mg	1/24/2020				
Lab 84	PE	PCB	6	water only	2000	5 mg	10 ug/g	100	9/20/2019	14:00			8 mg	1/24/2020				
Lab 52	Details Not Available																	
Lab 98	PDMS	PAH															PDMS were not part of the re-extraction process	
Lab 98	PDMS	PAH																
Lab 98	PDMS	PAH																
Lab 98	PDMS	PAH																
Lab 98	PDMS	PAH																
Lab 98	PDMS	PAH																
Lab 98	PDMS	PCB																
Lab 98	PDMS	PCB																
Lab 98	PDMS	PCB																
Lab 98	PDMS	PCB																
Lab 98	PDMS	PCB																
Lab 98	PDMS	PCB																
Lab 48	Data Not Available																	
Lab 15	Data Not Available																	

APPENDIX G-2
Extract Concentrations

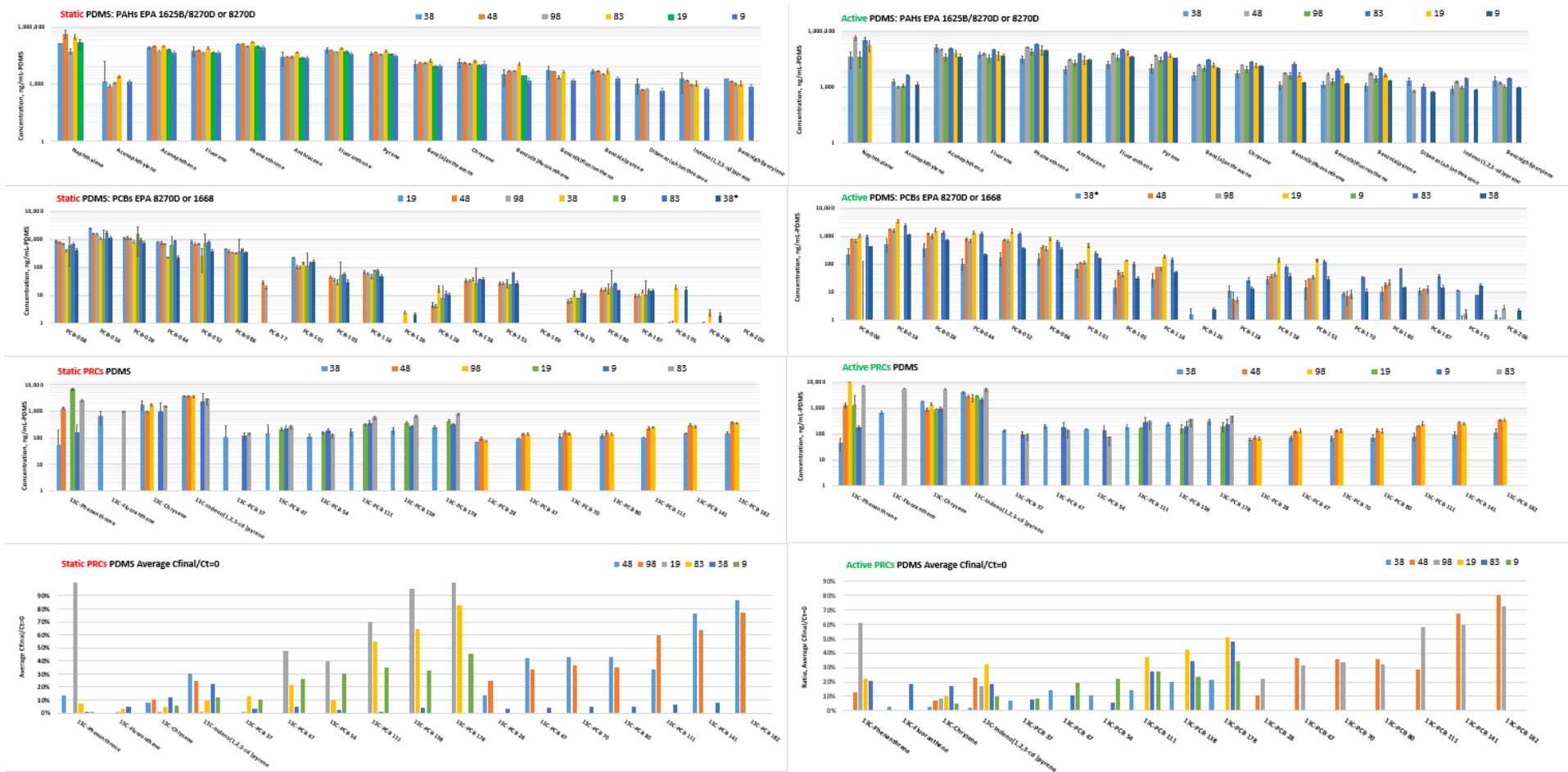


Figure G-2. Task 3 PDMS extract concentrations for active and static exposures

APPENDIX G-3
Data Validation Reports

Data Validation Report

Standardizing Polymeric Sampling for Measuring Freely Dissolved Organic Contaminants in Sediment Porewater ER 201735

Task 3 – Day Zero Loading and Analysis of Polyethylene Strips (First Study)

Prepared for:

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August 27, 2020

ACRONYMS

%D	percent difference
%D_f	percent drift
%R	percent recovery
%RSD	percent relative standard deviation
CCV	continuing calibration verification
COC	chain-of-custody
CS1	the first calibration standard
CS3	the third calibration standard
EDD	electronic data deliverable
EDL	estimated detection limit
EMPC	estimated maximum possible concentration
EPA	U.S. Environmental Protection Agency
HRGC/ HRMS	high-resolution gas chromatography/high-resolution mass spectrometry
ICAL	initial calibration
ICV	initial calibration verification
IPR	initial precision and recovery
LCL	lower control limit
LCS	laboratory control sample
LCSD	laboratory control sample duplicate
LDPE	low density polyethylene
LIMs	laboratory information management system
m/z	mass-to-charge ratio
MB	method blank
MDL	method detection limit
MIT	Massachusetts Institute of Technology
MS	matrix spike
MSD	matrix spike duplicate
ng/g	nanogram per gram
OPR	ongoing precision and recovery
PCB	polychlorinated biphenyl
PE	polyethylene
PFK	perfluorokerosene
PRC	performance reference compound
QA/QC	quality assurance/quality control
QAPP	quality assurance project plan
RF	response factor
RPD	relative percent difference
RRT	relative retention time
SDG	sample delivery group

SICP	selected ion current profile
S/N	signal-to-noise ratio
SOP	standard operating procedure
USACE	US Army Corps of Engineers

Each of the participating laboratories received 14 10cm polyethylene (PE) strips contained in a capped vial from the Massachusetts Institute of Technology (MIT). Six of the strips were subject for PCB performance reference compounds (PRCs) loading; six for PAH PRCs loading; and two samples designated as method blanks - one for each of the PCBs and PAHs analysis. Target PCB and PAH PRCs were identified in the Project Demonstration Plan (USACE *et. al.*, 2018), and the target PRCs and their concentrations for respective analytical methods are summarized as follows:

PCBs by EPA 1668C			PCBs by EPA 8270D-SIM				PAHs by EPA 8270D-SIM & EPA 1625C			
	Target ^(A) Concentration			Target ^(A) Concentration				Target ^(A) Concentration		
PRCs	(ng/g-LDPE)		PRCs	(ng/g-LDPE)			PRCs	(ng/g-LDPE)		
¹³ C-PCB 28	502	1000	¹³ C-PCB 37	500	522	1000	¹³ C ₆ -Phenanthrene ¹³ C ₆ -Fluoranthene ¹³ C ₆ -Chrysene ¹³ C ₆ -Indeno[1,2,3-cd]pyrene	500	498	991
¹³ C-PCB 47	532	1000	¹³ C-PCB 47	500	532	1000				
¹³ C-PCB 70	544	1000	¹³ C-PCB 54	500	423	1000				
¹³ C-PCB 80	516	1000	¹³ C-PCB 111	500	488	1000				
¹³ C-PCB 111	488	1000	¹³ C-PCB 138	500	531	1000				
¹³ C-PCB 141	517	1000	¹³ C-PCB 178	500	571	1000	500	521	1000	
¹³ C-PCB 182	913	1000					500	510	988	
							500	517	950	

(A) – Target concentrations were back-calculated based on LDPE sampler loading conditions determined by the laboratories and thus the concentrations varied with laboratories.

Participating commercial laboratories and respective analytical methodologies applied to this study are summarized as follows:

Participating Commercial Laboratory	Analytical Method	
	PCB Congeners	PAHs
Laboratory 58	SW846 Method 8270D Modified	SW846 Method 8270D Modified
Laboratory 84	EPA Method 1668C	SW846 Method 8270D Modified EPA Method 1625
Laboratory 52	EPA Method 1668C	SW846 Method 8270D Modified EPA Method 1625
Laboratory 34	SW846 Method 8270D Modified	SW846 Method 8270D Modified

Notes:

1. USEPA Method 1668C: *Chlorinated Biphenyl Congeners in Water, Soil, Sediment, Biosolids, and Tissue* by HRGC/HRMS. April 2010.
2. Method 1625C: *Semi-volatile Organic Compounds by Isotope Dilution GCMS*. June 1989.
3. SW846 - USEPA Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Third Edition, December 1996.

Laboratories throughout this report are referred to using random number assignments to ensure the anonymity of participating commercial laboratories. Each participating laboratory was required to submit analytical deliverables for each analysis, including (1) a Level IV full data package containing reporting forms and all raw data supporting the reported sample and QC analyses results, and (2) an electronic data deliverable (EDD) in the Washington State Department of Ecology's Environmental Information Management System (EIMs) format. The laboratory could choose to submit the EDDs in Excel or csv. format. Each laboratory report and EDD were assigned a unique sample delivery group (SDG) number. Laboratory deliverables, after fully validated, were archive in the project file at the US Army Corps of Engineers Seattle District. SDG numbers assigned by each laboratory are summarized as follows:

Participating Commercial Laboratory	Sample Delivery Group or Laboratory Identification Number	
	PCB Congeners	PAHs
Laboratory 58	19I0479	19I0479
Laboratory 84	140-17156	140-17156
Laboratory 52	DPWG71530	DPWG71255
Laboratory 34	DP-19-0980	DP-19-0981

Final sample results were reported as ng/g-LDPE, based on the conversion conventions provided by MIT. Values reported in the laboratory reports did not present this conversion, but

in separate EDDs due to the limitations posed by the laboratories' information management systems (LIMs).

A Stage 4 validation (as defined by EPA 2009) was performed on all PCB congener and PAHs data. The validation followed guidance specified by EPA (2014, 2016 & 2017), with modifications to accommodate respective analytical methods and requirements specified in the Standard Operating Procedures (SOPs) provided by the participating commercial laboratories. The numerical quality assurance/quality control (QA/QC) criteria applied to the validation were in accordance with method requirements and the current performance-based control limits established by the laboratory (laboratory control limits). Instrument calibration, frequency of QC analyses, and analytical sequence requirements were evaluated against the respective analytical methods. QC Criteria are summarized in *Appendix A, Tables A1 and A2*.

Validation findings are discussed in each section pertinent to the QC parameter for each type of analysis. Qualified data with applied data qualifiers are summarized in the **Summary** section at the end of this report.

DATA VALIDATION FINDINGS

1. PCB Congeners by EPA Method 1668C: High-resolution Gas Chromatography and High-resolution Mass Spectrometry (HRGC/HRMS)

Two participating commercial laboratories – Laboratory 52 and Laboratory 84 chose to use EPA Method 1668C for the study. Note that neither EPA Method 1668C nor laboratory SOPs specified evaluation criteria for carbon-labeled PCBs. However, unless noted otherwise, criteria set forth for non-labeled PCBs in the method and SOPs were applied for carbon-labeled PCB data quality and method compliance evaluation.

1.1 Sample Management and Holding time

No anomalies were noted by the laboratories in relation to sample packaging, transportation, handling, preservation, and integrity upon sample receipt in the laboratories.

EPA Method 1668C does not specify holding time requirements for PE samples (submerged in loading solution). Holding time requirements for solid samples (one year from collection to extraction, 40 days from extraction to analysis) were applied as a guideline for sample and extract holding time evaluation. Samples were extracted and analyzed within the holding times by both laboratories.

1.2 HRGC/HRMS Instrument Performance Check

The EPA Method 1668C criteria for instrument performance checks are as follows:

Mass Spectrometer Resolution: (1) The resolution check should be performed, using perfluorokerosene (PFK) or equivalent standard materials, prior to initial calibration and at the start and end of each 12-hour shift, (2) the resolution should be $\geq 8,000$ throughout the mass range and $\geq 10,000$ resolving power at m/z 330.9792 (or any other significant PFK fragments in the range of 300 to 350), and (3) the deviation between the exact m/z and the theoretical m/z must be less than 5 ppm for monitored isomers.

Column Performance: (1) A combined 209 congener standard should be analyzed prior to initial calibration and continuing calibration verification, (2) peak for congener 34 should be resolved from 23 and peak for congener 187 resolved from 182 peak with a valley of $\leq 40\%$, (3) congeners 156 and 157 should co-elute within 2 seconds at their peak maximum, and (4) the absolute retention time (RT) for congener 209 should be >55 minute for SPB-octyl or an alternate column.

In addition to the method requirements, laboratories imposed more criteria based on their specific instrumentation. HRGC/HRMS instrument performance checks met the method and SOP criteria for these laboratories.

1.3 Initial Calibration (ICAL)

Laboratory 84 chose to fully follow the EPA Method 1668C initial calibration (ICAL) for the ^{13}C -labeled PCB PRCs. The EPA Method 1668C criteria for initial calibration are: (1) a minimum of five standards should be employed for native congeners and labeled compounds, (2) the percent relative standard deviation (%RSD) of isomer response should be $\leq 20\%$, (3) the ion abundance ratios should be within the control limits listed in EPA Method 1668C, Table 8, (4) the signal-to-noise (S/N) ratio should be >10 for all native and labeled compounds in the first calibration standard (CS1), and (5) response factor (RF) should be determined using one- point calibration for congeners quantitated with internal standard method. Initial calibrations met the criteria. An initial calibration verification (second source) standard was analyzed to verify the calibration curve. The percent difference (%D) values were less than or equal to 30% and the initial calibration was considered valid.

Laboratory 52 followed their SOP to establish ICAL for the ^{13}C -labeled PCB PRCs. A mid-point calibration standard was analyzed at the beginning and the end of the analytical sequence. The response factor RPD values for the target compounds and surrogate compounds should be within 20%, and RT within 3 seconds between the two analyses. The ICAL met the laboratory SOP requirements.

1.4 Calibration Verification (CCV)

The EPA Method 1668C criteria require that: (1) continuing calibration verifications be performed at the beginning of each 12-hour shift using the mid-point calibration standard (CS3), (2) the %D value should be within the control limits listed in EPA Method 1668C, Table 6, and (3) the ion abundance ratios, retention times, relative retention times, and S/N ratio should meet the same criteria as for initial calibrations. Note that the method did not specify ion abundance ratios for ^{13}C -labeled PRCs; laboratory-specified criteria were applied for data quality determination. All CCVs met the laboratory control criteria.

1.5 Method Blanks

The Laboratory 84 Method Blank was not extracted with a media, but with solvent only. The method blank serves as a 'reagent blank' to monitor background contamination not associated with the PRC loading process. PCB PRCs were not detected at or above the estimated detection limits (EDLs) in the reagent blank.

PCB PRCs were detected in Laboratory 52 Method Blank WG70637-101 at levels comparable to those in the actual PE strips. The blank strip appeared mistakenly exposed to the loading solution, along with those designated for PRC loading. Based on the previous study conducted in Task 2 and the Secondary Study conducted in Task 3, detections in the blanks were all at trace levels and had no effects on data usability. No further data qualifying action was taken in this case, other than noting this anomaly herein.

1.6 Initial Precision and Recovery Study (IPR)

IPR study results are normally maintained in the laboratory and were not included in data packages. This information will be required in data packages reported for the following phases of this study as needed.

1.7 Ongoing Precision and Recovery (OPR)

OPR was prepared and analyzed for PRC PCBs at the adequate frequency by Laboratory 52. The %R values met the laboratory control criteria.

1.8 Laboratory Control Sample (LCS)

Since no matrix-specific (*i.e.*, LDPE in this case) LCS was available to be processed along with the samples, the laboratories analyzed/reported laboratory-made standards as LCS. Due to the limited supplier and the excessive cost of the ¹³C-labelled PRCs, the LCS analyzed/reported by Laboratory 84 did not contain the target PRCs. However, the %R values in LCS were all within the laboratory control criteria.

OPR was prepared and analyzed in lieu of LCS by Laboratory 52. See discussion above.

1.9 Labeled Compound Recovery

Labeled internal standards were added to all samples as required by the analytical method and laboratory SOPs. The labeled internal standards and cleanup standards percent recoveries all met the method and laboratory SOP requirements.

Laboratory 52 noted that due to interference from high level PRC analyte, the labelled surrogate ¹³C-PCB 77L was not quantifiable for all the QC samples and client samples, and this surrogate has been flagged with 'NQ' on reports. Target analytes were quantified against alternative surrogates. No data qualifying action was taken. See discussion below in Section 1.11.

1.10 Target Compound Identification

Target compound identification was evaluated by examining if: (1) the signals for the two exact m/z's being monitored were present, and maximized within ± 2 seconds of one another (± 3 seconds for Laboratory 52), (2) the S/N ratio of each of the two exact m/z's must be greater than or equal to 2.5, (3) the ion abundance ratios were within the method control limits, and (4) the relative retention time (RRT) or retention time (RT) of the peaks were within the method control limits or laboratory control limits. No anomalies were found in relation to target compound identification.

1.11 Reporting Limits, Estimated Detection Limits (EDLs) and Compound Quantitation

Correct internal standards, quantitation ions, and average RFs were used to quantitate target

compound detections. The MRLs were supported with adequate ICAL calibration concentrations. The project goal for quantitation limits were attained to in these cases.

A verification calculation was performed on 10% of the reported calibration, laboratory QC analyses, and sample results. No anomalies were found. The verification calculation worksheets were maintained in project files for requests.

Response peak integrations were primarily performed automatically with computer software. In cases where peak shifting, signal interferences, and/or peak tailing occurred, manual integrations were performed. Manual integrations criteria and approaches were consistent justifiable across the analyses; no anomalies were identified in relation to compound identification and quantitation.

Laboratory 52 noted that due to interference from high level PRC analyte, the labelled surrogate ^{13}C -PCB 77L was not quantifiable for all the QC samples and client samples, and this surrogate has been flagged with 'NQ' on reports. The PRC analytes ^{13}C -PCB 47L, ^{13}C -PCB 70L and ^{13}C -PCB 80L were re-quantified against ^{13}C -PCB 54L and ^{13}C -PCB 81L instead of ^{13}C -PCB 54L, ^{13}C -PCB 77L and ^{13}C -PCB 81L. Since this alternative quantitation approach was applied throughout the analytical sequence, including all QC and actual samples, the results for the affected PRC analytes, ^{13}C -PCB 47L, ^{13}C -PCB 70L and ^{13}C -PCB 80L were unlikely biased significantly. No further data qualifying action was taken other than noting this deviation herein.

1.12 Overall Assessment of PCB Congener Data Usability

PCB congener data were of known quality and acceptable for use with the acknowledgement of deviations and anomalies discussion above.

2. PCB Congeners by GC/MS - SIM (EPA Method SW8270D-SIM)

Two laboratories, Laboratory 58 and Laboratory 34, chose to use EPA Method SW8270D-SIM for PCB congeners analysis. Note that neither EPA Method 8270D nor laboratory SOPs specified evaluation criteria for carbon-labeled PCBs. However, unless noted otherwise, criteria set forth for non-labeled PCBs in the method and SOPs were applied for ^{13}C -labeled PCBs data quality and method compliance evaluation.

2.1 Sample Management and Holding Times

No anomalies were noted by the laboratories in relation to sample packaging, transportation, handling, preservation, and integrity upon sample receipt in the laboratories.

EPA Method 8270D does not specify holding time requirements for PE samples (submerged in loading solution). Holding time requirements for solid sample (one year from collection to extraction, 40 days from extraction to analysis) were applied as a guideline for sample and extract holding time evaluation. Samples were extracted and analyzed within the holding

times by both laboratories.

2.2 GC/MS Instrument Performance Check

The laboratories performed GC/MS tuning analysis as required by the analytical method and their SOPs. DFTPP tuning was performed within each 12-hour interval. All required ion abundance ratios met the method requirements.

2.3 Initial Calibration (ICAL)

EPA Method 8270D criteria require that (1) if a linear average RFs is chosen as the quantitation option, at least five standards at different concentrations should be analyzed and the %RSD of RFs be $\leq 15\%$ ($\leq 25\%$ for Laboratory 34) for the analyte, (2) if least-square linear regression is chosen for quantitation, the correlation coefficient (r) be > 0.995 , and (3) if six-point non-linear (quadratic) curve is chosen for quantitation, the coefficient of determination (r^2) be > 0.99 . All ICALs met the method and laboratory criteria.

An ICV standard (second source standard) was analyzed to verify the calibration curve. Due to limited suppliers and excessive cost of the ^{13}C -labeled PRCs, the second source standards used by both laboratories contained non-labelled PCBs rather than the ^{13}C -labeled PCB PRCs. The %D values were within ± 20 . The ICALs were considered valid.

2.4 Calibration Verification (CCV)

The analytical method requires that (1) continuing calibration verifications be analyzed at the beginning of each 12-hour analysis period prior to the analysis of method blank and samples, and (2) the %D be within $\pm 20\%$ ($\pm 25\%$ for Laboratory 34). All CCVs met the method and laboratory criteria.

2.5 Method Blanks

Method blanks were prepared and analyzed as required. Target PCB PRCs were not detected at or above the method detection limits (MDLs).

2.6 Surrogate Spikes

Surrogate spikes were added to all samples as required by the method. All surrogate spike %R values were within the control limits specified in the laboratory SOPs.

2.7 Matrix Spike (MS) and MS Duplicate (MSD)

MS and MSD analyses were not applicable for the calibration standard analysis.

2.8 Laboratory Control Sample (LCS) and LCS Duplicate (LCSD)

LCS/LCSD were not prepared by Laboratory 58. LCS was prepared and analyzed by

Laboratory 34. The %R values met the laboratory control limits.

2.9 Internal Standards

The method requires that (1) internal standard retention time be within ± 30 seconds from that of the associated 12-hour calibration standard, and (2) the area counts of all internal standards be within -50% to $+100\%$ of the associated 12-hour calibration standard. Laboratory 34 chose to use those of the mid-point ICAL standard for internal standard recovery control criteria. Internal standard recovery met the method or laboratory requirements.

2.10 Target Compound Identification

All chromatograms were properly displayed and scaled. No target compounds were detected in any of the field samples. No anomalies were found in relation to target compound identification.

2.11 Reporting Limits and Target Compound Quantitation

Re-calculation was performed on 10% of the instrument calibration and reported QC and sample analyses. No anomalies were found via the verification calculation. MRLs were supported with adequate initial calibration concentrations. In cases where target compound concentrations exceeded ICAL calibration ranges, extracts were diluted and re-analyzed for definitive quantitation..

Response peak integrations were primarily performed automatically with computer software. In cases where peak shifting, signal interferences, and/or peak tailing occurred, manual integrations were performed. Manual integrations criteria and approaches were consistent justifiable across the analyses; no anomalies were identified in relation to compound identification and quantitation.

2.12 Overall Assessment of PCB Congeners Data Usability

PCB Congeners data are of known quality and acceptable for use, with the acknowledgement of SOP deviations and anomalies stated above.

3. PAHs by Isotope Dilution GC/MS (EPA Method SW8270D Modified and EPA Method 1625 Modified)

Laboratory 52 and Laboratory 84 chose to use EPA Method SW8270D modified with EPA Method 1625 for this study. Note that neither EPA Method 8270D, EPA Method 1625 nor laboratory SOPs specified evaluation criteria for carbon-labeled PAHs. However, unless noted otherwise, criteria set forth for non-labeled PAHs in the methods and SOPs were applied for PAH PRC data quality and method compliance evaluation.

3.1 Sample Management and Holding Times

No anomalies were noted by the laboratories in relation to sample packaging, transportation, handling, preservation, and integrity upon sample receipt in the laboratories.

EPA Method 8270D does not specify holding time requirements for PE samples (submerged in loading solution). Holding time requirements for solid sample (one year from collection to extraction, 40 days from extraction to analysis) were applied as a guideline for sample and extract holding time evaluation. Samples were extracted and analyzed within the holding times by both laboratories.

3.2 GC/MS Instrument Performance Check

The method requires that DFTPP tuning be performed within each 12-hour interval. All required ion abundance ratios should meet the requirements in the method. Each of the laboratories specified GC/MS tuning procedures and requirements in their SOPs. However, tuning reports were not included in their data package in this task. This information will be required for all data packages in future sample analyses for this study.

3.3 Initial Calibration (ICAL)

Laboratory 84 chose to fully follow the method requirements to establish ICAL for $^{13}\text{C}_6$ -Labeled PAH PRCs. The method ICAL criteria require that (1) if linear average RF is chosen as the quantitation option, , (2) if least-square linear regression is chosen for quantitation, the correlation coefficient (r) be >0.995 , and (3) if six-point non-linear (quadratic) curve is chosen for quantitation, the coefficient of determination (r^2) be >0.99 . An ICV standard (second source standard) was analyzed to verify the calibration curve. The %D values were within $\pm 20\%$. The ICALs were considered valid.

Laboratory 52 followed their SOP to establish ICAL for the $^{13}\text{C}_6$ -Labeled PAH PRCs. A mid-point calibration standard was analyzed at the beginning and the end of the analytical sequence. The response factor %RSD values for the target compounds and surrogate compounds should be within 20%, and RT within 3 seconds between the two analyses. The ICAL met the laboratory SOP requirements.

3.4 Calibration Verification (CCV)

The analytical method requires that (1) continuing calibration verifications be analyzed at the beginning of each 12-hour analysis period prior to the analysis of method blank and samples, and (2) the %D be within $\pm 20\%$. All CCVs or OPRs met the laboratory control criteria.

3.5 Method Blanks

Method blanks were prepared and analyzed as required. Target PAH PRCs were not detected at or above the MDLs for Laboratory 84. PAH PRCs were detected in Laboratory 52 Method

Blank WG70638-101 at levels comparable to those in the actual PE strips. The blank strip appeared mistakenly exposed to the loading solution, along with those designated for PRC loading. Based on the previous study conducted in Task 2 and the Secondary Study conducted in Task 3, detections in the blanks were all at trace levels and had no effects on data usability. No further data qualifying action was taken in this case, other than noting this anomaly herein.

3.6 Surrogate Spikes

Surrogate spikes were added to all samples as required by the method. All surrogate spike %R values were within the control limits specified in the laboratory SOPs.

3.7 Laboratory Control Sample (LCS)

Since no matrix-specific (i.e., LDPE in this case) LCS was available to be processed along with the samples, the laboratories analyzed/reported laboratory-made standards as LCS. Due to the limited supplier and the excessive cost of the ¹³C-labelled PRCs, the LCS analyzed/reported by Laboratory 84 did not contain the target PRCs. However, the %R values in LCS were all within the laboratory control criteria.

OPR was prepared and analyzed in lieu of LCS by Laboratory 52. See discussion below.

3.8 Ongoing Precision and Recovery (OPR)

OPR was prepared and analyzed for PRC PCBs at the adequate frequency by Laboratory 52. The %R values met the laboratory control criteria.

3.9 Labeled Compound Recovery

Labeled internal standards were added to all samples as required by the analytical method and laboratory SOPs. The labeled internal standards percent recoveries all met the method and laboratory SOP requirements.

3.10 Target Compound Identification

All chromatograms were properly displayed and scaled. No target compounds were detected in any of the field samples. No anomalies were found in relation to target compound identification.

3.11 Reporting Limits and Target Compound Quantitation

Re-calculation was performed on 10% of the instrument calibration and reported QC and sample analyses. No anomalies were found via the verification calculation. MRLs were supported with adequate initial calibration concentrations. In cases where target compound concentrations exceeded ICAL calibration ranges.

Response peak integrations were primarily performed automatically with computer software. In cases where peak shifting, signal interferences, and/or peak tailing occurred, manual integrations were performed. Manual integrations criteria and approaches were consistent justifiable across the analyses; no anomalies were identified in relation to compound identification and quantitation.

3.12 Overall Assessment of PAHs Data Usability

PAHs data are of known quality and acceptable for use, with the acknowledgement of SOP deviations and anomalies stated above.

4. PAHs by GC/MS - SIM (EPA Method SW8270D-SIM)

Laboratory 58 and Laboratory 34 chose to use this methodology for PAHs analysis. Neither EPA Method 8270D nor laboratory SOPs specified evaluation criteria for ¹³C₆-labelled labeled PAHs. However, unless noted otherwise, criteria set forth for non-labeled PAHs in the method and SOPs were applied for carbon-labeled PAHs data quality and method compliance evaluation.

4.1 Sample Management and Holding Times

No anomalies were noted by the laboratories in relation to sample packaging, transportation, handling, preservation, and integrity upon sample receipt in the laboratories.

EPA Method 8270D does not specify holding time requirements for PE samples (submerged in loading solution). Holding time requirements for solid sample (one year from collection to extraction, 40 days from extraction to analysis) were applied as a guideline for sample and extract holding time evaluation. Samples were extracted and analyzed within the holding times by both laboratories.

4.2 GC/MS Instrument Performance Check

The laboratories performed GC/MS tuning analysis as required by the analytical method and their SOPs. DFTPP tuning was performed within each 12-hour interval. All required ion abundance ratios met the method requirements.

4.3 Initial Calibration (ICAL)

The EPA Method 8270D criteria require that (1) if linear average RFs is chosen as the quantitation option, at least five standards at different concentrations should be analyzed and the %RSD of RFs be $\leq 20\%$ for the analyte, (2) if least-square linear regression is chosen for quantitation, the correlation coefficient (r) be > 0.995 , and (3) if six-point non-linear (quadratic) curve is chosen for quantitation, the coefficient of determination (r^2) be > 0.99 . Laboratory 34's criteria vary slightly from the method requirements. All ICALs met the method and laboratory criteria.

An ICV standard (second source standard) was analyzed to verify the calibration curve. Due to limited suppliers and excessive cost of the carbon-labeled PRCs, the second source standards used by both laboratories contained non-labelled PCBs rather than the carbon-labeled PRCs. The %D values were within ± 20 . The ICALs were considered valid.

4.4 Calibration Verification (CCV)

The analytical method requires that (1) continuing calibration verifications be analyzed at the beginning of each 12-hour analysis period prior to the analysis of method blank and samples, and (2) the %D be within $\pm 20\%$ (25% for Laboratory 34). The laboratories met the CCV criteria.

4.5 Method Blanks

Method blanks were prepared and analyzed as required. Target PAH PRCs were not detected at or above the MDLs for Laboratory 34.

PAH PRCs were detected in Laboratory 58's Method Blank BHJ0196-BLK1 at levels approximately one tenth of those in the actual PE strips. The levels of PAH PRCs detected in the method blank had no significant effects on data usability given the low levels of the detections comparing to those in the samples. No further data qualifying action was taken in this case, other than noting this anomaly herein.

4.6 Surrogate Spikes

Surrogate spikes were added to all samples as required by the method. All surrogate spike %R values were within the control limits specified in laboratory SOPs.

4.7 Matrix Spike (MS) and MS Duplicate (MSD)

MS and MSD analyses were not applicable for this calibration standard analysis

4.8 Laboratory Control Sample (LCS)

LCS was not prepared by Laboratory 58. LCS was prepared and analyzed by Laboratory 34. The %R values met the laboratory control limits.

4.9 Internal Standards

The method requires that (1) internal standard retention time be within ± 30 seconds from that of the associated 12-hour calibration standard, and (2) the area counts of all internal standards be within -50% to $+100\%$ of the associated 12-hour calibration standard. Laboratory 34 chose to use those of the mid-point ICAL standard for internal standard recovery control criteria. Internal standard recovery met the method or laboratory requirements.

4.10 Target Compound Identification

All chromatograms were properly displayed and scaled. No target compounds were detected in any of the field samples. No anomalies were found in relation to target compound identification.

4.11 Reporting Limits and Target Compound Quantitation

Re-calculation was performed on 10% of the instrument calibration and reported QC and sample analyses. No anomalies were found via the verification calculation. MRLs were supported with adequate initial calibration concentrations. Response peak integrations were primarily performed automatically with computer software. In cases where peak shifting, signal interferences, and/or peak tailing occurred, manual integrations were performed. Manual integrations criteria and approaches were consistent justifiable across the analyses; no anomalies were identified in relation to compound identification and quantitation.

4.12 Overall Assessment of PAHs Data Usability

PAHs data are of known quality and acceptable for use with the acknowledgement of SOP deviations and anomalies stated above.

SUMMARY

Table 1. Data Affected by QC Anomalies

Sample ID	Analyte	Data Qualifier	Reason	Report Section
No data qualifiers were assigned as results of QC failure.				

REFERENCES

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APPENDIX A

Quality Control Criteria for Analytical Methods

Table A1 – PCB Congeners Analysis Quality Control Evaluation Criteria Summary

QC Parameters and Performance Frequency	Laboratory and Referenced Analytical Method			
	Laboratory 58 (EPA 8270D)	Laboratory 52(EPA 1668C)	Laboratory 34 (EPA 8270D Modified)	Laboratory 84 (EPA 1668C)
Tuning (Resolution Check) At the beginning and the end of each 12-hour period of analysis.	Same as Method	Same as Method	Prior to initial calibration. Prior to CCV if system idle for >24 hrs. Criteria same as 8270D.	Same as Method
GC Column Performance Check Prior to ICAL or calibration verification.	N/A	Same as Method	N/A	Same as Method
Initial Calibration (ICAL) Prior to sample analysis; as needed if failure of calibration verification; or a new lot is used as standard source.	Same as Method	- Same as Method - Standards' result values are within 15% of true values.	Same as 8270D.	Same as Method
Calibration Verification (CCV), Ongoing Precision Recovery (OPR), or Verification (VER) At the beginning of each 12-hour period.	Same as Method	- Same as Methods. - SOP Tables 4a and 4b.	At the beginning and end of 10 injections or each 24 hour period (whichever is more frequent)	Same as Method
Method Blank One per preparatory batch, run after calibration standards and before samples.	No analytes detected $\geq \frac{1}{2}$ limit of quantitation or $\geq 5\%$ of the associated regulatory limit for the analyte or $\geq 10\%$ of the sample result for the analyte, whichever is greater, per method.	Analyte amounts in blank samples for PCB congeners 77, 81, 114, 123, 126 and 169 must be ≤ 2 pg/congener/sample, amounts of PCB congeners 156, 157, 167 and 189 must be ≤ 10 pg/congener/sample, and the maximal amount of PCB 11 must be ≤ 150 pg/sample. Amounts of all other individual PCB congeners or coelutions must be ≤ 50 pg/congener/sample in blank samples. The sum of all 209 congeners should be ≤ 300 pg/sample. Higher levels are acceptable where sample concentrations exceed 10 times blank levels.	Analyte concentration in PB should be $< \text{MDL}$ and must be $< 5\text{xMDL}$ No analytes detected $> \frac{1}{2}$ RL. For common laboratory contaminants, no analytes detected $> \text{RL}$.	Target analytes must be less than estimated maximum levels (EMLs) in SOP Table 4
Instrument Blank At the beginning of each 12-hour period.	Same as Method Blank.	Same as Method Blank.	Same as Method Blank.	Target analytes must be less than EMLs in SOP Table 4

Laboratory Control Sample (LCS) One per preparatory batch.	%R value should be within 70-130% of the true value	SOP Tables 4a and 4b.	70 to 130% recovery vs. SIS 40 to 120% recovery vs. IS	Within control limits for OPR (SOP Tables 10A and 10B).
Matrix Spike (MS) (OPTIONAL)	%R value should be within 70-130% of the true value	N/A	70 to 130% recovery vs. SIS 40 to 120% recovery vs. IS Spiked target analyte concentration must be > 5 x the level in the background sample.	NA
Sample Duplicate or MS Duplicate (MSD)	RPD ≤ 30%	RPD ≤ 20% (applicable to concentrations ≥10 times the DL)	RPD ≤ 30%	N/A
Extraction Standards and Cleanup Standards Every field sample, standard, and QC sample.	- Same as Method for Internal standard recovery - Surrogate Spike recovery is within 70 - 130%.	Same as Method SOP Tables 4a and 4b.	Surrogate spike recovery 40 - 120%	Same as Method
Compound Identification	Same as Method	Same as Method	Same as 8270D	Same as Method

Notes:

N/A: Not applicable

EPA 8270D - USEPA. 1998. *Test Methods for Evaluating Solid Waste (SW 846). Third Edition and Revised Update IIIA. Method 8000 and Method 8270D. Office of Solid Waste and Emergency Response, Washington, D.C. April 1998 and Updates.*

EPA 1668C - USEPA Method 1668C - *Chlorinated Biphenyl Congeners in Water, Soil, Sediment, Biosolids, and Tissue by HRGC/HRMS. April 2010.*

Table A2 – PAHs Analysis Quality Control Evaluation Criteria Summary

QC Parameter & Performance Frequency	Laboratory and Referenced Method			
	Laboratory 58EPA 8270D-SIM	Laboratory 52EPA 8720C-SIM EPA 1625 (HRGC/MS)	Laboratory 34 (EPA 8270D Modified)	Laboratory 84 EPA 8270C-SIM EPA 1625 (GC/MS)
Relative Retention Time (RRT) Evaluation Each Sample	RRT of each target analyte in each calibration standard within ± 0.05 RRT units.	- RT within ± 3 seconds of the predicted retention time determined from the calibration standard and adjusted relative to the peak retention time reference (i.e. labelled surrogate). - A second requirement is that an authentic elute after its labelled analog.	RT window for an analyte is ± 15 s from the determined RT of the analyte in the ICAL.	N/A
Initial Calibration (ICAL) Prior to sample analysis; as needed if failure of calibration verification; or a new lot is used as standard source.	- A minimum of five points. - Analytes' RRFs must meet method limits across calibration range. - Analytes %RSDs must be less than or equal to 20%, or the analyte must employ a linear or non-linear calibration model with a coefficient of determination (r^2) greater than 0.99. - Up to 10% of the total analytes may fail 1 and 2 above. - Verify ICAL with one second-source standard at mid-point concentration. Value for all analytes within $\pm 30\%$ of expected value.	- Calibration standard solutions are presented in SOP Table 6. - Linearity is demonstrated by a 5-point calibration over the working concentration range with a relative standard deviation of the RRFs $\leq 20\%$ for targets with a labelled analog present and all labelled compounds, $\leq 35\%$ for targets with no labelled analog present.	- A minimum of five points. - Analyte RF %RSDs must be less than or equal to 25% average RF. - Verify ICAL with one second-source standard. Value for all analytes within $\pm 25\%$ of expected value.	- SOP Table 3 lists ICAL concentrations. %RSD must be $\leq 30\%$ for analytes and internal standards. - Verify ICAL with one second-source standard at mid-point (CS4) concentration. Value for all analytes within $\pm 30\%$ of expected value.

QC Parameter & Performance Frequency	Laboratory and Referenced Method			
	Laboratory 58EPA 8270D-SIM	Laboratory 52EPA 8720C-SIM EPA 1625 (HRGC/MS)	Laboratory 34 (EPA 8270D Modified)	Laboratory 84 EPA 8270C-SIM EPA 1625 (GC/MS)
Calibration verification (CCV) Before sample analysis, and every 12 hours of analysis time	- Average RRFs for analytes must meet the method defined limits. %Difference/Drift for analytes $\leq 20\%$ - Up to 20% of the target analytes may fail the criteria in 1 and 2 so long as the sample analyses associated with the CCVS are J flagged.	- Opening Cal Ver: Concentrations of native compounds and labelled surrogates must be within $\pm 25\%$ of expected values for all targets. - Closing Cal Ver: Concentrations of native compounds must be within $\pm 25\%$ of expected values. - Concentrations of labelled surrogates must be within $\pm 25\%$ of expected values, with any two (2) values allowed to be within $\pm 40\%$. - Ion ratios for authentic and labelled dibenz[ah]anthracene, indeno[1,2,3-cd]pyrene and benzo[ghi]perylene must be within $\pm 35\%$ of the mid-point of the I-CAL. - All other native analytes and labelled surrogates must be within $\pm 20\%$ of the mid-point of the I-CAL.	- Average RRFs for analytes must meet the method defined limits. - CCV after every 10 injections of 24 hrs – whichever is shorter. - Individual % difference $\leq 25\%$ - Grand mean of % difference $\leq 15\%$. - IS area has not changed by more than a factor of two (-50% to +100% from the area found in level 3 of the ICAL.	%Difference/Drift for analytes must be $\leq 30\%$ (SOP Table 7). - The recovery standard response must be within 50- 200% of the response in the corresponding CS4 calibration level of the initial calibration. - New ICAL is needed if this criterion is not met.
Internal Standards Every field sample, standard, and QC sample	- Retention time ± 30 seconds from retention time of the midpoint standard in the ICAL or CCV. - EICP area within - 50% to +100% of ICAL midpoint standard	Within -50% to +100% of ICAL midpoint standard.	IS area has not changed by more than a factor of two (-50% to +100% from the area found in level 3 of the ICAL.	The recovery standard response must be within 50- 200% of the response in the corresponding CS4 calibration level of the initial calibration.
Method blank One per preparation batch of 20 or less samples	No analytes detected > $\frac{1}{2}$ RL. For common laboratory contaminants, no analytes detected $\geq$ RL.	SOP Table 8.	Analyte concentration in PB should be < MDL and must be < 5 MDL No analytes detected > $\frac{1}{2}$ RL. For common laboratory contaminants, no analytes detected > RL.	No analytes detected > RL ($\frac{1}{2}$ RL for DoD projects).

QC Parameter & Performance Frequency	Laboratory and Referenced Method			
	Laboratory 58EPA 8270D-SIM	Laboratory 52EPA 8720C-SIM EPA 1625 (HRGC/MS)	Laboratory 34 (EPA 8270D Modified)	Laboratory 84 EPA 8270C-SIM EPA 1625 (GC/MS)
Laboratory control sample (LCS) One per preparation batch of 20 or less samples	See Laboratory QA Plan (LQAP). Reported along with LCS results	SOP Table 8.	70 to 130% recovery vs. SIS 40 to 120% recovery vs. IS	SOP Table 7
Matrix Spike (MS) and MS Duplicate (MSD)	- For matrix evaluation, see LQAP. MS recovery is advisory. - RPD $\leq$ 30% (MS/MSD or sample duplicate). Limits are advisory.	SOP Table 8.	70 to 130% recovery vs. SIS 40 to 120% recovery vs. IS RPD $\leq$ 30%	N/A
Surrogate Spikes Every field and QC sample	QC acceptance criteria for LCS specified by DoD, if available; otherwise method- specified criteria or laboratory's own in-house criteria (No more than 1 acid surrogate or 1 base surrogate is allowed out of control, all surrogate recoveries must be > 10%.)	SOP Table 8 for SPMD samples, including criteria for PRCs.	40 - 120% recovery	SOP Table 7
Laboratory Duplicates (Optional)	N/A	Duplicates must fall within $\pm 20\%$ of the mean (applicable to concentrations ≥ 10 times the DL). (Note that $\pm 20\%$ of the mean is equivalent to 40 relative percent difference)	$\leq 30\%$ RPD	N/A

QC Parameter & Performance Frequency	Laboratory and Referenced Method			
	Laboratory 58EPA 8270D-SIM	Laboratory 52EPA 8720C-SIM EPA 1625 (HRGC/MS)	Laboratory 34 (EPA 8270D Modified)	Laboratory 84 EPA 8270C-SIM EPA 1625 (GC/MS)
Compound Identification	Same as Method	- Peak responses must be at least three times the background noise level. - The retention time (RT) must be within three seconds of that predicted from the calibration run and the sample retention time reference (labelled compound). - Peak maxima for the quantification and confirmation ions must coincide within two seconds. - The relative ion abundance ratios must be within 20% of the opening calibration values.	- Primary SIM ion must be present. - Peak responses must be at least three times the background noise level. - RT must fall within established RT window.	- The internal standard quantitation ions must be present. - The relative intensities of confirmation ions should agree to within $\pm 30\%$ between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 20% and 80%). The absence of confirmation ions should be considered carefully when making decisions regarding qualitative identification. Confirmation ions may have lower response than quantitation ions and may not always be present at lower concentrations. Their absence in this case may not be cause for determining that the analyte is not present. The absence of confirmation ions at higher levels where they should have been detectable may be cause for determination that an analyte is not present. - The sample component retention time must compare to within ± 0.2 min. of the retention time of the internal standard component. For reference, the standard must be run within the same 12- hour period as the sample. - If a compound cannot be verified by all the above criteria, but in the technical judgment of the analyst the identification is correct, the analyst shall report that identification and proceed with quantitation.

Notes:

N/A - Not applicable.; DoD – U.S. Department of Defense

EPA 8270D - USEPA. 1998. *Test Methods for Evaluating Solid Waste (SW 846). Third Edition and Revised Update IIIA. Method 8000 and Method 8270D. Office of Solid Waste and Emergency Response, Washington, D.C. April 1998 and Updates.*

EPA 1625 – 40CFR, Appendix A to Part 136, Method 1625 Revision B, Semivolatile Organic Compounds by Isotope Dilution GC/MS

HRGC/MS – High resolution gas chromatography coping with mass spectrometry

GC/MS – Gas chromatography coping with mass spectrometry

RL – Reporting Limit

Data Validation Report

Standardizing Polymeric Sampling for Measuring Freely Dissolved Organic Contaminants in Sediment Porewater ER 201735

Task 3 – Day Zero Loading and Analysis of Solid Phase Microextraction (SPME) Fiber (First Study)

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ACRONYMS

%D	percent difference
%D_f	percent drift
%R	percent recovery
%RSD	percent relative standard deviation
CCV	continuing calibration verification
COC	chain-of-custody
CS1	the first calibration standard
CS3	the third calibration standard
EDD	electronic data deliverable
EDL	estimated detection limit
EMPC	estimated maximum possible concentration
EPA	U.S. Environmental Protection Agency
HRGC/ HRMS	high-resolution gas chromatography/high-resolution mass spectrometry
ICAL	initial calibration
ICV	initial calibration verification
IPR	initial precision and recovery
LCL	lower control limit
LCS	laboratory control sample
LCSD	laboratory control sample duplicate
LIMs	laboratory information management system
m/z	mass-to-charge ratio
MB	method blank
MDL	method detection limit
MS	matrix spike
MSD	matrix spike duplicate
ng/g	nanogram per gram
ng/L	nanogram per liter
ng/mL-PDMS	nanogram per milliliter of polydimethylsiloxane
OPR	ongoing precision and recovery
PCB	polychlorinated biphenyl
PDMS	polydimethylsiloxane
PFK	perfluorokerosene
PRC	performance reference compound
QA/QC	quality assurance/quality control
QAPP	quality assurance project plan
RF	response factor
RPD	relative percent difference
RRT	relative retention time
SDG	sample delivery group

SICP	selected ion current profile
S/N	signal-to-noise ratio
SOP	standard operating procedure
SPME	solid phase microextraction
TTU	Texas Technology University
USACE	US Army Corps of Engineers

INTRODUCTION

This report presents the findings of the data validation performed on analytical data for the Day Zero Loading and Analysis of Solid Phase Microextraction (SPME) Fiber submitted by participating commercial laboratories, as part of the effort for Task 3 identified in the Project Demonstration Plan (USACE et. al., 2018).

Each of the participating laboratories received 28 5cm solid phase microextraction (SPME) fibers coated with polydimethylsiloxane (PDMS) from the Texas Tech University (TTU). The SPME fibers were divided into 14 samples (two fibers per sample) - six of the samples were subject for PCB performance reference compounds (PRCs) loading; six for PAH PRC loading; and one as a method blank for each of the PCBs and PAHs analyses. Specific PRCs for each types of analyses were identified in the Project Demonstration Plan (USACE et. al., 2018), and the target PRCs and their concentrations for respective analytical methods are summarized as follows:

PCBs by EPA 1668C		PCBs by EPA 8270D-SIM			PAHs by EPA 8270D-SIM & EPA 1625C	
PRCs	Target Concentration (ng/mL-PDMS)	PRCs	Target ^(A) Concentration (ng/mL-PDMS)		PRCs	Target Concentration (ng/g-PDMS)
¹³ C-PCB 28	1184	¹³ C-PCB 37	1184	5922	¹³ C ₆ -Phenanthrene	1184
¹³ C-PCB 47	1184	¹³ C-PCB 47	1184	5922	¹³ C ₆ -Fluoranthene	1184
¹³ C-PCB 70	1184	¹³ C-PCB 54	1184	5922	¹³ C ₆ -Chrysene	1184
¹³ C-PCB 80	1184	¹³ C-PCB 111	1184	5922	¹³ C ₆ -Indeno[1,2,3-cd]pyrene	1184
¹³ C-PCB 111	1184	¹³ C-PCB 138	1184	5922		
¹³ C-PCB 141	1184	¹³ C-PCB 178	1184	5922		
¹³ C-PCB 182	1184					

Notes:

ng/mL-PDMS: nanogram per milliliter of PDMS

^(A) – Target concentrations were back-calculated based on PDMS sampler loading conditions determined by the laboratories and thus the concentrations varied with laboratories.

Samples (excluding the method blanks) then underwent the PRC loading process following the guidelines provided by the TTU (TTU, 2018). Once the loading process was completed, the samples (including method blanks) were subject for solvent extraction. Upon extraction, the fiber was rinsed with DI water then blot or air dried. Each segment was placed into a 2 mL amber vial prefilled with hexane then sonicated and brought to desired final extract volume to complete the extraction. The extracts were then subjected for instrumental analyses.

Participating commercial laboratories and respective analytical methodologies applied to this study are summarized as follows:

Participating Commercial Laboratory	Analytical Method	
	PCB Congeners	PAHs
Laboratory 19	SW846 Method 8270D Modified - SIM	SW846 Method 8270D Modified _SIM
Laboratory 98	EPA Method 1668C (Full Scan)	SW846 Method 8270D Modified EPA Method 1625 (Full Scan)
Laboratory 48	EPA Method 1668C - SIM	SW846 Method 8270D Modified EPA Method 1625 -SIM
Laboratory 83	SW846 Method 8270D Modified - SIM	SW846 Method 8270D Modified - SIM

Notes:

1. USEPA Method 1668C: *Chlorinated Biphenyl Congeners in Water, Soil, Sediment, Biosolids, and Tissue by HRGC/HRMS*. April 2010.
2. Method 1625C: *Semi-volatile Organic Compounds by Isotope Dilution GCMS*. June 1989.
3. SW846 - USEPA Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Third Edition, December 1996.

SIM – Selective ion monitoring

Laboratories throughout this report are referred to using random number assignments to ensure the anonymity of participating commercial laboratories. Each participating laboratory was required to submit analytical deliverables for each analysis, including (1) a Level IV full data package containing reporting forms and all raw data supporting the reported sample and QC analyses results, and (2) an electronic data deliverable (EDD) in the Washington State Department of Ecology's Environmental Information Management System (EIMS) format. The laboratory could choose to submit the EDDs in Excel or csv. format. Each laboratory report and EDD were assigned a unique sample delivery group (SDG) number. Laboratory deliverables, after fully validated, were archive in the project file at the US Army Corps of Engineers, Seattle District. SDG numbers assigned by each laboratory are summarized as follows:

Participating Commercial Laboratory	Sample Delivery Group or Laboratory Identification Number	
	PCB Congeners	PAHs
Laboratory 19	19I0479	19I0479
Laboratory 98	140-17156	140-17156
Laboratory 48	DPWG71529	DPWG71585
Laboratory 83	DP-19-0973	DP-19-0972

Final sample results were reported as ng/mL-PDMS, based on the conversion conventions provided by TTU. Values reported in the laboratory reports did not present this conversion, but in

separate EDDs due to the limitations posed by the laboratories' information management systems (LIMs).

A Stage 4 validation (as defined by EPA, 2009) was performed on all PCB congener and PAHs data. The validation followed guidance specified by EPA (2014, 2016 & 2017), with modifications to accommodate respective analytical methods and requirements specified in the Standard Operating Procedures (SOPs) provided by the participating commercial laboratories. The numerical quality assurance/quality control (QA/QC) criteria applied to the validation were in accordance with method requirements and the current performance-based control limits established by the laboratory (laboratory control limits). Instrument calibration, frequency of QC analyses, and analytical sequence requirements were evaluated against the respective analytical methods. QC Criteria are summarized in *Appendix A, Tables A1 and A2*.

Validation findings are discussed in each section pertinent to the QC parameter for each type of analysis. Qualified data with applied data qualifiers are summarized in the **Summary** section at the end of this report.

DATA VALIDATION FINDINGS

1. PCB Congeners by EPA Method 1668C: High-resolution Gas Chromatography and High-resolution Mass Spectrometry (HRGC/HRMS)

Two participating commercial laboratories, Laboratory 48 and Laboratory 98, chose to use EPA Method 1668C for the study. Note that neither EPA Method 1668C nor laboratory SOPs specified evaluation criteria for carbon-labeled PCBs. However, unless noted otherwise, criteria set forth for non-labeled PCBs in the method and SOPs were applied for carbon-labeled PCB data quality and method compliance evaluation.

1.1 Sample Management and Holding time

No anomalies were noted by the laboratories in relation to sample packaging, transportation, handling, preservation, and integrity upon sample receipt in the laboratories.

EPA Method 1668C does not specify holding time requirements for SPME samples (submerged in loading solution). Holding time requirements for solid samples (one year from collection to extraction, 40 days from extraction to analysis) were applied as a guideline for sample and extract holding time evaluation. Samples were extracted and analyzed within the holding times by both laboratories.

1.2 HRGC/HRMS Instrument Performance Check

The EPA Method 1668C criteria for instrument performance checks are as follows:

Mass Spectrometer Resolution: (1) The resolution check should be performed, using perfluorokerosene (PFK) or equivalent standard materials, prior to initial calibration and at the start and end of each 12-hour shift, (2) the resolution should be $\geq 8,000$ throughout the mass range and $\geq 10,000$ resolving power at m/z 330.9792 (or any other significant PFK fragments in the range of 300 to 350), and (3) the deviation between the exact m/z and the theoretical m/z must be less than 5 ppm for monitored isomers.

Column Performance: (1) A combined 209 congener standard should be analyzed prior to initial calibration and continuing calibration verification, (2) peak for congener 34 should be resolved from 23 and peak for congener 187 resolved from 182 peak with a valley of $\leq 40\%$, (3) congeners 156 and 157 should co-elute within 2 seconds at their peak maximum, and (4) the absolute retention time (RT) for congener 209 should be >55 minute for SPB-octyl or an alternate column.

In addition to the method requirements, laboratories imposed more criteria based on their specific instrumentation. HRGC/HRMS instrument performance checks met the method and SOP criteria for these laboratories.

1.3 Initial Calibration (ICAL)

Laboratory 98 chose to fully follow the EPA Method 1668C initial calibration (ICAL) for the ^{13}C -labeled PCB PRCs. The EPA Method 1668C criteria for initial calibration are: (1) a minimum of five standards should be employed for native congeners and labeled compounds, (2) the percent relative standard deviation (%RSD) of isomer response should be $\leq 20\%$, (3) the ion abundance ratios should be within the control limits listed in EPA Method 1668C, Table 8, (4) the signal-to-noise (S/N) ratio should be >10 for all native and labeled compounds in the first calibration standard (CS1), and (5) response factor (RF) should be determined using one- point calibration for congeners quantitated with internal standard method. Initial calibrations met the criteria. An initial calibration verification (second source) standard was analyzed to verify the calibration curve. The percent difference (%D) values were less than or equal to 30% and the initial calibration was considered valid.

Laboratory 48 followed their SOP to establish ICAL for the ^{13}C -labeled PCB PRCs. A mid-point calibration standard was analyzed at the beginning and the end of the analytical sequence. The response factor %RSD values for the target compounds and surrogate compounds should be within laboratory criteria, and RT within 3 seconds between the two analyses. The ICAL met the laboratory SOP requirements.

1.4 Calibration Verification (CCV)

The EPA Method 1668C criteria require that: (1) continuing calibration verifications be performed at the beginning of each 12-hour shift using the mid-point calibration standard (CS3), (2) the %D value should be within the control limits listed in EPA Method 1668C, Table 6, and (3) the ion abundance ratios, retention times, relative retention times, and S/N ratio should meet the same criteria as for initial calibrations. Note that the method did not specify ion abundance ratios for ^{13}C -labeled PCB PRCs; laboratory-specified criteria were applied for data quality determination. All CCVs met the laboratory control criteria.

1.5 Method Blanks

The Laboratory 98 Method Blank was not extracted with a media, but with solvent only. The method blank serves as a 'reagent blank' to monitor background contamination not associated with the PRC loading process. PCB PRCs were not detected at or above the estimated detection limits (EDLs) in the reagent blank.

PCB PRCs were detected in Laboratory 48 Method Blank WG70637-101 at levels comparable to those in the actual PE strips. The blank strip appeared mistakenly exposed to the loading solution, along with those designated for PRC loading. Based on the previous study conducted in Task 2 and the Secondary Study conducted in Task 3, detections in the blanks were all at trace levels and had no effects on data usability. No further data qualifying action was taken in this case, other than noting this anomaly herein.

1.6 Initial Precision and Recovery Study (IPR)

IPR study results are normally maintained in the laboratory and were not included in data packages. This information will be required in data packages reported for the following phases of this study as needed.

1.7 Laboratory Control Sample (LCS)

Since no matrix-specific (i.e., LDPE in this case) LCS was available to be processed along with the samples, the laboratories analyzed/reported laboratory-made standards as LCS. Due to the limited supplier and the excessive cost of the ^{13}C -labelled PRCs, the LCS analyzed/reported by Laboratory 98 did not contain the target PRCs. However, the %R values in LCS were all within the laboratory control criteria.

OPR was prepared and analyzed in lieu of LCS by Laboratory 48. See discussion below.

1.8 Ongoing Precision and Recovery (OPR)

OPR was prepared and analyzed for PRC PCBs at the adequate frequency by Laboratory 48. The %R values met the laboratory control criteria.

1.9 Labeled Compound Recovery

Labeled internal standards were added to all samples as required by the analytical method and laboratory SOPs. The labeled internal standards and cleanup standards percent recoveries all met the method and laboratory SOP requirements.

1.10 Target Compound Identification

Target compound identification was evaluated by examining if: (1) the signals for the two exact m/z 's being monitored were present, and maximized within ± 2 seconds of one another (± 3 seconds for Laboratory 48), (2) the S/N ratio of each of the two exact m/z 's must be greater than or equal to 2.5, (3) the ion abundance ratios were within the method control limits, and (4) the relative retention time (RRT) or retention time (RT) of the peaks were within the method control limits or laboratory control limits. No anomalies were found in relation to target compound identification.

1.11 Reporting Limits, Estimated Detection Limits (EDLs) and Compound Quantitation

Correct internal standards, quantitation ions, and average RFs were used to quantitate target compound detections. The MRLs were supported with adequate ICAL calibration concentrations. The project goal for quantitation limits were attained to in these cases. Response peak integrations were primarily performed automatically with computer software. In cases where peak shifting, signal interferences, and/or peak tailing occurred, manual integrations were performed. Manual integrations criteria and approaches were consistent justifiable across the analyses; no anomalies were identified in relation to compound identification and quantitation.

A verification calculation was performed on 10% of the reported calibration, laboratory QC analyses, and sample results. No anomalies were found. The verification calculation worksheets were maintained in project files for requests.

1.12 Overall Assessment of PCB Congener Data Usability

PCB congener data were of known quality and acceptable for use with the acknowledgement of deviations and anomalies discussion above.

2. PCB Congeners by GC/MS - SIM (EPA Method SW8270D-SIM)

Two laboratories, Laboratory 19 and Laboratory 83, chose to use EPA Method SW8270D-SIM for PCB congeners analysis. Note that neither EPA Method 8270D nor laboratory SOPs specified evaluation criteria for carbon-labeled PCBs. However, unless noted otherwise, criteria set forth for non-labeled PCBs in the method and SOPs were applied for carbon-labeled PCBs data quality and method compliance evaluation.

2.1 Sample Management and Holding Times

No anomalies were noted by the laboratories in relation to sample packaging, transportation, handling, preservation, and integrity upon sample receipt in the laboratories.

EPA Method 8270D does not specify holding time requirements for SPME samples (submerged in loading solution). Holding time requirements for solid samples (one year from collection to extraction, 40 days from extraction to analysis) were applied as a guideline for sample and extract holding time evaluation. Samples were extracted and analyzed within the holding times by both laboratories.

2.2 GC/MS Instrument Performance Check

The laboratories performed GC/MS tuning analysis as required by the analytical method and their SOPs. DFTPP tuning was performed within each 12-hour interval. All required ion abundance ratios met the method requirements.

2.3 Initial Calibration (ICAL)

EPA Method 8270D criteria require that (1) if a linear average RFs is chosen as the quantitation option, at least five standards at different concentrations should be analyzed and the %RSD of RFs be $\leq 15\%$ ($\leq 25\%$ for Laboratory 83) for the analyte, (2) if least-square linear regression is chosen for quantitation, the correlation coefficient (r) be > 0.995 , and (3) if six-point non-linear (quadratic) curve is chosen for quantitation, the coefficient of determination (r^2) be > 0.99 . All ICALs met the method and laboratory criteria.

An ICV standard (second source standard) was analyzed to verify the calibration curve. Due to limited suppliers and excessive cost of the ^{13}C -labeled PRCs, the second source standards

used by both laboratories contained non-labelled PCBs rather than the ^{13}C -labeled PCB PRCs. The %D values were within ± 20 . The ICALs were considered valid.

2.4 Calibration Verification (CCV)

The analytical method requires that (1) continuing calibration verifications be analyzed at the beginning of each 12-hour analysis period prior to the analysis of method blank and samples, and (2) the %D be within $\pm 20\%$ ($\pm 25\%$ for Laboratory 83). All CCVs met the method and laboratory criteria.

2.5 Method Blanks

Method blanks were prepared and analyzed as required. Target PCB PRCs were not detected at or above the method detection limits (MDLs).

2.6 Surrogate Spikes

Surrogate spikes were added to all samples as required by the method. All surrogate spike %R values were within the control limits specified in the laboratory SOPs.

2.7 Matrix Spike (MS) and MS Duplicate (MSD)

MS and MSD analyses were not applicable for the calibration standard analysis.

2.8 Laboratory Control Sample (LCS)

LCS/LCSD were not prepared by Laboratory 19. LCS was prepared and analyzed by Laboratory 83. The %R values met the laboratory control limits.

2.9 Internal Standards

The method requires that (1) internal standard retention time be within ± 30 seconds from that of the associated 12-hour calibration standard, and (2) the area counts of all internal standards be within -50% to $+100\%$ of the associated 12-hour calibration standard. Laboratory 83 chose to use those of the mid-point ICAL standard for internal standard recovery control criteria. Internal standard recovery met the method or laboratory requirements for Laboratory 19.

2.10 Target Compound Identification

All chromatograms and ion spectrum were properly displayed and scaled. No anomalies were found in relation to target compound identification.

2.11 Reporting Limits and Target Compound Quantitation

Re-calculation was performed on 10% of the instrument calibration and reported QC and sample analyses. No anomalies were found via the verification calculation. MRLs were

supported with adequate initial calibration concentrations. In cases where target compound concentrations exceeded ICAL calibration ranges, extracts were diluted and re-analyzed for definitive quantitation.

Response peak integrations were primarily performed automatically with computer software. In cases where peak shifting, signal interferences, and/or peak tailing occurred, manual integrations were performed. Manual integrations criteria and approaches were consistent justifiable across the analyses; no anomalies were identified in relation to compound identification and quantitation.

2.12 Overall Assessment of PCB Congeners Data Usability

PCB Congeners data are of known quality and acceptable for use, with the acknowledgement of SOP deviations and anomalies stated above.

3. PAHs by Isotope Dilution GC/MS (EPA Method SW8270D Modified and EPA Method 1625 Modified)

Laboratory 48 and Laboratory 98 chose to use EPA Method SW8270D modified with EPA Method 1625 for this study. Note that neither EPA Method 8270D, EPA Method 1625 nor laboratory SOPs specified evaluation criteria for carbon-labeled PAHs. However, unless noted otherwise, criteria set forth for non-labeled PAHs in the methods and SOPs were applied for PAH PRC data quality and method compliance evaluation.

3.1 Sample Management and Holding Times

No anomalies were noted by the laboratories in relation to sample packaging, transportation, handling, preservation, and integrity upon sample receipt in the laboratories.

EPA Method 8270D does not specify holding time requirements for SPME samples (submerged in loading solution). Holding time requirements for solid sample (one year from collection to extraction, 40 days from extraction to analysis) were applied as a guideline for sample and extract holding time evaluation. Samples were extracted and analyzed within the holding times by both laboratories.

3.2 GC/MS Instrument Performance Check

The method requires that MS tuning be performed within each 12-hour interval. All required ion abundance ratios should meet the requirements in the method. Each of the laboratories specified GC/MS tuning procedures and requirements in their SOPs. However, tuning reports were not included in their data package in this task. This information will be required for all data packages in future sample analyses for this study.

3.3 Initial Calibration (ICAL)

Laboratory 98 chose to fully follow the method requirements to establish ICAL for $^{13}\text{C}_6$ -Labeled PAH PRCs. The method ICAL criteria require that (1) if linear average RF is chosen as the quantitation option, at least five standards at different concentrations should be analyzed and the %RSD of RFs be $\leq 20\%$ for the analyte, (2) if least-square linear regression is chosen for quantitation, the correlation coefficient (r) be > 0.995 , and (3) if six-point non-linear (quadratic) curve is chosen for quantitation, the coefficient of determination (r^2) be > 0.99 . An ICV standard (second source standard) was analyzed to verify the calibration curve. The %D values were within $\pm 20\%$. The ICALs were considered valid.

Laboratory 48 followed their SOP to establish ICAL for the $^{13}\text{C}_6$ -Labeled PAH PRCs. A mid-point calibration standard was analyzed at the beginning and the end of the analytical sequence. The response factor RPD values for the target compounds and surrogate compounds should be within 20%, and RT within 3 seconds between the two analyses. The ICAL met the laboratory SOP requirements.

3.4 Calibration Verification (CCV)

The analytical method requires that (1) continuing calibration verifications be analyzed at the beginning of each 12-hour analysis period prior to the analysis of method blank and samples, and (2) the %D be within $\pm 20\%$. All CCVs or OPRs met the laboratory control criteria.

3.5 Method Blanks

Method blanks were prepared and analyzed as required. Target PAH PRCs were not detected at or above the MDLs.

3.6 Surrogate Spikes

Surrogate spikes were added to all samples as required by the method. All surrogate spike %R values were within the control limits specified in the laboratory SOPs.

3.7 Ongoing Precision and Recovery (OPR)

OPR was prepared and analyzed for PRC PCBs at the adequate frequency by Laboratory 48. The %R values met the laboratory control criteria.

3.8 Laboratory Control Sample (LCS)

Since no matrix-specific (i.e., LDPE in this case) LCS was available to be processed along with the samples, the laboratories analyzed/reported laboratory-made standards as LCS. Due to the limited supplier and the excessive cost of the ^{13}C -labelled PRCs, the LCS analyzed/reported by Laboratory 98 did not contain the target PRCs. However, the %R values in LCS were all within the laboratory control criteria.

OPR was prepared and analyzed in lieu of LCS by Laboratory 48. See discussion above.

3.9 Labeled Compound Recovery

Labeled internal standards were added to all samples as required by the analytical method and laboratory SOPs. The labeled internal standards percent recoveries all met the method and laboratory SOP requirements.

3.10 Target Compound Identification

All chromatograms and ion spectrum were properly displayed and scaled. No target compounds were detected in any of the field samples. No anomalies were found in relation to target compound identification.

3.11 Reporting Limits and Target Compound Quantitation

Re-calculation was performed on 10% of the instrument calibration and reported QC and sample analyses. No anomalies were found via the verification calculation. MRLs were supported with adequate initial calibration concentrations. In cases where target compound concentrations exceeded ICAL calibration ranges.

Response peak integrations were primarily performed automatically with computer software. In cases where peak shifting, signal interferences, and/or peak tailing occurred, manual integrations were performed. Manual integrations criteria and approaches were consistent justifiable across the analyses; no anomalies were identified in relation to compound identification and quantitation.

3.12 Overall Assessment of PAHs Data Usability

PAHs data are of known quality and acceptable for use with the acknowledgement of deviations and anomalies stated above.

4. PAHs by GC/MS - SIM (EPA Method SW8270D-SIM)

Laboratory 19 and Laboratory 83 chose to use this methodology for PAHs analysis. Neither EPA Method 8270D nor laboratory SOPs specified evaluation criteria for carbon-labeled PAHs. However, unless noted otherwise, criteria set forth for non-labeled PAHs in the method and SOPs were applied for carbon-labeled PAHs data quality and method compliance evaluation.

4.1 Sample Management and Holding Times

No anomalies were noted by the laboratories in relation to sample packaging, transportation, handling, preservation, and integrity upon sample receipt in the laboratories.

EPA Method 8270D does not specify holding time requirements for SPME samples (submerged in loading solution). Holding time requirements for solid sample (one year from collection to extraction, 40 days from extraction to analysis) were applied as a guideline for sample and extract holding time evaluation. Samples were extracted and analyzed within the holding times by both laboratories.

4.2 GC/MS Instrument Performance Check

The laboratories performed GC/MS tuning analysis as required by the analytical method and

their SOPs. DFTPP tuning was performed within each 12-hour interval. All required ion abundance ratios met the method requirements.

4.3 Initial Calibration (ICAL)

EPA Method 8270D criteria require that (1) if a linear average RFs is chosen as the quantitation option, at least five standards at different concentrations should be analyzed and the %RSD of RFs be $\leq 15\%$ ($\leq 25\%$ for Laboratory 83) for the analyte, (2) if least-square linear regression is chosen for quantitation, the correlation coefficient (r) be > 0.995 , and (3) if six-point non-linear (quadratic) curve is chosen for quantitation, the coefficient of determination (r^2) be > 0.99 . All ICALs met the method and laboratory criteria.

An ICV standard (second source standard) was analyzed to verify the calibration curve. Due to limited suppliers and excessive cost of the $^{13}\text{C}_6$ -labeled PRCs, the second source standards used by both laboratories contained non-labelled PCBs rather than the carbon-labeled PRCs. The %D values were within ± 20 . The ICALs were considered valid.

4.4 Calibration Verification (CCV)

The analytical method requires that (1) continuing calibration verifications be analyzed at the beginning of each 12-hour analysis period prior to the analysis of method blank and samples, and (2) the %D be within $\pm 20\%$ (25% for Laboratory 83). The laboratories met the CCV criteria.

4.5 Method Blanks

Method blanks were prepared and analyzed as required. Target PAH PRCs were not detected at or above the MDLs.

4.6 Surrogate Spikes

Surrogate spikes were added to all samples as required by the method. All surrogate spike %R values were within the control limits specified in laboratory SOPs.

4.7 Matrix Spike (MS) and MS Duplicate (MSD)

MS and MSD analyses were not applicable for this calibration standard analysis

4.8 Laboratory Control Sample (LCS)

LCS was not prepared by Laboratory 19. LCS was prepared and analyzed by Laboratory 83. The %R values met the laboratory control limits.

4.9 Internal Standards

The method requires that (1) internal standard retention time be within ± 30 seconds from that

of the associated 12-hour calibration standard, and (2) the area counts of all internal standards be within –50% to +100% of the associated 12-hour calibration standard. Laboratory 83 chose to use those of the mid-point ICAL standard for internal standard recovery control criteria. Internal standard recovery met the method or laboratory requirements.

4.10 Target Compound Identification

All chromatograms were properly displayed and scaled. No target compounds were detected in any of the field samples. No anomalies were found in relation to target compound identification.

4.11 Reporting Limits and Target Compound Quantitation

Re-calculation was performed on 10% of the instrument calibration and reported QC and sample analyses. No anomalies were found via the verification calculation. MRLs were supported with adequate initial calibration concentrations.

Response peak integrations were primarily performed automatically with computer software. In cases where peak shifting, signal interferences, and/or peak tailing occurred, manual integrations were performed. Manual integrations criteria and approaches were consistent justifiable across the analyses; no anomalies were identified in relation to compound identification and quantitation.

4.12 Overall Assessment of PAHs Data Usability

PAHs data are of known quality and acceptable for use with the acknowledgement of SOP deviations and anomalies stated above.

SUMMARY

Table 1. Data Affected by QC Anomalies

Sample ID	Analyte	Data Qualifier	Reason	Report Section
No data qualifiers were assigned as results of QC failure.				

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- USEPA. 2010. *Method 1668A: Chlorinated Biphenyl Congeners in Water, Soil, Sediment, Biosolids, and Tissue by HRGC/HRMS*. April 2010. USEPA-820-R-10-005.
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- USEPA. 1996. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Third Edition, December 1996.
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APPENDIX A

Quality Control Criteria for Analytical Methods

Table A1 – PCB Congeners Analysis Quality Control Evaluation Criteria Summary

QC Parameters and Performance Frequency	Laboratory and Referenced Analytical Method			
	Laboratory 19 (EPA 8270D)	Laboratory 48 (EPA 1668C)	Laboratory 83 (EPA 8270D Modified)	Laboratory 98 (EPA 1668C)
Tuning (Resolution Check) At the beginning and the end of each 12-hour period of analysis.	Same as Method	Same as Method	Prior to initial calibration. Prior to CCV if system idle for >24 hrs. Criteria same as 8270D.	Same as Method
GC Column Performance Check Prior to ICAL or calibration verification.	N/A	Same as Method	N/A	Same as Method
Initial Calibration (ICAL) Prior to sample analysis; as needed if failure of calibration verification; or a new lot is used as standard source.	Same as Method	- Same as Method - Standards' result values are within 15% of true values.	Same as 8270D.	Same as Method
Calibration Verification (CCV), Ongoing Precision Recovery (OPR), or Verification (VER) At the beginning of each 12-hour period.	Same as Method	- Same as Methods. - SOP Tables 4a and 4b.	At the beginning and end of 10 injections or each 24 hour period (whichever is more frequent)	Same as Method
Method Blank One per preparatory batch, run after calibration standards and before samples.	No analytes detected $\geq \frac{1}{2}$ limit of quantitation or $\geq 5\%$ of the associated regulatory limit for the analyte or $\geq 10\%$ of the sample result for the analyte, whichever is greater, per method.	Analyte amounts in blank samples for PCB congeners 77, 81, 114, 123, 126 and 169 must be ≤ 2 pg/congener/sample, amounts of PCB congeners 156, 157, 167 and 189 must be ≤ 10 pg/congener/sample, and the maximal amount of PCB 11 must be ≤ 150 pg/sample. Amounts of all other individual PCB congeners or coelutions must be ≤ 50 pg/congener/sample in blank samples. The sum of all 209 congeners should be ≤ 300 pg/sample. Higher levels are acceptable where sample concentrations exceed 10 times blank levels.	Analyte concentration in PB should be < MDL and must be < 5xMDL No analytes detected > $\frac{1}{2}$ RL. For common laboratory contaminants, no analytes detected > RL.	Target analytes must be less than estimated maximum levels (EMLs) in SOP Table 4
Instrument Blank At the beginning of each 12-hour period.	Same as Method Blank.	Same as Method Blank.	Same as Method Blank.	Target analytes must be less than EMLs in SOP Table 4
Laboratory Control Sample (LCS) One per preparatory batch.	%R value should be within 70-130% of the true value	SOP Tables 4a and 4b.	70 to 130% recovery vs. SIS 40 to 120% recovery vs. IS	Within control limits for OPR (SOP Tables 10A and 10B).

Matrix Spike (MS) (OPTIONAL)	%R value should be within 70-130% of the true value	N/A	70 to 130% recovery vs. SIS 40 to 120% recovery vs. IS Spiked target analyte concentration must be > 5 x the level in the background sample.	NA
Sample Duplicate or MS Duplicate (MSD)	RPD ≤ 30%	RPD ≤ 20% (applicable to concentrations ≥10 times the DL)	RPD ≤ 30%	N/A
Extraction Standards and Cleanup Standards Every field sample, standard, and QC sample.	- Same as Method for Internal standard recovery - Surrogate Spike recovery is within 70 - 130%.	Same as Method SOP Tables 4a and 4b.	Surrogate spike recovery 40 - 120%	Same as Method
Compound Identification	Same as Method	Same as Method	Same as 8270D	Same as Method

Notes:

N/A: Not applicable

EPA 8270D - USEPA. 1998. *Test Methods for Evaluating Solid Waste (SW 846). Third Edition and Revised Update IIIA. Method 8000 and Method 8270D. Office of Solid Waste and Emergency Response, Washington, D.C. April 1998 and Updates.*

EPA 1668C - USEPA Method 1668C - *Chlorinated Biphenyl Congeners in Water, Soil, Sediment, Biosolids, and Tissue by HRGC/HRMS. April 2010.*

Table A2 – PAHs Analysis Quality Control Evaluation Criteria Summary

QC Parameter & Performance Frequency	Laboratory and Referenced Method			
	Laboratory 19 EPA 8270D-SIM	Laboratory 48 EPA 8720C-SIM EPA 1625 (HRGC/MS)	Laboratory 83 (EPA 8270D Modified)	Laboratory 98 EPA 8270C-SIM EPA 1625 (GC/MS)
Relative Retention Time (RRT) Evaluation Each Sample	RRT of each target analyte in each calibration standard within ± 0.05 RRT units.	- RT within ± 3 seconds of the predicted retention time determined from the calibration standard and adjusted relative to the peak retention time reference (i.e. labelled surrogate). - A second requirement is that an authentic elute after its labelled analog.	RT window for an analyte is ± 15 s from the determined RT of the analyte in the ICAL.	N/A
Initial Calibration (ICAL) Prior to sample analysis; as needed if failure of calibration verification; or a new lot is used as standard source.	- A minimum of five points. - Analytes' RRFs must meet method limits across calibration range. - Analytes %RSDs must be less than or equal to 20%, or the analyte must employ a linear or non-linear calibration model with a coefficient of determination (r^2) greater than 0.99. - Up to 10% of the total analytes may fail 1 and 2 above. - Verify ICAL with one second-source standard at mid- point concentration. Value for all analytes within $\pm 30\%$ of expected value.	- Calibration standard solutions are presented in SOP Table 6. - Linearity is demonstrated by a 5-point calibration over the working concentration range with a relative standard deviation of the RRFs $\leq 20\%$ for targets with a labelled analog present and all labelled compounds, $\leq 35\%$ for targets with no labelled analog present.	- A minimum of five points. - Analyte RF %RSDs must be less than or equal to 25% average RF. - Verify ICAL with one second- source standard. Value for all analytes within $\pm 25\%$ of expected value.	- SOP Table 3 lists ICAL concentrations. %RSD must be $\leq 30\%$ for analytes and internal standards. - Verify ICAL with one second-source standard at mid-point (CS4) concentration. Value for all analytes within $\pm 30\%$ of expected value.
Calibration verification (CCV) Before sample analysis, and every 12 hours of analysis time	- Average RRFs for analytes must meet the method defined limits. %Difference/Drift for analytes $\leq 20\%$ - Up to 20% of the target analytes may fail the criteria in 1 and 2 so long as the sample analyses associated with the CCVS are J flagged.	- Opening Cal Ver: Concentrations of native compounds and labelled surrogates must be within $\pm 25\%$ of expected values for all targets. - Closing Cal Ver: Concentrations of native compounds must be within $\pm 25\%$ of expected values. - Concentrations of labelled surrogates must be within $\pm 25\%$ of expected values, with any two (2) values allowed to be within $\pm 40\%$. - Ion ratios for authentic and labelled dibenz[ah]anthracene, indeno[1,2,3-cd]pyrene and benzo[ghi]perylene must be within $\pm 35\%$ of the mid-point of the I-CAL. - All other native analytes and labelled surrogates must be within $\pm 20\%$ of the mid-point of the I-CAL.	- Average RRFs for analytes must meet the method defined limits. - CCV after every 10 injections of 24 hrs – whichever is shorter. - Individual % difference $\leq 25\%$ - Grand mean of % difference $\leq 15\%$. - IS area has not changed by more than a factor of two (-50% to +100% from the area found in level 3 of the ICAL.	%Difference/Drift for analytes must be $\leq 30\%$ (SOP Table 7). - The recovery standard response must be within 50- 200% of the response in the corresponding CS4 calibration level of the initial calibration. - New ICAL is needed if this criterion is not met.

QC Parameter & Performance Frequency	Laboratory and Referenced Method			
	Laboratory 19 EPA 8270D-SIM	Laboratory 48 EPA 8720C-SIM EPA 1625 (HRGC/MS)	Laboratory 83 (EPA 8270D Modified)	Laboratory 98 EPA 8270C-SIM EPA 1625 (GC/MS)
Internal Standards Every field sample, standard, and QC sample	- Retention time ± 30 seconds from retention time of the midpoint standard in the ICAL or CCV. - EICP area within - 50% to +100% of ICAL midpoint standard	Within -50% to +100% of ICAL midpoint standard.	IS area has not changed by more than a factor of two (-50% to +100% from the area found in level 3 of the ICAL.	The recovery standard response must be within 50- 200% of the response in the corresponding CS4 calibration level of the initial calibration.
Method blank One per preparation batch of 20 or less samples	No analytes detected > $\frac{1}{2}$ RL. For common laboratory contaminants, no analytes detected $\geq$ RL.	SOP Table 8.	Analyte concentration in PB should be < MDL and must be < 5 MDL No analytes detected > $\frac{1}{2}$ RL. For common laboratory contaminants, no analytes detected > RL.	No analytes detected > RL ($\frac{1}{2}$ RL for DoD projects).
Laboratory control sample (LCS) One per preparation batch of 20 or less samples	See Laboratory QA Plan (LQAP). Reported along with LCS results	SOP Table 8.	70 to 130% recovery vs. SIS 40 to 120% recovery vs. IS	SOP Table 7
Matrix Spike (MS) and MS Duplicate (MSD)	- For matrix evaluation, see LQAP. MS recovery is advisory. - RPD $\leq$ 30% (MS/ MSD or sample duplicate). Limits are advisory.	SOP Table 8.	70 to 130% recovery vs. SIS 40 to 120% recovery vs. IS RPD $\leq$ 30%	N/A
Surrogate Spikes Every field and QC sample	QC acceptance criteria for LCS specified by DoD, if available; otherwise method- specified criteria or laboratory's own in- house criteria (No more than 1 acid surrogate or 1 base surrogate is allowed out of control, all surrogate recoveries must be > 10%.)	SOP Table 8 for SPMD samples, including criteria for PRCs.	40 - 120% recovery	SOP Table 7
Laboratory Duplicates (Optional)	N/A	Duplicates must fall within $\pm 20\%$ of the mean (applicable to concentrations ≥ 10 times the DL). (Note that $\pm 20\%$ of the mean is equivalent to 40 relative percent difference)	$\leq 30\%$ RPD	N/A

QC Parameter & Performance Frequency	Laboratory and Referenced Method			
	Laboratory 19 EPA 8270D-SIM	Laboratory 48 EPA 8720C-SIM EPA 1625 (HRGC/MS)	Laboratory 83 (EPA 8270D Modified)	Laboratory 98 EPA 8270C-SIM EPA 1625 (GC/MS)
Compound Identification	Same as Method	• Peak responses must be at least three times the background noise level. • The retention time (RT) must be within three seconds of that predicted from the calibration run and the sample retention time reference (labelled compound). • Peak maxima for the quantification and confirmation ions must coincide within two seconds. • The relative ion abundance ratios must be within 20% of the opening calibration values.	• Primary SIM ion must be present. • Peak responses must be at least three times the background noise level. • RT must fall within established RT window.	• The internal standard quantitation ions must be present. • The relative intensities of confirmation ions should agree to within $\pm 30\%$ between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 20% and 80%). The absence of confirmation ions should be considered carefully when making decisions regarding qualitative identification. Confirmation ions may have lower response than quantitation ions and may not always be present at lower concentrations. Their absence in this case may not be cause for determining that the analyte is not present. The absence of confirmation ions at higher levels where they should have been detectable may be cause for determination that an analyte is not present. • The sample component retention time must compare to within ± 0.2 min. of the retention time of the internal standard component. For reference, the standard must be run within the same 12- hour period as the sample. • If a compound cannot be verified by all the above criteria, but in the technical judgment of the analyst the identification is correct, the analyst shall report that identification and proceed with quantitation.

Notes:

N/A - Not applicable.; DoD – U.S. Department of Defense

EPA 8270D - USEPA. 1998. *Test Methods for Evaluating Solid Waste (SW 846). Third Edition and Revised Update IIIA. Method 8000 and Method 8270D. Office of Solid Waste and Emergency Response, Washington, D.C. April 1998 and Updates.*

EPA 1625 – 40CFR, Appendix A to Part 136, Method 1625 Revision B, Semivolatile Organic Compounds by Isotope Dilution GC/MS

HRGC/MS – High resolution gas chromatography coping with mass spectrometry

GC/MS – Gas chromatography coping with mass spectrometry

RL – Reporting Limit

Data Validation Report

Standardizing Polymeric Sampling for Measuring Freely Dissolved Organic Contaminants in Sediment Porewater ER 201735

Task 3 – Day Zero Loading and Analysis of Polyethylene Strips (Second Study)

Prepared for:

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ACRONYMS

%D	percent difference
%D _f	percent drift
%R	percent recovery
%RSD	percent relative standard deviation
CCV	continuing calibration verification
COC	chain-of-custody
CS1	the first calibration standard
CS3	the third calibration standard
EDD	electronic data deliverable
EDL	estimated detection limit
EMPC	estimated maximum possible concentration
EPA	U.S. Environmental Protection Agency
HRGC/ HRMS	high-resolution gas chromatography/high-resolution mass spectrometry
ICAL	initial calibration
ICV	initial calibration verification
IPR	initial precision and recovery
LCL	lower control limit
LCS	laboratory control sample
LCSD	laboratory control sample duplicate
LDPE	low density polyethylene
LIMs	laboratory information management system
m/z	mass-to-charge ratio
MB	method blank
MDL	method detection limit
MIT	Massachusetts Institute of Technology
MS	matrix spike
MSD	matrix spike duplicate
ng/g	nanogram per gram
OPR	ongoing precision and recovery
PCB	polychlorinated biphenyl
PE	polyethylene
PFK	perfluorokerosene
PRC	performance reference compound
QA/QC	quality assurance/quality control
QAPP	quality assurance project plan
RF	response factor
RPD	relative percent difference
RRT	relative retention time

SDG	sample delivery group
SICP	selected ion current profile
S/N	signal-to-noise ratio
SOP	standard operating procedure
USACE	US Army Corps of Engineers

INTRODUCTION

This report presents the findings of the data validation performed on analytical data for the second study of the Day Zero Loading and Analysis of Polyethylene Strip, submitted by participating commercial laboratories, as part of the effort for Task 3 identified in the Project Demonstration Plan (USACE et. al., 2018). As a follow-up with the first study, the loading conditions for the polyethylene strips were further optimized in this study.

Each of the participating laboratories received 14 10cm polyethylene (PE) strips contained in a capped vial from the Massachusetts Institute of Technology (MIT). Six of the strips were subject for PCB performance reference compounds (PRCs) loading; six for PAH PRCs loading; and two samples designated as method blanks - one for each of the PCBs and PAHs analysis. Target PCB and PAH PRCs were identified in the Project Demonstration Plan (USACE et. al., 2018), and the target PRCs and their concentrations for respective analytical methods are summarized as follows:

PCBs by EPA 1668C			PCBs by EPA 8270D-SIM				PAHs by EPA 8270D-SIM & EPA 1625C			
PRCs	Target ^(A) Concentration (ng/g-LDPE)		PRCs	Target ^(A) Concentration (ng/g-LDPE)			PRCs	Target ^(A) Concentration (ng/g-LDPE)		
¹³ C-PCB 28	502	1000	¹³ C-PCB 37	500	522	1000	¹³ C ₆ -Phenanthrene ¹³ C ₆ -Fluoranthene ¹³ C ₆ -Chrysene ¹³ C ₆ -Indeno[1,2,3-cd]pyrene	500	498	991
¹³ C-PCB 47	532	1000	¹³ C-PCB 47	500	532	1000		500	521	1000
¹³ C-PCB 70	544	1000	¹³ C-PCB 54	500	423	1000		500	510	988
¹³ C-PCB 80	516	1000	¹³ C-PCB 111	500	488	1000		500	517	950
¹³ C-PCB 111	488	1000	¹³ C-PCB 138	500	531	1000				
¹³ C-PCB 141	517	1000	¹³ C-PCB 178	500	571	1000				
¹³ C-PCB 182	913	1000								

Notes:

ng/g-LDPE: nanogram per gram of LDPE

^(A) – Target concentrations were back-calculated based on LDPE sampler loading conditions determined by the laboratories and thus the concentrations varied with laboratories.

The samples (excluding the method blanks) underwent the PRC loading process following the guidelines provided by MIT (MIT 2017). Once the loading was completed, samples (including the method blank strips) were subject for solvent extraction. Upon extraction, the strips were rinsed with DI water then blot or air dried. Each strip was placed into a 2 mL amber vial prefilled with hexane then sonicated and brought to desired final extract volume to complete the extraction. The extracts were then subjected for instrumental analyses.

Participating commercial laboratories and respective analytical methodologies applied to this study are summarized as follows:

Participating Commercial Laboratory	Analytical Method	
	PCB Congeners	PAHs
Laboratory 58	SW846 Method 8270D Modified	SW846 Method 8270D Modified
Laboratory 84	EPA Method 1668C	SW846 Method 8270D Modified EPA Method 1625
Laboratory 52	EPA Method 1668C	SW846 Method 8270D Modified EPA Method 1625
Laboratory 34	SW846 Method 8270D Modified	SW846 Method 8270D Modified

Notes:

1. USEPA Method 1668C: *Chlorinated Biphenyl Congeners in Water, Soil, Sediment, Biosolids, and Tissue by HRGC/HRMS*. April 2010.
2. Method 1625C: *Semi-volatile Organic Compounds by Isotope Dilution GCMS*. June 1989.
3. SW846 - USEPA Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Third Edition, December 1996.

Laboratories throughout this report are referred to using random number assignments to ensure the anonymity of participating commercial laboratories. Each participating laboratory was required to submit analytical deliverables for each analysis, including (1) a Level IV full data package containing reporting forms and all raw data supporting the reported sample and QC analyses results, and (2) an electronic data deliverable (EDD) in the Washington State Department of Ecology's Environmental Information Management System (EIMs) format. The laboratory could choose to submit the EDDs in Excel or csv. format. Each laboratory report and EDD were assigned a unique sample delivery group (SDG) number. Laboratory deliverables, after fully validated, were archive in the project file at the US Army Corps of Engineers Seattle District. SDG numbers assigned by each laboratory are summarized as follows:

Participating Commercial Laboratory	Sample Delivery Group or Laboratory Identification Number	
	PCB Congeners	PAHs
Laboratory 58	20A0347	20A0347
Laboratory 84	140-18041-1	140-18041-1
Laboratory 52	DPWG71530	DPWG71255
Laboratory 34	DP-20-0545	DP-20-0547

Final sample results were reported as ng/g-LDPE, based on the conversion conventions provided by MIT. Values reported in the laboratory reports did not present this conversion, but in separate EDDs due to the limitations posed by the laboratories' information management systems (LIMs). A Stage 4 validation (as defined by EPA 2009) was performed on all PCB congener and PAHs data. The validation followed guidance specified by EPA (2014, 2016 & 2017), with modifications to accommodate respective analytical methods and requirements specified in the Standard Operating

Procedures (SOPs) provided by the participating commercial laboratories. The numerical quality assurance/quality control (QA/QC) criteria applied to the validation were in accordance with method requirements and the current performance-based control limits established by the laboratory (laboratory control limits). Instrument calibration, frequency of QC analyses, and analytical sequence requirements were evaluated against the respective analytical methods. Laboratory-specific QC Criteria are summarized in *Appendix A, Tables A1 and A2*.

Validation findings are discussed in each section pertinent to the QC parameter for each type of analysis. Qualified data with applied data qualifiers are summarized in the **Summary** section at the end of this report.

DATA VALIDATION FINDINGS

1. PCB Congeners by EPA Method 1668C: High-resolution Gas Chromatography and High-resolution Mass Spectrometry (HRGC/HRMS)

Two participating commercial laboratories – Laboratory 52 and Laboratory 84 chose to use EPA Method 1668C for the study. Note that neither EPA Method 1668C nor laboratory SOPs specified evaluation criteria for carbon-labeled PCBs. However, unless noted otherwise, criteria set forth for non-labeled PCBs in the method and SOPs were applied for carbon-labeled PCB data quality and method compliance evaluation.

1.1 Sample Management and Holding time

No anomalies were noted by the laboratories in relation to sample packaging, transportation, handling, preservation, and integrity upon sample receipt in the laboratories.

EPA Method 1668C does not specify holding time requirements for PE samples (submerged in loading solution). Holding time requirements for solid samples (one year from collection to extraction, 40 days from extraction to analysis) were applied as a guideline for sample and extract holding time evaluation. Samples were extracted and analyzed within the holding times by both laboratories.

1.2 HRGC/HRMS Instrument Performance Check

The EPA Method 1668C criteria for instrument performance checks are as follows:

Mass Spectrometer Resolution: (1) The resolution check should be performed, using perfluorokerosene (PFK) or equivalent standard materials, prior to initial calibration and at the start and end of each 12-hour shift, (2) the resolution should be $\geq 8,000$ throughout the mass range and $\geq 10,000$ resolving power at m/z 330.9792 (or any other significant PFK fragments in the range of 300 to 350), and (3) the deviation between the exact m/z and the theoretical m/z must be less than 5 ppm for monitored isomers.

Column Performance: (1) A combined 209 congener standard should be analyzed prior to initial calibration and continuing calibration verification, (2) peak for congener 34 should be resolved from 23 and peak for congener 187 resolved from 182 peak with a valley of $\leq 40\%$, (3) congeners 156 and 157 should co-elute within 2 seconds at their peak maximum, and (4) the absolute retention time (RT) for congener 209 should be >55 minute for SPB-octyl or an alternate column.

In addition to the method requirements, laboratories imposed more criteria based on their specific instrumentation. HRGC/HRMS instrument performance checks met the method and SOP criteria for these laboratories.

1.3 Initial Calibration (ICAL)

Laboratory 84 chose to fully follow the EPA Method 1668C initial calibration (ICAL) for the ^{13}C -labeled PCB PRCs. The EPA Method 1668C criteria for initial calibration are: (1) a minimum of five standards should be employed for native congeners and labeled compounds, (2) the percent relative standard deviation (%RSD) of isomer response should be $\leq 20\%$, (3) the ion abundance ratios should be within the control limits listed in EPA Method 1668C, Table 8, (4) the signal-to-noise (S/N) ratio should be >10 for all native and labeled compounds in the first calibration standard (CS1), and (5) response factor (RF) should be determined using one-point calibration for congeners quantitated with internal standard method. Initial calibrations met the criteria. An initial calibration verification (second source) standard was analyzed to verify the calibration curve. The percent difference (%D) values were less than or equal to 30% and the initial calibration was considered valid.

Laboratory 52 followed their SOP to establish ICAL for the ^{13}C -labeled PCB PRCs. A mid-point calibration standard was analyzed at the beginning and the end of the analytical sequence. The response factor RPD values for the target compounds and surrogate compounds should be within 20%, and RT within 3 seconds between the two analyses. The ICAL met the laboratory SOP requirements.

1.4 Calibration Verification (CCV)

The EPA Method 1668C criteria require that: (1) continuing calibration verifications be performed at the beginning of each 12-hour shift using the mid-point calibration standard (CS3), (2) the %D value should be within the control limits listed in EPA Method 1668C, Table 6, and (3) the ion abundance ratios, retention times, relative retention times, and S/N ratio should meet the same criteria as for initial calibrations. Note that the method did not specify ion abundance ratios for ^{13}C -labeled PRCs; laboratory-specified criteria were applied for data quality determination. All CCVs met the laboratory control criteria.

1.5 Method Blanks

A method blank was prepared and analyzed by Laboratory 52. Target PCB PRCs were not detected at or above the method reporting limits (MRLs). A method blank was not prepared/analyzed by Laboratory 84. Based on the historical method blank results (*i.e.*, Task 2), detections of PCB PRCs, if any, were at trace levels and had not significant effects on data usability. No data qualifying action was taken other than noting the anomaly herein.

1.6 Initial Precision and Recovery Study (IPR)

IPR study results are normally maintained in the laboratory and were not included in data packages. This information will be required in data packages reported for the following phases of this study as needed.

1.7 Ongoing Precision and Recovery (OPR)

OPR was prepared and analyzed for PRC PCBs at the adequate frequency by Laboratory 52. The %R values met the laboratory control criteria.

1.8 Laboratory Control Sample (LCS)

LCS was not prepared/analyzed by Laboratory 84. Analytical precision was evaluated via the %R values of surrogate spikes and CCVs. No data qualifying action was taken other than noting the anomaly herein.

OPR was prepared and analyzed in lieu of LCS by Laboratory 52. See discussion above.

1.9 Labeled Compound Recovery

Labeled internal standards were added to all samples as required by the analytical method and laboratory SOPs. The labeled internal standards and cleanup standards percent recoveries all met the method and laboratory SOP requirements.

1.10 Target Compound Identification

Target compound identification was evaluated by examining if: (1) the signals for the two exact m/z's being monitored were present, and maximized within ± 2 seconds of one another (± 3 seconds for Laboratory 52), (2) the S/N ratio of each of the two exact m/z's must be greater than or equal to 2.5, (3) the ion abundance ratios were within the method control limits, and (4) the relative retention time (RRT) or retention time (RT) of the peaks were within the method control limits or laboratory control limits. No anomalies were found in relation to target compound identification.

1.11 Reporting Limits, Estimated Detection Limits (EDLs) and Compound Quantitation

Correct internal standards, quantitation ions, and average RFs were used to quantitate target compound detections. The MRLs were supported with adequate ICAL calibration concentrations. The project goal for quantitation limits were attained to in these cases.

A verification calculation was performed on 10% of the reported calibration, laboratory QC analyses, and sample results. No anomalies were found. The verification calculation worksheets were maintained in project files for requests.

Response peak integrations were primarily performed automatically with computer software. In cases where peak shifting, signal interferences, and/or peak tailing occurred, manual integrations were performed. Manual integrations criteria and approaches were consistent justifiable across the analyses; no anomalies were identified in relation to compound identification and quantitation.

1.12 Overall Assessment of PCB Congener Data Usability

PCB congener data were of known quality and acceptable for use with the acknowledgement of deviations and anomalies discussion above.

2. PCB Congeners by GC/MS - SIM (EPA Method SW8270D-SIM)

Two laboratories, Laboratory 58 and Laboratory 34, chose to use EPA Method SW8270D-SIM for PCB congeners analysis. Note that neither EPA Method 8270D nor laboratory SOPs specified evaluation criteria for carbon-labeled PCBs. However, unless noted otherwise, criteria set forth for non-labeled PCBs in the method and SOPs were applied for ^{13}C -labeled PCBs data quality and method compliance evaluation.

2.1 Sample Management and Holding Times

No anomalies were noted by the laboratories in relation to sample packaging, transportation, handling, preservation, and integrity upon sample receipt in the laboratories.

EPA Method 8270D does not specify holding time requirements for PE samples (submerged in loading solution). Holding time requirements for solid sample (one year from collection to extraction, 40 days from extraction to analysis) were applied as a guideline for sample and extract holding time evaluation. Samples were extracted and analyzed within the holding times by both laboratories.

2.2 GC/MS Instrument Performance Check

The laboratories performed GC/MS tuning analysis as required by the analytical method and their SOPs. DFTPP tuning was performed within each 12-hour interval. All required ion abundance ratios met the method requirements.

2.3 Initial Calibration (ICAL)

EPA Method 8270D criteria require that (1) if a linear average RFs is chosen as the quantitation option, at least five standards at different concentrations should be analyzed and the %RSD of RFs be $\leq 15\%$ ($\leq 25\%$ for Laboratory 34) for the analyte, (2) if least-square linear regression is chosen for quantitation, the correlation coefficient (r) be > 0.995 , and (3) if six-point non-linear (quadratic) curve is chosen for quantitation, the coefficient of determination (r^2) be > 0.99 . All ICALs met the method and laboratory criteria.

An ICV standard (second source standard) was analyzed to verify the calibration curve. Due to limited suppliers and excessive cost of the ^{13}C -labeled PRCs, the second source standards used by both laboratories contained non-labelled PCBs rather than the ^{13}C -labeled PCB PRCs. The %D values were within ± 20 . The ICALs were considered valid.

2.4 Calibration Verification (CCV)

The analytical method requires that (1) continuing calibration verifications be analyzed at the beginning of each 12-hour analysis period prior to the analysis of method blank and samples, and (2) the %D be within $\pm 20\%$ ($\pm 25\%$ for Laboratory 34). All CCVs met the method and laboratory criteria.

2.5 Method Blanks

Method blanks were prepared and analyzed as required. Target PCB PRCs were not detected at or above the method detection limits (MDLs).

2.6 Surrogate Spikes

Surrogate spikes were added to all samples as required by the method. All surrogate spike %R values were within the control limits specified in the laboratory SOPs.

2.7 Matrix Spike (MS) and MS Duplicate (MSD)

MS and MSD analyses were not applicable for the calibration standard analysis.

2.8 Laboratory Control Sample (LCS)

LCS was not prepared/analyzed by Laboratory 58. LCS was prepared and analyzed by Laboratory 34. The %R values met the laboratory control limits.

2.9 Internal Standards

The method requires that (1) internal standard retention time be within ± 30 seconds from that of the associated 12-hour calibration standard, and (2) the area counts of all internal standards be within -50% to $+100\%$ of the associated 12-hour calibration standard. Laboratory 34 chose to use those of the mid-point ICAL standard for internal standard recovery control criteria. Internal standard recovery met the method or laboratory requirements.

2.10 Target Compound Identification

All chromatograms were properly displayed and scaled. No target compounds were detected in any of the field samples. No anomalies were found in relation to target compound identification.

2.11 Reporting Limits and Target Compound Quantitation

Re-calculation was performed on 10% of the instrument calibration and reported QC and sample analyses. No anomalies were found via the verification calculation. MRLs were supported with adequate initial calibration concentrations. In cases where target compound concentrations exceeded ICAL calibration ranges, extracts were diluted and re-analyzed for definitive quantitation.

Response peak integrations were primarily performed automatically with computer software. In cases where peak shifting, signal interferences, and/or peak tailing occurred, manual integrations were performed. Manual integrations criteria and approaches were consistent justifiable across the analyses; no anomalies were identified in relation to compound identification and quantitation.

2.12 Overall Assessment of PCB Congeners Data Usability

PCB Congeners data are of known quality and acceptable for use, with the acknowledgement of SOP deviations and anomalies stated above.

3. PAHs by Isotope Dilution GC/MS (EPA Method SW8270D Modified and EPA Method 1625 Modified)

Laboratory 52 and Laboratory 84 chose to use EPA Method SW8270D modified with EPA Method 1625 for this study. Note that neither EPA Method 8270D, EPA Method 1625 nor laboratory SOPs specified evaluation criteria for carbon-labeled PAHs. However, unless noted otherwise, criteria set forth for non-labeled PAHs in the methods and SOPs were applied for PAH PRC data quality and method compliance evaluation.

3.1 Sample Management and Holding Times

No anomalies were noted by the laboratories in relation to sample packaging, transportation, handling, preservation, and integrity upon sample receipt in the laboratories.

EPA Method 8270D does not specify holding time requirements for PE samples (submerged in loading solution). Holding time requirements for solid sample (one year from collection to extraction, 40 days from extraction to analysis) were applied as a guideline for sample and extract holding time evaluation. Samples were extracted and analyzed within the holding times by both laboratories.

3.2 GC/MS Instrument Performance Check

The method requires that DFTPP tuning be performed within each 12-hour interval. All required ion abundance ratios should meet the requirements in the method. Each of the laboratories specified GC/MS tuning procedures and requirements in their SOPs. However, tuning reports were not included in their data package in this task. This information will be required for all data packages in future sample analyses for this study.

3.3 Initial Calibration (ICAL)

Laboratory 84 chose to fully follow the method requirements to establish ICAL for $^{13}\text{C}_6$ -Labeled PAH PRCs. The method ICAL criteria require that (1) if linear average RF is chosen as the quantitation option, at least five standards at different concentrations should be analyzed and the %RSD of RFs be $\leq 20\%$ for the analyte, (2) if least-square linear regression is chosen for quantitation, the correlation coefficient (r) be > 0.995 , and (3) if six-point non-linear (quadratic)

curve is chosen for quantitation, the coefficient of determination (r^2) be >0.99 . An ICV standard (second source standard) was analyzed to verify the calibration curve. The %D values were within $\pm 20\%$. The ICALs were considered valid.

Laboratory 52 followed their SOP to establish ICAL for the $^{13}\text{C}_6$ -Labeled PAH PRCs. A mid-point calibration standard was analyzed at the beginning and the end of the analytical sequence. The response factor %RSD values for the target compounds and surrogate compounds should be within 20%, and RT within 3 seconds between the two analyses. The ICAL met the laboratory SOP requirements.

3.4 Calibration Verification (CCV)

The analytical method requires that (1) continuing calibration verifications be analyzed at the beginning of each 12-hour analysis period prior to the analysis of method blank and samples, and (2) the %D be within $\pm 20\%$. All CCVs or OPRs met the laboratory control criteria.

3.5 Method Blanks

A method blank was prepared and analyzed by Laboratory 52. Target PCB PRCs were not detected at or above the method reporting limits (MRLs). A method blank was not prepared/analyzed by TetsAmerica. Based on the historical method blank results (*i.e.*, Task 2), detections of PAH PRCs, if any, were at trace levels and had not significant effects on data usability. No data qualifying action was taken other than noting the anomaly herein.

3.6 Surrogate Spikes

Surrogate spikes were added to all samples as required by the method. All surrogate spike %R values were within the control limits specified in the laboratory SOPs.

3.7 Laboratory Control Sample (LCS)

Since no matrix-specific (*i.e.*, LDPE in this case) LCS was available to be processed along with the samples, the laboratories analyzed/reported laboratory-made standards as LCS. Due to the limited supplier and the excessive cost of the ^{13}C -labelled PRCs, the LCS analyzed/reported by Laboratory 84 did not contain the target PRCs. However, the %R values in LCS were all within the laboratory control criteria.

OPR was prepared and analyzed in lieu of LCS by Laboratory 52. See discussion below.

3.8 Ongoing Precision and Recovery (OPR)

OPR was prepared and analyzed for PRC PCBs at the adequate frequency by Laboratory 52. The %R values met the laboratory control criteria.

3.9 Labeled Compound Recovery

Labeled internal standards were added to all samples as required by the analytical method and laboratory SOPs. The labeled internal standards percent recoveries all met the method and laboratory SOP requirements.

3.10 Target Compound Identification

All chromatograms were properly displayed and scaled. No target compounds were detected in any of the field samples. No anomalies were found in relation to target compound identification.

3.11 Reporting Limits and Target Compound Quantitation

Re-calculation was performed on 10% of the instrument calibration and reported QC and sample analyses. No anomalies were found via the verification calculation. MRLs were supported with adequate initial calibration concentrations. In cases where target compound concentrations exceeded ICAL calibration ranges, extracts were diluted and re-analyzed for definitive quantitation.

Response peak integrations were primarily performed automatically with computer software. In cases where peak shifting, signal interferences, and/or peak tailing occurred, manual integrations were performed. Manual integrations criteria and approaches were consistent justifiable across the analyses; no anomalies were identified in relation to compound identification and quantitation.

3.12 Overall Assessment of PAHs Data Usability

PAHs data are of known quality and acceptable for use, with the acknowledgement of SOP deviations and anomalies stated above.

4. PAHs by GC/MS - SIM (EPA Method SW8270D-SIM)

Laboratory 58 and Laboratory 34 chose to use this methodology for PAHs analysis. Neither EPA Method 8270D nor laboratory SOPs specified evaluation criteria for ¹³C₆-labelled labeled PAHs. However, unless noted otherwise, criteria set forth for non-labeled PAHs in the method and SOPs were applied for carbon-labeled PAHs data quality and method compliance evaluation.

4.1 Sample Management and Holding Times

No anomalies were noted by the laboratories in relation to sample packaging, transportation, handling, preservation, and integrity upon sample receipt in the laboratories.

EPA Method 8270D does not specify holding time requirements for PE samples (submerged in loading solution). Holding time requirements for solid sample (one year from collection to extraction, 40 days from extraction to analysis) were applied as a guideline for sample and extract holding time evaluation. Samples were extracted and analyzed within the holding times by both laboratories.

4.2 GC/MS Instrument Performance Check

The laboratories performed GC/MS tuning analysis as required by the analytical method and their SOPs. DFTPP tuning was performed within each 12-hour interval. All required ion abundance ratios met the method requirements.

4.3 Initial Calibration (ICAL)

The EPA Method 8270D criteria require that (1) if linear average RFs is chosen as the quantitation option, at least five standards at different concentrations should be analyzed and the %RSD of RFs be $\leq 20\%$ for the analyte, (2) if least-square linear regression is chosen for quantitation, the correlation coefficient (r) be >0.995 , and (3) if six-point non-linear (quadratic) curve is chosen for quantitation, the coefficient of determination (r^2) be >0.99 . Laboratory 34's criteria vary slightly from the method requirements. All ICALs met the method and laboratory criteria.

An ICV standard (second source standard) was analyzed to verify the calibration curve. Due to limited suppliers and excessive cost of the carbon-labeled PRCs, the second source standards used by both laboratories contained non-labelled PCBs rather than the carbon-labeled PRCs. The %D values were within ± 20 . The ICALs were considered valid.

4.4 Calibration Verification (CCV)

The analytical method requires that (1) continuing calibration verifications be analyzed at the beginning of each 12-hour analysis period prior to the analysis of method blank and samples, and (2) the %D be within $\pm 20\%$ (25% for Laboratory 34). The laboratories met the CCV criteria.

4.5 Method Blanks

Method blanks were prepared and analyzed as required. Target PAH PRCs were not detected at or above the MDLs.

4.6 Surrogate Spikes

Surrogate spikes were added to all samples as required by the method. All surrogate spike %R values were within the control limits specified in laboratory SOPs.

4.7 Matrix Spike (MS) and MS Duplicate (MSD)

MS and MSD analyses were not applicable for this calibration standard analysis

4.8 Laboratory Control Sample (LCS)

LCS was not prepared by Laboratory 58. LCS was prepared and analyzed by Laboratory 34. The %R values met the laboratory control limits.

4.9 Internal Standards

The method requires that (1) internal standard retention time be within ± 30 seconds from that of the associated 12-hour calibration standard, and (2) the area counts of all internal standards be within -50% to $+100\%$ of the associated 12-hour calibration standard. Laboratory 34 chose to use those of the mid-point ICAL standard for internal standard recovery control criteria. Internal standard recovery met the method or laboratory requirements.

4.10 Target Compound Identification

All chromatograms were properly displayed and scaled. No target compounds were detected in any of the field samples. No anomalies were found in relation to target compound identification.

4.11 Reporting Limits and Target Compound Quantitation

Re-calculation was performed on 10% of the instrument calibration and reported QC and sample analyses. No anomalies were found via the verification calculation. MRLs were supported with adequate initial calibration concentrations. Response peak integrations were primarily performed automatically with computer software. In cases where peak shifting, signal interferences, and/or peak tailing occurred, manual integrations were performed. Manual integrations criteria and approaches were consistent justifiable across the analyses; no anomalies were identified in relation to compound identification and quantitation.

4.12 Overall Assessment of PAHs Data Usability

PAHs data are of known quality and acceptable for use with the acknowledgement of SOP deviations and anomalies stated above.

SUMMARY

Table 1. Data Affected by QC Anomalies

Sample ID	Analyte	Data Qualifier	Reason	Report Section
No data were significantly affected by QC anomalies that required data qualification.				

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APPENDIX A

QUALITY CONTROL CRITERIA FOR ANALYTICAL METHODS

Table A1 – PCB Congeners Analysis Quality Control Evaluation Criteria Summary

QC Parameters and Performance Frequency	Laboratory and Referenced Analytical Method			
	Laboratory 58 (EPA 8270D)	Laboratory 52 (EPA 1668C)	Laboratory 34 (EPA 8270D Modified)	Laboratory 84 (EPA 1668C)
Tuning (Resolution Check) At the beginning and the end of each 12-hour period of analysis.	Same as Method	Same as Method	Prior to initial calibration. Prior to CCV if system idle for >24 hrs. Criteria same as 8270D.	Same as Method
GC Column Performance Check Prior to ICAL or calibration verification.	N/A	Same as Method	N/A	Same as Method
Initial Calibration (ICAL) Prior to sample analysis; as needed if failure of calibration verification; or a new lot is used as standard source.	Same as Method	- Same as Method - Standards' result values are within 15% of true values.	Same as 8270D.	Same as Method
Calibration Verification (CCV), Ongoing Precision Recovery (OPR), or Verification (VER) At the beginning of each 12-hour period.	Same as Method	- Same as Methods. - SOP Tables 4a and 4b.	At the beginning and end of 10 injections or each 24 hour period (whichever is more frequent)	Same as Method
Method Blank One per preparatory batch, run after calibration standards and before samples.	No analytes detected $\geq \frac{1}{2}$ limit of quantitation or $\geq 5\%$ of the associated regulatory limit for the analyte or $\geq 10\%$ of the sample result for the analyte, whichever is greater, per method.	Analyte amounts in blank samples for PCB congeners 77, 81, 114, 123, 126 and 169 must be ≤ 2 pg/congener/sample, amounts of PCB congeners 156, 157, 167 and 189 must be ≤ 10 pg/congener/sample, and the maximal amount of PCB 11 must be ≤ 150 pg/sample. Amounts of all other individual PCB congeners or coelutions must be ≤ 50 pg/congener/sample in blank samples. The sum of all 209 congeners should be ≤ 300 pg/sample. Higher levels are acceptable where sample concentrations exceed 10 times blank levels.	Analyte concentration in PB should be $< \text{MDL}$ and must be $< 5 \times \text{MDL}$ No analytes detected $> \frac{1}{2}$ RL. For common laboratory contaminants, no analytes detected $> \text{RL}$.	Target analytes must be less than estimated maximum levels (EMLs) in SOP Table 4

Instrument Blank At the beginning of each 12-hour period.	Same as Method Blank.	Same as Method Blank.	Same as Method Blank.	Target analytes must be less than EMLs in SOP Table 4
Laboratory Control Sample (LCS) One per preparatory batch.	%R value should be within 70-130% of the true value	SOP Tables 4a and 4b.	70 to 130% recovery vs. SIS 40 to 120% recovery vs. IS	Within control limits for OPR (SOP Tables 10A and 10B).
Matrix Spike (MS) (OPTIONAL)	%R value should be within 70-130% of the true value	N/A	70 to 130% recovery vs. SIS 40 to 120% recovery vs. IS Spiked target analyte concentration must be > 5 x the level in the background sample.	NA
Sample Duplicate or MS Duplicate (MSD)	RPD ≤ 30%	RPD ≤ 20% (applicable to concentrations ≥10 times the DL)	RPD ≤ 30%	N/A
Extraction Standards and Cleanup Standards Every field sample, standard, and QC sample.	- Same as Method for Internal standard recovery - Surrogate Spike recovery is within 70 - 130%.	Same as Method SOP Tables 4a and 4b.	Surrogate spike recovery 40 - 120%	Same as Method
Compound Identification	Same as Method	Same as Method	Same as 8270D	Same as Method

Notes:

N/A: Not applicable

EPA 8270D - USEPA. 1998. *Test Methods for Evaluating Solid Waste (SW 846). Third Edition and Revised Update IIIA. Method 8000 and Method 8270D. Office of Solid Waste and Emergency Response, Washington, D.C. April 1998 and Updates.*

EPA 1668C - USEPA Method 1668C - *Chlorinated Biphenyl Congeners in Water, Soil, Sediment, Biosolids, and Tissue by HRGC/HRMS. April 2010.*

Table A2 – PAHs Analysis Quality Control Evaluation Criteria Summary

QC Parameter & Performance Frequency	Laboratory and Referenced Method			
	Laboratory 58 EPA 8270D-SIM	Laboratory 52 EPA 8720C-SIM EPA 1625 (HRGC/MS)	Laboratory 34 (EPA 8270D Modified)	Laboratory 84 EPA 8270C-SIM EPA 1625 (GC/MS)
Relative Retention Time (RRT) Evaluation Each Sample	RRT of each target analyte in each calibration standard within ± 0.05 RRT units.	- RT within ± 3 seconds of the predicted retention time determined from the calibration standard and adjusted relative to the peak retention time reference (i.e. labelled surrogate). - A second requirement is that an authentic elute after its labelled analog.	RT window for an analyte is ± 15 s from the determined RT of the analyte in the ICAL.	N/A
Initial Calibration (ICAL) Prior to sample analysis; as needed if failure of calibration verification; or a new lot is used as standard source.	- A minimum of five points. - Analytes' RRFs must meet method limits across calibration range. - Analytes %RSDs must be less than or equal to 20%, or the analyte must employ a linear or non-linear calibration model with a coefficient of determination (r^2) greater than 0.99. - Up to 10% of the total analytes may fail 1 and 2 above. - Verify ICAL with one second-source standard at mid- point concentration. Value for all analytes within $\pm 30\%$ of expected value.	- Calibration standard solutions are presented in SOP Table 6. - Linearity is demonstrated by a 5-point calibration over the working concentration range with a relative standard deviation of the RRFs $\leq 20\%$ for targets with a labelled analog present and all labelled compounds, $\leq 35\%$ for targets with no labelled analog present.	- A minimum of five points. - Analyte RF %RSDs must be less than or equal to 25% average RF. - Verify ICAL with one second-source standard. Value for all analytes within $\pm 25\%$ of expected value.	- SOP Table 3 lists ICAL concentrations. %RSD must be $\leq 30\%$ for analytes and internal standards. - Verify ICAL with one second-source standard at mid-point (CS4) concentration. Value for all analytes within $\pm 30\%$ of expected value.
Calibration verification (CCV) Before sample analysis, and every 12 hours of analysis time	- Average RRFs for analytes must meet the method defined limits. %Difference/Drift for analytes $\leq 20\%$ - Up to 20% of the target analytes may fail the criteria in 1 and 2 so long as the sample analyses associated with the CCVS are J flagged.	- Opening Cal Ver: Concentrations of native compounds and labelled surrogates must be within $\pm 25\%$ of expected values for all targets. - Closing Cal Ver: Concentrations of native compounds must be within $\pm 25\%$ of expected values. - Concentrations of labelled surrogates must be within $\pm 25\%$ of expected values, with any two (2) values allowed to be within $\pm 40\%$. - Ion ratios for authentic and labelled dibenz[ah]anthracene, indeno[1,2,3-cd]pyrene and benzo[ghi]perylene must be within $\pm 35\%$ of the mid-point of the I-CAL. - All other native analytes and labelled surrogates must be within $\pm 20\%$ of the mid-point of the I-CAL.	- Average RRFs for analytes must meet the method defined limits. - CCV after every 10 injections of 24 hrs – whichever is shorter. - Individual % difference $\leq 25\%$ - Grand mean of % difference $\leq 15\%$. - IS area has not changed by more than a factor of two (-50% to +100% from the area found in level 3 of the ICAL.	%Difference/Drift for analytes must be $\leq 30\%$ (SOP Table 7). - The recovery standard response must be within 50- 200% of the response in the corresponding CS4 calibration level of the initial calibration. - New ICAL is needed if this criterion is not met.

QC Parameter & Performance Frequency	Laboratory and Referenced Method			
	Laboratory 58 EPA 8270D-SIM	Laboratory 52 EPA 8720C-SIM EPA 1625 (HRGC/MS)	Laboratory 34 (EPA 8270D Modified)	Laboratory 84 EPA 8270C-SIM EPA 1625 (GC/MS)
Internal Standards Every field sample, standard, and QC sample	- Retention time ± 30 seconds from retention time of the midpoint standard in the ICAL or CCV. - EICP area within - 50% to +100% of ICAL midpoint standard	Within -50% to +100% of ICAL midpoint standard.	IS area has not changed by more than a factor of two (-50% to +100% from the area found in level 3 of the ICAL.	The recovery standard response must be within 50- 200% of the response in the corresponding CS4 calibration level of the initial calibration.
Method blank One per preparation batch of 20 or less samples	No analytes detected > $\frac{1}{2}$ RL. For common laboratory contaminants, no analytes detected $\geq$ RL.	SOP Table 8.	Analyte concentration in PB should be < MDL and must be < 5 MDL No analytes detected > $\frac{1}{2}$ RL. For common laboratory contaminants, no analytes detected > RL.	No analytes detected > RL ($\frac{1}{2}$ RL for DoD projects).
Laboratory control sample (LCS) One per preparation batch of 20 or less samples	See Laboratory QA Plan (LQAP). Reported along with LCS results	SOP Table 8.	70 to 130% recovery vs. SIS 40 to 120% recovery vs. IS	SOP Table 7
Matrix Spike (MS) and MS Duplicate (MSD)	- For matrix evaluation, see LQAP. MS recovery is advisory. - RPD $\leq 30\%$ (MS/MSD or sample duplicate). Limits are advisory.	SOP Table 8.	70 to 130% recovery vs. SIS 40 to 120% recovery vs. IS RPD $\leq 30\%$	N/A
Surrogate Spikes Every field and QC sample	QC acceptance criteria for LCS specified by DoD, if available; otherwise method- specified criteria or laboratory's own in-house criteria (No more than 1 acid surrogate or 1 base surrogate is allowed out of control, all surrogate recoveries must be > 10%.)	SOP Table 8 for SPMD samples, including criteria for PRCs.	40 - 120% recovery	SOP Table 7
Laboratory Duplicates (Optional)	N/A	Duplicates must fall within $\pm 20\%$ of the mean (applicable to concentrations ≥ 10 times the DL). (Note that $\pm 20\%$ of the mean is equivalent to 40 relative percent difference)	$\leq 30\%$ RPD	N/A

QC Parameter & Performance Frequency	Laboratory and Referenced Method			
	Laboratory 58 EPA 8270D-SIM	Laboratory 52 EPA 8720C-SIM EPA 1625 (HRGC/MS)	Laboratory 34 (EPA 8270D Modified)	Laboratory 84 EPA 8720C-SIM EPA 1625 (GC/MS)
Compound Identification	Same as Method	• Peak responses must be at least three times the background noise level. • The retention time (RT) must be within three seconds of that predicted from the calibration run and the sample retention time reference (labelled compound). • Peak maxima for the quantification and confirmation ions must coincide within two seconds. • The relative ion abundance ratios must be within 20% of the opening calibration values.	• Primary SIM ion must be present. • Peak responses must be at least three times the background noise level. • RT must fall within established RT window.	• The internal standard quantitation ions must be present. • The relative intensities of confirmation ions should agree to within $\pm 30\%$ between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 20% and 80%). The absence of confirmation ions should be considered carefully when making decisions regarding qualitative identification. Confirmation ions may have lower response than quantitation ions and may not always be present at lower concentrations. Their absence in this case may not be cause for determining that the analyte is not present. The absence of confirmation ions at higher levels where they should have been detectable may be cause for determination that an analyte is not present. • The sample component retention time must compare to within ± 0.2 min. of the retention time of the internal standard component. For reference, the standard must be run within the same 12- hour period as the sample. • If a compound cannot be verified by all the above criteria, but in the technical judgment of the analyst the identification is correct, the analyst shall report that identification and proceed with quantitation.

Notes:

N/A - Not applicable.; DoD – U.S. Department of Defense

EPA 8270D - USEPA. 1998. *Test Methods for Evaluating Solid Waste (SW 846). Third Edition and Revised Update IIIA. Method 8000 and Method 8270D. Office of Solid Waste and Emergency Response, Washington, D.C. April 1998 and Updates.*

EPA 1625 – 40CFR, Appendix A to Part 136, Method 1625 Revision B, Semivolatile Organic Compounds by Isotope Dilution GC/MS

HRGC/MS – High resolution gas chromatography coping with mass spectrometry

GC/MS – Gas chromatography coping with mass spectrometry

RL – Reporting Limit

Data Validation Report

Standardizing Polymeric Sampling for Measuring Freely Dissolved Organic Contaminants in Sediment Porewater ER 201735

Task 3 – Day Zero Loading and Analysis of Solid Phase Microextraction (SPME) Fiber (Second Study)

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ACRONYMS

%D	percent difference
%D_f	percent drift
%R	percent recovery
%RSD	percent relative standard deviation
CCV	continuing calibration verification
COC	chain-of-custody
CS1	the first calibration standard
CS3	the third calibration standard
EDD	electronic data deliverable
EDL	estimated detection limit
EMPC	estimated maximum possible concentration
EPA	U.S. Environmental Protection Agency
HRGC/ HRMS	high-resolution gas chromatography/high-resolution mass spectrometry
ICAL	initial calibration
ICV	initial calibration verification
IPR	initial precision and recovery
LCL	lower control limit
LCS	laboratory control sample
LCSD	laboratory control sample duplicate
LIMs	laboratory information management system
m/z	mass-to-charge ratio
MB	method blank
MDL	method detection limit
MS	matrix spike
MSD	matrix spike duplicate
ng/g	nanogram per gram
ng/L	nanogram per liter
ng/mL-PDMS	nanogram per milliliter of polydimethylsiloxane
OPR	ongoing precision and recovery
PCB	polychlorinated biphenyl
PDMS	polydimethylsiloxane
PFK	perfluorokerosene
PRC	performance reference compound
QA/QC	quality assurance/quality control
QAPP	quality assurance project plan
RF	response factor
RPD	relative percent difference
RRT	relative retention time
SDG	sample delivery group

SICP	selected ion current profile
S/N	signal-to-noise ratio
SOP	standard operating procedure
SPME	solid phase microextraction
TTU	Texas Technology University
USACE	US Army Corps of Engineers

INTRODUCTION

This report presents the findings of the data validation performed on analytical data for the study of the Day Zero Loading and Analysis of Solid Phase Microextraction (SPME) Fiber submitted by participating commercial laboratories, as part of the effort for Task 3 identified in the Project Demonstration Plan (USACE et. al., 2018). As a follow-up with the first study, the loading conditions for the SPME fibers were further optimized in this study.

Each of the participating laboratories received 28 5cm solid phase microextraction (SPME) fibers coated with polydimethylsiloxane (PDMS) from the Texas Tech University (TTU). The SPME fibers were divided into 14 samples (two fibers per sample) - six of the samples were subject for PCB performance reference compounds (PRCs) loading; six for PAH PRC loading; and one as a method blank for each of the PCBs and PAHs analyses. Specific PRCs for each types of analyses were identified in the Project Demonstration Plan (USACE et. al., 2018), and the target PRCs and their concentrations for respective analytical methods are summarized as follows:

PCBs by EPA 1668C		PCBs by EPA 8270D-SIM		PAHs by EPA 8270D-SIM & EPA 1625C	
PRCs	Target Concentration (ng/mL-PDMS)	PRCs	Target ^(A) Concentration (ng/mL-PDMS)	PRCs	Target Concentration (ng/mL-PDMS)
¹³ C-PCB 28	1184	¹³ C-PCB 37	1579	¹³ C ₆ -Phenanthrene	39480
¹³ C-PCB 47	1184	¹³ C-PCB 47	1579	¹³ C ₆ -Fluoranthene	39480
¹³ C-PCB 70	1184	¹³ C-PCB 54	1579	¹³ C ₆ -Chrysene	39480
¹³ C-PCB 80	1184	¹³ C-PCB 111	1579	¹³ C ₆ -Indeno[1,2,3-cd]pyrene	39480
¹³ C-PCB 111	1184	¹³ C-PCB 138	1579		
¹³ C-PCB 141	1184	¹³ C-PCB 178	1579		
¹³ C-PCB 182	1184				

Notes:

ng/mL-PDMS: nanogram per milliliter of PDMS

^(A) – Target concentrations were back-calculated based on PDMS sampler loading conditions determined by the laboratories and thus the concentrations varied with laboratories.

Samples (excluding the method blanks) then underwent the PRC loading process following the guidelines provided by the TTU (TTU, 2018). Once the loading process was completed, the samples (including method blanks) were subject for solvent extraction. Upon extraction, the fiber was rinsed with DI water then blot or air dried. Each segment was placed into a 2 mL amber vial prefilled with hexane then sonicated and brought to desired final extract volume to complete the extraction. The extracts were then subjected for instrumental analyses.

Participating commercial laboratories and respective analytical methodologies applied to this study are summarized as follows:

Participating Commercial Laboratory	Analytical Method	
	PCB Congeners	PAHs
Laboratory 48	EPA Method 1668C -SIM	SW846 Method 8270D Modified EPA Method 1625 -SIM
Laboratory 83	SW846 Method 8270D Modified - SIM	SW846 Method 8270D Modified - SIM

Notes:

1. USEPA Method 1668C: *Chlorinated Biphenyl Congeners in Water, Soil, Sediment, Biosolids, and Tissue by HRGC/HRMS*. April 2010.
2. Method 1625C: *Semi-volatile Organic Compounds by Isotope Dilution GCMS*. June 1989.
3. SW846 - USEPA Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Third Edition, December 1996.

SIM – Selective ion monitoring

Laboratories throughout this report are referred to using random number assignments to ensure the anonymity of participating commercial laboratories. Each participating laboratory was required to submit analytical deliverables for each analysis, including (1) a Level IV full data package containing reporting forms and all raw data supporting the reported sample and QC analyses results, and (2) an electronic data deliverable (EDD) in the Washington State Department of Ecology's Environmental Information Management System (EIMS) format. The laboratory could choose to submit the EDDs in Excel or csv. format. Each laboratory report and EDD were assigned a unique sample delivery group (SDG) number. Laboratory deliverables, after fully validated, were archive in the project file at the US Army Corps of Engineers, Seattle District. SDG numbers assigned by each laboratory are summarized as follows:

Participating Commercial Laboratory	Sample Delivery Group or Laboratory Identification Number	
	PCB Congeners	PAHs
Laboratory 48	DPWG72500	DPWG72434
Laboratory 83	DP-20-0549	DP-20-0551

Final sample results were reported as ng/mL-PDMS, based on the conversion conventions provided by TTU. Values reported in the laboratory reports did not present this conversion, but in separate EDDs due to the limitations posed by the laboratories' information management systems (LIMs). A Stage 4 validation (as defined by EPA, 2009) was performed on all PCB congener and PAHs data. The validation followed guidance specified by EPA (2014, 2016 & 2017), with modifications to accommodate respective analytical methods and requirements specified in the Standard Operating Procedures (SOPs) provided by the participating commercial laboratories. The numerical quality assurance/quality control (QA/QC) criteria applied to the validation were in accordance with method requirements and the current performance-based control limits established by the laboratory (laboratory control limits). Instrument calibration, frequency of QC analyses, and analytical sequence requirements were evaluated against the respective analytical methods. Laboratory-specific QC Criteria are summarized in **Appendix A, Tables A1 and A2**.

Validation findings are discussed in each section pertinent to the QC parameter for each type of analysis. Qualified data with applied data qualifiers are summarized in the **Summary** section at the end of this report.

DATA VALIDATION FINDINGS

1. PCB Congeners by EPA Method 1668C: High-resolution Gas Chromatography and High-resolution Mass Spectrometry (HRGC/HRMS)

One participating commercial laboratory, Laboratory 48 participate in this phase of study using EPA Method 1668C for the study. Note that neither EPA Method 1668C nor laboratory SOPs specified evaluation criteria for carbon-labeled PCBs. However, unless noted otherwise, criteria set forth for non-labeled PCBs in the method and SOPs were applied for carbon-labeled PCB data quality and method compliance evaluation.

1.1 Sample Management and Holding time

No anomalies were noted by the laboratories in relation to sample packaging, transportation, handling, preservation, and integrity upon sample receipt in the laboratories.

EPA Method 1668C does not specify holding time requirements for SPME samples (submerged in loading solution). Holding time requirements for solid samples (one year from collection to extraction, 40 days from extraction to analysis) were applied as a guideline for sample and extract holding time evaluation. Samples were extracted and analyzed within the holding times by both laboratories.

1.2 HRGC/HRMS Instrument Performance Check

The EPA Method 1668C criteria for instrument performance checks are as follows:

Mass Spectrometer Resolution: (1) The resolution check should be performed, using perfluorokerosene (PFK) or equivalent standard materials, prior to initial calibration and at the start and end of each 12-hour shift, (2) the resolution should be $\geq 8,000$ throughout the mass range and $\geq 10,000$ resolving power at m/z 330.9792 (or any other significant PFK fragments in the range of 300 to 350), and (3) the deviation between the exact m/z and the theoretical m/z must be less than 5 ppm for monitored isomers.

Column Performance: (1) A combined 209 congener standard should be analyzed prior to initial calibration and continuing calibration verification, (2) peak for congener 34 should be resolved from 23 and peak for congener 187 resolved from 182 peak with a valley of $\leq 40\%$, (3) congeners 156 and 157 should co-elute within 2 seconds at their peak maximum, and (4) the absolute retention time (RT) for congener 209 should be >55 minute for SPB-octyl or an alternate column.

In addition to the method requirements, laboratories imposed more criteria based on their specific instrumentation. HRGC/HRMS instrument performance checks met the method and SOP criteria for Laboratory 48.

1.3 Initial Calibration (ICAL)

Laboratory 48 followed their SOP to establish ICAL for the ^{13}C -labeled PCB PRCs. A mid-point calibration standard was analyzed at the beginning and the end of the analytical sequence. The ion

abundance ratios, signal/noise (S/N) ratios, and the response factor %RSD ($\leq 20\%$) values and retention time (RT) difference between the two analyses met the laboratory control criteria for the target compounds and surrogate compounds were within laboratory criteria. The ICAL met the laboratory SOP requirements and is valid for compound quantitation.

1.4 Calibration Verification (CCV) – Ongoing Precision and Recovery (OPR)

An ongoing precision and recovery (OPR) analysis was performed in lieu of continuing calibration verification. The ion abundance ratios, signal/noise (S/N) ratios, and the percent recovery (%R) values met the laboratory control criteria for the target compounds and surrogate compounds were within laboratory criteria.

1.5 Method Blanks

A method blank was prepared and analyzed. PCB PRCs were not detected at or above the method detection limits (MDLs).

1.6 Initial Precision and Recovery Study (IPR)

IPR study results are normally maintained in the laboratory and were not included in data packages. This information will be required in data packages reported for the following phases of this study as needed.

1.7 Laboratory Control Sample (LCS)

OPR was prepared and analyzed in lieu of LCS. The %R values met the laboratory control criteria.

1.8 Labeled Compound Recovery

Labeled internal standards were added to all samples as required by the analytical method and the laboratory SOP. The labeled internal standards and cleanup standards percent recoveries all met the laboratory SOP requirements.

1.9 Target Compound Identification

Target compound identification was evaluated by examining if: (1) the signals for the two exact m/z's being monitored were present, and maximized within ± 3 seconds of one another, (2) the S/N ratio of each of the two exact m/z's must be greater than or equal to 2.5, (3) the ion abundance ratios were within the method control limits, and (4) the relative retention time (RRT) or retention time (RT) of the peaks were within the laboratory control limits. No anomalies were found in relation to target compound identification.

1.10 Reporting Limits, Estimated Detection Limits (EDLs) and Compound Quantitation

Correct internal standards, quantitation ions, and average RFs were used to quantitate target compound detections. The MRLs were supported with adequate ICAL calibration concentrations.

The project goal for quantitation limits were attained to in these cases. Response peak integrations were primarily performed automatically with computer software. In cases where peak shifting, signal interferences, and/or peak tailing occurred, manual integrations were performed. Manual integrations criteria and approaches were consistent justifiable across the analyses; no anomalies were identified in relation to compound identification and quantitation.

A verification calculation was performed on 10% of the reported calibration, laboratory QC analyses, and sample results. No anomalies were found. The verification calculation worksheets were maintained in project files for requests.

1.11 Overall Assessment of PCB Congener Data Usability

PCB congener data were of known quality and acceptable for use with the acknowledgement of deviations and anomalies discussion above.

2. PCB Congeners by GC/MS - SIM (EPA Method SW8270D-SIM)

One laboratory, Laboratory 83, participated this phase of the study using EPA Method SW8270D-SIM for PCB congeners analysis. Note that neither EPA Method 8270D nor the laboratory SOP specified evaluation criteria for carbon-labeled PCBs. However, unless noted otherwise, criteria set forth for non-labeled PCBs in the method and the laboratory SOP were applied for carbon-labeled PCBs data quality and method compliance evaluation.

2.1 Sample Management and Holding Times

No anomalies were noted by the laboratories in relation to sample packaging, transportation, handling, preservation, and integrity upon sample receipt in the laboratories.

EPA Method 8270D does not specify holding time requirements for SPME samples (submerged in loading solution). Holding time requirements for solid samples (one year from collection to extraction, 40 days from extraction to analysis) were applied as a guideline for sample and extract holding time evaluation. Samples were extracted and analyzed within the holding times by both laboratories.

2.2 GC/MS Instrument Performance Check

The laboratories performed GC/MS tuning analysis as required by the analytical method and their SOPs. DFTPP tuning was performed within each 12-hour interval. All required ion abundance ratios met the method requirements.

2.3 Initial Calibration (ICAL)

EPA Method 8270D criteria require that (1) if a linear average RFs is chosen as the quantitation option, at least five standards at different concentrations should be analyzed and the %RSD of RFs be $\leq 25\%$ for the analyte, (2) if least-square linear regression is chosen for quantitation, the

correlation coefficient (r) be >0.995 , and (3) if six-point non-linear (quadratic) curve is chosen for quantitation, the coefficient of determination (r^2) be >0.99 . All ICALs met the method and laboratory criteria.

2.4 Calibration Verification (CCV)

The analytical method and the laboratory SOP require that (1) continuing calibration verifications be analyzed at the beginning of each 12-hour analysis period prior to the analysis of method blank and samples, and (2) the %D be within $\pm 25\%$. All CCVs met the method and laboratory criteria.

2.5 Method Blank

A method blank was prepared and analyzed. Target PCB PRCs were not detected at or above the MDLs.

2.6 Surrogate Spikes

Surrogate spikes were added to all samples as required by the method. All surrogate spike %R values were within the laboratory control limits.

2.7 Matrix Spike (MS) and MS Duplicate (MSD)

MS and MSD analyses were not applicable for the calibration standard analysis.

2.8 Laboratory Control Sample (LCS)

LCS was prepared and analyzed. The %R values met the laboratory control limits.

2.9 Internal Standards

The method requires that (1) internal standard retention time be within ± 30 seconds from that of the associated 12-hour calibration standard, and (2) the area counts of all internal standards be within -50% to $+100\%$ of the associated 12-hour calibration standard. Laboratory 83 chose to use those of the mid-point ICAL standard for internal standard recovery control criteria. Internal standard recovery met the method or laboratory requirements for ARI.

2.10 Target Compound Identification

All chromatograms and ion spectrum were properly displayed and scaled. No anomalies were found in relation to target compound identification.

2.11 Reporting Limits and Target Compound Quantitation

Re-calculation was performed on 10% of the instrument calibration and reported QC and sample analyses. No anomalies were found via the verification calculation. MRLs were supported with

adequate initial calibration concentrations. In cases where target compound concentrations exceeded ICAL calibration ranges, extracts were diluted and re-analyzed for definitive quantitation.

Response peak integrations were primarily performed automatically with computer software. In cases where peak shifting, signal interferences, and/or peak tailing occurred, manual integrations were performed. Manual integrations criteria and approaches were consistent justifiable across the analyses; no anomalies were identified in relation to compound identification and quantitation.

2.12 Overall Assessment of PCB Congeners Data Usability

PCB Congeners data are of known quality and acceptable for use, with the acknowledgement of SOP deviations and anomalies stated above.

3. PAHs by Isotope Dilution GC/MS (EPA Method SW8270D Modified and EPA Method 1625 Modified)

Laboratory 48 participated this phase of the study using EPA Method SW8270D modified with EPA Method 1625 for this study. Note that neither EPA Method 8270D, EPA Method 1625 nor laboratory SOPs specified evaluation criteria for carbon-labeled PAHs. However, unless noted otherwise, criteria set forth for non-labeled PAHs in the methods and SOPs were applied for PAH PRC data quality and method compliance evaluation.

3.1 Sample Management and Holding Times

No anomalies were noted by the laboratories in relation to sample packaging, transportation, handling, preservation, and integrity upon sample receipt in the laboratories.

EPA Method 8270D does not specify holding time requirements for SPME samples (submerged in loading solution). Holding time requirements for solid sample (one year from collection to extraction, 40 days from extraction to analysis) were applied as a guideline for sample and extract holding time evaluation. Samples were extracted and analyzed within the holding times by both laboratories.

3.2 GC/MS Instrument Performance Check

The method requires that MS tuning be performed within each 12-hour interval. All required ion abundance ratios should meet the requirements in the method. Each of the laboratories specified GC/MS tuning procedures and requirements in their SOPs. However, tuning reports were not included in their data package in this task. This information will be required for all data packages in future sample analyses for this study.

3.3 Initial Calibration (ICAL)

Laboratory 48 followed their SOP to establish ICAL for the ¹³C-labeled PCB PRCs. A mid-point calibration standard was analyzed at the beginning and the end of the analytical sequence. The ion

abundance ratios, signal/noise (S/N) ratios, and the response factor %RSD ($\leq 20\%$) values and retention time (RT) difference between the two analyses met the laboratory control criteria for the target compounds and surrogate compounds were within laboratory criteria. The ICAL met the laboratory SOP requirements and is valid for compound quantitation.

3.4 Calibration Verification (CCV) – Ongoing Precision and Recovery

An ongoing precision and recovery (OPR) analysis was performed in lieu of continuing calibration verification. The ion abundance ratios, signal/noise (S/N) ratios, and the percent recovery (%R) values met the laboratory control criteria for the target compounds and surrogate compounds were within laboratory criteria.

3.5 Method Blanks

A method blank was prepared and analyzed as required. Target PAH PRCs were not detected at or above the MDLs.

3.6 Surrogate Spikes

Surrogate spikes were added to all samples as required by the method. All surrogate spike %R values were within the control limits specified in the laboratory SOPs.

3.7 Laboratory Control Sample (LCS)

OPR was prepared and analyzed in lieu of LCS. All %R values were within the laboratory control limits.

3.8 Labeled Compound Recovery

Labeled internal standards were added to all samples as required by the analytical method and laboratory SOPs. The labeled internal standards percent recoveries all met the method and laboratory SOP requirements.

3.9 Target Compound Identification

All chromatograms and ion spectrum were properly displayed and scaled. No target compounds were detected in any of the field samples. No anomalies were found in relation to target compound identification.

3.10 Reporting Limits and Target Compound Quantitation

Re-calculation was performed on 10% of the instrument calibration and reported QC and sample analyses. No anomalies were found via the verification calculation. MRLs were supported with adequate initial calibration concentrations. In cases where target compound concentrations exceeded ICAL calibration ranges, extracts were diluted and re-analyzed for definitive quantitation.

Response peak integrations were primarily performed automatically with computer software. In cases where peak shifting, signal interferences, and/or peak tailing occurred, manual integrations were performed. Manual integrations criteria and approaches were consistent justifiable across the analyses; no anomalies were identified in relation to compound identification and quantitation.

3.11 Overall Assessment of PAHs Data Usability

PAHs data are of known quality and acceptable for use with the acknowledgement of deviations and anomalies stated above.

4. PAHs by GC/MS - SIM (EPA Method SW8270D-SIM)

Laboratory 83 participated in this phase of the study, using EPA Method 8270D-SIM. Neither EPA Method 8270D nor the laboratory SOP specified evaluation criteria for carbon-labeled PAHs. Unless noted otherwise, criteria set forth for non-labeled PAHs in the method and SOP were applied for carbon-labeled PAHs data quality and method compliance evaluation.

4.1 Sample Management and Holding Times

No anomalies were noted by the laboratories in relation to sample packaging, transportation, handling, preservation, and integrity upon sample receipt in the laboratories.

EPA Method 8270D does not specify holding time requirements for SPME samples (submerged in loading solution). Holding time requirements for solid sample (one year from collection to extraction, 40 days from extraction to analysis) were applied as a guideline for sample and extract holding time evaluation. Samples were extracted and analyzed within the holding times by both laboratories.

4.2 GC/MS Instrument Performance Check

The laboratory performed GC/MS tuning analysis as required by the analytical method and their SOP. DFTPP tuning was performed within each 12-hour interval. All required ion abundance ratios met the method requirements.

4.3 Initial Calibration (ICAL)

EPA Method 8270D criteria require that (1) if a linear average RFs is chosen as the quantitation option, at least five standards at different concentrations should be analyzed and the %RSD of RFs be $\leq 25\%$ for the analyte, (2) if least-square linear regression is chosen for quantitation, the correlation coefficient (r) be >0.995 , and (3) if six-point non-linear (quadratic) curve is chosen for quantitation, the coefficient of determination (r^2) be >0.99 . All ICALs met the method and laboratory criteria.

4.4 Calibration Verification (CCV)

The analytical method requires that (1) continuing calibration verifications be analyzed at the beginning of each 12-hour analysis period prior to the analysis of method blank and samples, and (2) the %D be within $\pm 25\%$. The laboratories met the CCV criteria.

4.5 Method Blanks

A method blank was prepared and analyzed as required. Target PAH PRCs were not detected at or above the MDLs.

4.6 Surrogate Spikes

Surrogate spikes were added to all samples as required by the method. All surrogate spike %R values were within the control limits specified in laboratory SOP.

4.7 Matrix Spike (MS) and MS Duplicate (MSD)

MS and MSD analyses were not applicable for this calibration standard analysis

4.8 Laboratory Control Sample (LCS)

LCS was not prepared by ARI. LCS was prepared and analyzed by Laboratory 83. The %R values met the laboratory control limits.

4.9 Internal Standards

The method requires that (1) internal standard retention time be within ± 30 seconds from that of the associated 12-hour calibration standard, and (2) the area counts of all internal standards be within -50% to $+100\%$ of the associated 12-hour calibration standard. Laboratory 83 chose to use those of the mid-point ICAL standard for internal standard recovery control criteria. Internal standard recovery met the method or laboratory requirements.

4.10 Target Compound Identification

All chromatograms were properly displayed and scaled. No target compounds were detected in any of the field samples. No anomalies were found in relation to target compound identification.

4.11 Reporting Limits and Target Compound Quantitation

Re-calculation was performed on 10% of the instrument calibration and reported QC and sample analyses. No anomalies were found via the verification calculation. MRLs were supported with adequate initial calibration concentrations.

Response peak integrations were primarily performed automatically with computer software. In cases where peak shifting, signal interferences, and/or peak tailing occurred, manual integrations

were performed. Manual integrations criteria and approaches were consistent justifiable across the analyses; no anomalies were identified in relation to compound identification and quantitation.

4.12 Overall Assessment of PAHs Data Usability

PAHs data are of known quality and acceptable for use with the acknowledgement of SOP deviations and anomalies stated above.

SUMMARY

Table 1. Data Affected by QC Anomalies

Sample ID	Analyte	Data Qualifier	Reason	Report Section
No data qualifiers were assigned as results of QC failure.				

REFERENCES

- TTU. 2018. *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*. Department of Civil, Environmental and Construction Engineering, Texas Technology University. 2018.
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- USEPA. 2014. *R10 Data Validation and Review Guidelines for Polychlorinated Dibenzo-p-Dioxin and Polychlorinated Dibenzofuran Data (PCDD/PCDF) Using Method 1613B and SW846 Method 8290A*. USEPA Region 10, Office of Environmental Assessment. Seattle, Washington. May 2014. EPA-910-R-14-003.
- USEPA. 2010. *Method 1668A: Chlorinated Biphenyl Congeners in Water, Soil, Sediment, Biosolids, and Tissue by HRGC/HRMS*. April 2010. USEPA-820-R-10-005.
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- USEPA. 1996. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Third Edition, December 1996.
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APPENDIX A

QUALITY CONTROL CRITERIA FOR ANALYTICAL METHODS

Table A1 – PCB Congeners Analysis Quality Control Evaluation Criteria Summary

QC Parameters and Performance Frequency	Laboratory and Referenced Analytical Method	
	Laboratory 48 (EPA 1668C)	Laboratory 83 (EPA 8270D Modified)
Tuning (Resolution Check) At the beginning and the end of each 12-hour period of analysis.	Same as Method	Prior to initial calibration. Prior to CCV if system idle for >24 hrs. Criteria same as 8270D.
GC Column Performance Check Prior to ICAL or calibration verification.	Same as Method	N/A
Initial Calibration (ICAL) Prior to sample analysis; as needed if failure of calibration verification; or a new lot is used as standard source.	- Same as Method - Standards' result values are within 15% of true values.	Same as 8270D.
Calibration Verification (CCV), Ongoing Precision Recovery (OPR), or Verification (VER)	- Same as Methods. - SOP Tables 4a and 4b.	At the beginning and end of 10 injections or each 24 hour period (whichever is more frequent)
Method Blank One per preparatory batch, run after calibration standards and before samples.	Analyte amounts in blank samples for PCB congeners 77, 81, 114, 123, 126 and 169 must be ≤ 2 pg/congener/sample, amounts of PCB congeners 156, 157, 167 and 189 must be ≤ 10 pg/congener/sample, and the maximal amount of PCB 11 must be ≤ 150 pg/sample. Amounts of all other individual PCB congeners or coelutions must be ≤ 50 pg/congener/sample in blank samples. The sum of all 209 congeners should be ≤ 300 pg/sample. Higher levels are acceptable where sample concentrations exceed 10 times blank levels.	Analyte concentration in PB should be $< \text{MDL}$ and must be $< 5 \times \text{MDL}$ No analytes detected $> \frac{1}{2}$ RL. For common laboratory contaminants, no analytes detected $> \text{RL}$.
Instrument Blank At the beginning of each 12-hour period.	Same as Method Blank.	Same as Method Blank.
Laboratory Control Sample (LCS) One per preparatory batch.	SOP Tables 4a and 4b.	70 to 130% recovery vs. SIS 40 to 120% recovery vs. IS
Matrix Spike (MS) (OPTIONAL)	N/A	70 to 130% recovery vs. SIS 40 to 120% recovery vs. IS Spiked target analyte concentration must be $> 5 \times$ the level in the background sample.
Sample Duplicate or MS Duplicate (MSD)	$\text{RPD} \leq 20\%$ (applicable to concentrations ≥ 10 times the DL)	$\text{RPD} \leq 30\%$
Extraction Standards and Cleanup Standards Every field sample, standard, and QC sample.	- Same as Method - SOP Tables 4a and 4b.	Surrogate spike recovery 40 - 120%
Compound Identification	Same as Method	Same as 8270D

Notes:

N/A: Not applicable

EPA 8270D - USEPA. 1998. *Test Methods for Evaluating Solid Waste (SW 846). Third Edition and Revised Update IIIA. Method 8000 and Method 8270D. Office of Solid Waste and Emergency Response, Washington, D.C. April 1998 and Updates.*

EPA 1668C - *USEPA Method 1668C - Chlorinated Biphenyl Congeners in Water, Soil, Sediment, Biosolids, and Tissue by HRGC/HRMS. April 2010.*

Table A2 – PAHs Analysis Quality Control Evaluation Criteria Summary

QC Parameter & Performance Frequency	Laboratory and Referenced Method	
	Laboratory 48 EPA 8720C-SIM EPA 1625 (HRGC/MS)	Laboratory 83 (EPA 8270D Modified)
Relative Retention Time (RRT) Evaluation Each Sample	- RT within ± 3 seconds of the predicted retention time determined from the calibration standard and adjusted relative to the peak retention time reference (i.e. labelled surrogate). - A second requirement is that an authentic elute after its labelled analog.	RT window for an analyte is ± 15 s from the determined RT of the analyte in the ICAL.
Initial Calibration (ICAL) Prior to sample analysis; as needed if failure of calibration verification; or a new lot is used as standard source.	- Calibration standard solutions are presented in SOP Table 6. - Linearity is demonstrated by a 5-point calibration over the working concentration range with a relative standard deviation of the RRFs $\leq 20\%$ for targets with a labelled analog present and all labelled compounds, $\leq 35\%$ for targets with no labelled analog present.	- A minimum of five points. - Analyte RF %RSDs must be less than or equal to 25% average RF. - Verify ICAL with one second- source standard. Value for all analytes within $\pm 25\%$ of expected value.
Calibration verification (CCV) Before sample analysis, and every 12 hours of analysis time	- Opening Cal Ver: Concentrations of native compounds and labelled surrogates must be within $\pm 25\%$ of expected values for all targets. - Closing Cal Ver: Concentrations of native compounds must be within $\pm 25\%$ of expected values. - Concentrations of labelled surrogates must be within $\pm 25\%$ of expected values, with any two (2) values allowed to be within $\pm 40\%$. - Ion ratios for authentic and labelled dibenz[ah]anthracene, indeno[1,2,3-cd]pyrene and benzo[ghi]perylene must be within $\pm 35\%$ of the mid-point of the I-CAL. - All other native analytes and labelled surrogates must be within $\pm 20\%$ of the mid-point of the I-CAL.	- Average RRFs for analytes must meet the method defined limits. - CCV after every 10 injections of 24 hrs – whichever is shorter. - Individual % difference $\leq 25\%$ - Grand mean of % difference $\leq 15\%$. - IS area has not changed by more than a factor of two (-50% to +100% from the area found in level 3 of the ICAL.
Internal Standards Every field sample, standard, and QC sample	Within -50% to +100% of ICAL midpoint standard.	IS area has not changed by more than a factor of two (-50% to +100% from the area found in level 3 of the ICAL.
Method blank One per preparation batch of 20 or less samples	SOP Table 8.	Analyte concentration in PB should be < MDL and must be < 5 MDL No analytes detected > $\frac{1}{2}$ RL. For common laboratory contaminants, no analytes detected > RL.
Laboratory control sample (LCS) One per preparation batch of 20 or less samples	SOP Table 8.	70 to 130% recovery vs. SIS 40 to 120% recovery vs. IS
Matrix Spike (MS) and MS Duplicate (MSD)	SOP Table 8.	70 to 130% recovery vs. SIS 40 to 120% recovery vs. IS RPD $\leq 30\%$

QC Parameter & Performance Frequency	Laboratory and Referenced Method	
	Laboratory 48 EPA 8720C-SIM EPA 1625 (HRGC/MS)	Laboratory 83 (EPA 8270D Modified)
Surrogate Spikes Every field and QC sample	SOP Table 8 for SPMD samples, including criteria for PRCs.	40 - 120% recovery
Laboratory Duplicates (Optional)	Duplicates must fall within $\pm 20\%$ of the mean (applicable to concentrations ≥ 10 times the DL). (Note that $\pm 20\%$ of the mean is equivalent to 40 relative percent difference)	$\leq 30\%$ RPD
Compound Identification	- Peak responses must be at least three times the background noise level. - The retention time (RT) must be within three seconds of that predicted from the calibration run and the sample retention time reference (labelled compound). - Peak maxima for the quantification and confirmation ions must coincide within two seconds. - The relative ion abundance ratios must be within 20% of the opening calibration values.	- Primary SIM ion must be present. - Peak responses must be at least three times the background noise level. - RT must fall within established RT window.

Notes:

N/A - Not applicable.; DoD – U.S. Department of Defense

EPA 8270D - USEPA. 1998. *Test Methods for Evaluating Solid Waste (SW 846). Third Edition and Revised Update IIIA. Method 8000 and Method 8270D. Office of Solid Waste and Emergency Response, Washington, D.C. April 1998 and Updates.*

EPA 1625 – 40CFR, Appendix A to Part 136, Method 1625 Revision B, Semivolatile Organic Compounds by Isotope Dilution GC/MS

HRGC/MS – High resolution gas chromatography coping with mass spectrometry

GC/MS – Gas chromatography coping with mass spectrometry

RL – Reporting Limit

Data Validation Report

Standardizing Polymeric Sampling for Measuring Freely Dissolved Organic Contaminants in Sediment Porewater ER 201735

Task 3 – Low Density Polyethylene (LDPE) Passive Sampler *ex-situ* Sediment Exposure

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ACRONYMS

%D	percent difference
%D_f	percent drift
%R	percent recovery
%RSD	percent relative standard deviation
CCV	continuing calibration verification
COC	chain-of-custody
CS1	the first calibration standard
CS3	the third calibration standard
EDD	electronic data deliverable
EDL	estimated detection limit
EMPC	estimated maximum possible concentration
EPA	U.S. Environmental Protection Agency
HRGC/ HRMS	high-resolution gas chromatography/high-resolution mass spectrometry
ICAL	initial calibration
ICV	initial calibration verification
IPR	initial precision and recovery
LCL	lower control limit
LCS	laboratory control sample
LCSD	laboratory control sample duplicate
LDPE	low density polyethylene
LIMs	laboratory information management system
m/z	mass-to-charge ratio
MB	method blank
MDL	method detection limit
MIT	Massachusetts Institute of Technology
MS	matrix spike
MSD	matrix spike duplicate
ng/g	nanogram per gram
OPR	ongoing precision and recovery
PCB	polychlorinated biphenyl
PE	polyethylene
PFK	perfluorokerosene
PQL	practical quantitation limit
PRC	performance reference compound
QA/QC	quality assurance/quality control
QAPP	quality assurance project plan
RF	response factor
RPD	relative percent difference
RRT	relative retention time

SDG	sample delivery group
SICP	selected ion current profile
S/N	signal-to-noise ratio
SOP	standard operating procedure
USACE	US Army Corps of Engineers

INTRODUCTION

This report presents the findings of the data validation performed on analytical data submitted by participating commercial laboratories for the study of *ex-situ* Sediment Exposure using Low Density Polyethylene (LDPE) Passive Sampler. This sediment exposure study is final laboratory effort as part of the effort for Task 3 identified in the Project Demonstration Plan (USACE *et. al.*, 2018).

Each of the participating laboratories performed the *ex-situ* sediment exposure in their facilities. The sediment supplied for this study was homogenized and aliquoted into twelve jars – six for static (passive) exposure and six for active exposure. Six LDPE strips were loaded with PRCs (following the procedures developed in Task 2), merged into jars individually and the jars sealed. Static exposure jars were placed upright and stored properly during the entire course of exposure. The active exposure jars underwent continuous vertical shaking plus periodical manual shaking in various directions to mimic dynamic real environmental conditions. The exposure time varied with laboratories, ranging from 30 to 40 days (Laboratory 34's exposure time extended to approximately 3 months due to restricted access to the facility by the COVID-19 pandemic.) Once retrieved from the sediment jars, LDPE strips were wiped-cleaned and underwent solvent extractions following the procedures developed in Task 2. A method blank LDPE strip and, for selected laboratories, a laboratory control sample (LCS) and/or LCS duplicate (LCSD) spiked with known-concentration target analytes were extracted along with the sediment-exposed LDPE. The extracts were analyzed for target polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyl (PCB) congeners and performance reference compounds (PRCs), as defined in the Project Demonstration Plan (USACE *et. al.*, 2018).

Target polycyclic aromatic compounds (PAHs) include the 17 non-derivatives PAHs; target PCB congeners for this task are PCB-44, PCB-52, PCB-66, PCB-101, PCB-105, PCB-118, PCB-126, PCB-128, PCB-138, PCB-153, PCB-170, PCB-180, PCB-187, PCB-195, PCB-206, and PCB-209.

Participating commercial laboratories and respective analytical methodologies applied to this study are summarized as follows:

Participating Commercial Laboratory	Analytical Method	
	PCB Congeners	PAHs
Laboratory 58	SW846 Method 8270D Modified	SW846 Method 8270D Modified
Laboratory 84	EPA Method 1668C	SW846 Method 8270D Modified EPA Method 1625
Laboratory 52	EPA Method 1668C	SW846 Method 8270D Modified EPA Method 1625
Laboratory 34	SW846 Method 8270D Modified	SW846 Method 8270D Modified

Notes:

1. Method 1668C: *Chlorinated Biphenyl Congeners in Water, Soil, Sediment, Biosolids, and Tissue by HRGC/HRMS*. April 2010.

2. Method 1625C: *Semi-volatile Organic Compounds by Isotope Dilution GCMS*. June 1989.
3. SW846 - Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Third Edition, December 1996.

Laboratories throughout this report are referred to using random number assignments to ensure the anonymity of participating commercial laboratories. Each participating laboratory was required to submit analytical deliverables for each analysis, including (1) a Level IV full data package containing reporting forms and all raw data supporting the reported sample and QC analyses results, and (2) an electronic data deliverable (EDD) in the Washington State Department of Ecology's Environmental Information Management System (EIMs) format. The laboratory could choose to submit the EDDs in Excel or csv. format. Each laboratory report and EDD were assigned a unique sample delivery group (SDG) number. Laboratory deliverables, after fully validated, were archive in the project file at the US Army Corps of Engineers Seattle District. SDG numbers assigned by each laboratory are summarized as follows:

Participating Commercial Laboratory	Sample Delivery Group or Laboratory Identification Number	
	PCB Congeners	PAHs
Laboratory 58	20D0005	20D0005
Laboratory 84	140-18674-2	140-18674-2
Laboratory 52	DPWG72609	DPWG72470
Laboratory 34	DP-20-0546	DP-20-0548

Final sample results were reported as ng/g-LDPE, based on the conversion conventions provided by MIT. Values reported in the laboratory reports did not present this conversion, but in separate EDDs due to the limitations posed by the laboratories' information management systems (LIMs).

A Stage 4 validation (as defined by EPA 2009) was performed on all PCB congener and PAHs data. The validation followed guidance specified by EPA (2014, 2016 & 2017), with modifications to accommodate respective analytical methods and requirements specified in the Standard Operating Procedures (SOPs) provided by the participating commercial laboratories. The numerical quality assurance/quality control (QA/QC) criteria applied to the validation were in accordance with method requirements and the current performance-based control limits established by the laboratory (laboratory control limits). Instrument calibration, frequency of QC analyses, and analytical sequence requirements were evaluated against the respective analytical methods. Laboratory-specific QC Criteria are summarized in *Appendix A, Tables A1 and A2*.

Validation findings are discussed in each section pertinent to the QC parameter for each type of analysis. Qualified data with applied data qualifiers are summarized in the **Summary** section at the end of this report.

DATA VALIDATION FINDINGS

1. PCB Congeners by EPA Method 1668C: High-resolution Gas Chromatography and High-resolution Mass Spectrometry (HRGC/HRMS)

Two participating commercial laboratories – Laboratory 52 and Laboratory 84 chose to use EPA Method 1668C for the study. Note that neither EPA Method 1668C nor laboratory SOPs specified evaluation criteria for carbon-labeled PCBs (i.e., PRCs). However, unless noted otherwise, criteria set forth for non-labeled PCBs in the method and SOPs were applied for carbon-labeled PCB data quality and method compliance evaluation.

1.1 Sample Management and Holding time

No anomalies were noted by the laboratories in relation to sample packaging, transportation, handling, preservation, and integrity upon sample receipt in the laboratories.

EPA Method 1668C does not specify holding time requirements for PE samples (submerged in loading solution). Holding time requirements for solid samples (one year from collection to extraction, 40 days from extraction to analysis) were applied as a guideline for sample collection (the time the LDPE strips were retrieved from the sediment) and extract holding time evaluation. Samples were extracted and analyzed within the holding times by both laboratories.

1.2 HRGC/HRMS Instrument Performance Check

The EPA Method 1668C criteria for instrument performance checks are as follows:

Mass Spectrometer Resolution: (1) The resolution check should be performed, using perfluorokerosene (PFK) or equivalent standard materials, prior to initial calibration and at the start and end of each 12-hour shift, (2) the resolution should be $\geq 8,000$ throughout the mass range and $\geq 10,000$ resolving power at m/z 330.9792 (or any other significant PFK fragments in the range of 300 to 350), and (3) the deviation between the exact m/z and the theoretical m/z must be less than 5 ppm for monitored isomers.

Column Performance: (1) A combined 209 congener standard should be analyzed prior to initial calibration and continuing calibration verification, (2) peak for congener 34 should be resolved from 23 and peak for congener 187 resolved from 182 peak with a valley of $\leq 40\%$, (3) congeners 156 and 157 should co-elute within 2 seconds at their peak maximum, and (4) the absolute retention time (RT) for congener 209 should be >55 minute for SPB-octyl or an alternate column.

In addition to the method requirements, laboratories imposed more criteria based on their specific instrumentation. HRGC/HRMS instrument performance checks met the method and SOP criteria for these laboratories.

1.3 Initial Calibration (ICAL)

Laboratory 84 chose to fully follow the EPA Method 1668C initial calibration (ICAL) for regular and the ¹³C-labeled PCB PRCs. The EPA Method 1668C criteria for initial calibration are: (1) a minimum of five standards should be employed for native congeners and labeled compounds, (2) the percent relative standard deviation (%RSD) of isomer response should be $\leq 20\%$, (3) the ion abundance ratios should be within the control limits listed in EPA Method 1668C, Table 8, (4) the signal-to-noise (S/N) ratio should be >10 for all native and labeled compounds in the first calibration standard (CS1), and (5) response factor (RF) should be determined using one-point calibration for congeners quantitated with internal standard method. Initial calibrations met the criteria. An initial calibration verification (second source) standard was analyzed to verify the calibration curve. The percent difference (%D) values were less than or equal to 30% and the initial calibration was considered valid.

Laboratory 52 followed the EPA Method 1668C requirements for regular PCB congeners and their SOP to establish ICAL for the ¹³C-labeled PCB PRCs. For PCB PRCs, a mid-point calibration standard was analyzed at the beginning and the end of the analytical sequence. The response factor RPD values for the target compounds and surrogate compounds should be within 20%, and RT within 3 seconds between the two analyses. The ICAL met the laboratory SOP requirements.

1.4 Calibration Verification (CCV)

The EPA Method 1668C criteria require that: (1) continuing calibration verifications be performed at the beginning of each 12-hour shift using the mid-point calibration standard (CS3), (2) the %D value should be within the control limits listed in EPA Method 1668C, Table 6, and (3) the ion abundance ratios, retention times, relative retention times, and S/N ratio should meet the same criteria as for initial calibrations. Note that the method did not specify ion abundance ratios for ¹³C-labeled PRCs; laboratory-specified criteria were applied for data quality determination.

All CCVs met the laboratory control criteria, except that the relative retention times (RRTs) for selected compounds slightly went outside the RRT window in Laboratory 84's CCVs. The chromatograms and ion spectrums were examined; no anomalies were found as far as compound identification. The %D values were all well within the control limits. The RRT shifting had no significant effects on data quality. No data qualifying action was taken in these cases.

1.5 Method Blanks

A method blank was prepared and analyzed by both laboratories. PRCs were not detected at or above the method detection limits (MDLs). Selected target PCB congeners were detected in method blanks at levels less than the practical quantitation limits (PQLs) but greater than their MDLs for both laboratories. Sample results for target PCB congeners detected in the method blank were all, except one data point, greater than five times the levels found in the method blank; the detections in method blanks were considered no effects on data usability. No data qualifying actions were taken in these cases. PCB-209 result in AXYs sample Active Test 3 (1.63 ng/g) was less than five times the level found in the method blank (0.45 ng/g). This result is qualified (U) as non-detected at the reported level.

1.6 Initial Precision and Recovery Study (IPR)

IPR study results are normally maintained in the laboratory and were not included in data packages. This information will be required in data packages reported for the following phases of this study as needed.

1.7 Ongoing Precision and Recovery (OPR)

OPR was prepared and analyzed for PRC PCBs at the adequate frequency by Laboratory 52. The %R values met the laboratory control criteria.

1.8 Laboratory Control Sample (LCS) and LCS Duplicate (LCSD)

Since no matrix-specific (i.e., LDPE in this case) LCS was available to be processed along with the samples, the laboratories analyzed/reported laboratory-made standards as LCS. Due to the limited supplier and the excessive cost of the ¹³C-labelled PRCs, the LCS analyzed/reported by Laboratory 84 did not contain the target PRCs. However, the %R values in LCS were all within the laboratory control criteria. The %R values for selected labeled compounds in LCS 140-38863/13-B and LCSD 140-38863/14-B. Since the %R values for the target compounds were within the control criteria; no data qualifying action was taken in this case.

OPR was prepared and analyzed in lieu of LCS by Laboratory 52. See discussion above.

1.9 Labeled Compound Recovery

Labeled internal standards were added to all samples as required by the analytical method and laboratory SOPs. The labeled internal standards and cleanup standards percent recoveries all met the method and laboratory SOP requirements, except for those discussed above related to the LCS and LCSD analyses by Laboratory 84 (see Section 1.8).

1.10 Target Compound Identification

Target compound identification was evaluated by examining if: (1) the signals for the two exact m/z's being monitored were present, and maximized within ± 2 seconds of one another (± 3 seconds for Laboratory 52), (2) the S/N ratio of each of the two exact m/z's must be greater than or equal to 2.5, (3) the ion abundance ratios were within the method control limits, and (4) the relative retention time (RRT) or retention time (RT) of the peaks were within the method control limits or laboratory control limits. No anomalies were found in relation to target compound identification, except that ion abundance ratios did not fully meet the method criteria for selected results. These results were reported as estimated maximum possible concentration (EMPC). The ion spectra were evaluated and determined that the anomaly in ion abundance ratios did not significantly affect data usability for these results. No data qualifying actions were taken.

1.11 Reporting Limits, Estimated Detection Limits (EDLs) and Compound Quantitation

Correct internal standards, quantitation ions, and average RFs were used to quantitate target compound detections. The MRLs were supported with adequate ICAL calibration concentrations. The project goal for quantitation limits were attained to in these cases.

A verification calculation was performed on 10% of the reported calibration, laboratory QC analyses, and sample results. No anomalies were found. The verification calculation worksheets were maintained in project files for requests.

Response peak integrations were primarily performed automatically with computer software. In cases where peak shifting, signal interferences, and/or peak tailing occurred, manual integrations were performed. Manual integrations criteria and approaches were consistent justifiable across the analyses; no anomalies were identified in relation to compound identification and quantitation.

1.12 Overall Assessment of PCB Congener Data Usability

PCB congener data were of known quality and acceptable for use as qualified, with the acknowledgement of deviations and anomalies discussion above.

2. PCB Congeners by GC/MS - SIM (EPA Method SW8270D-SIM)

Two laboratories, Laboratory 58 and Laboratory 34, chose to use EPA Method SW8270D-SIM for PCB congeners analysis. Note that neither EPA Method 8270D nor laboratory SOPs specified evaluation criteria for carbon-labeled PCBs. However, unless noted otherwise, criteria set forth for non-labeled PCBs in the method and SOPs were applied for ¹³C-labeled PCBs data quality and method compliance evaluation.

2.1 Sample Management and Holding Times

No anomalies were noted by the laboratories in relation to sample packaging, transportation, handling, preservation, and integrity upon sample receipt in the laboratories.

EPA Method 8270D does not specify holding time requirements for PE samples (submerged in loading solution). Holding time requirements for solid samples (one year from collection to extraction, 40 days from extraction to analysis) were applied as a guideline for sample collection (the time the LDPE strips were retrieved from the sediment) and extract holding time evaluation. Samples were extracted and analyzed within the holding times by both laboratories.

2.2 GC/MS Instrument Performance Check

The laboratories performed GC/MS tuning analysis as required by the analytical method and their SOPs. DFTPP tuning was performed within each 12-hour interval. All required ion abundance ratios met the method requirements.

2.3 Initial Calibration (ICAL)

EPA Method 8270D criteria require that (1) if a linear average RFs is chosen as the quantitation option, at least five standards at different concentrations should be analyzed and the %RSD of RFs be $\leq 15\%$ ($\leq 25\%$ for Laboratory 34) for the analyte, (2) if least-square linear regression is chosen for quantitation, the correlation coefficient (r) be > 0.995 , and (3) if six-point non-linear (quadratic) curve is chosen for quantitation, the coefficient of determination (r^2) be > 0.99 . All ICALs met the method and laboratory criteria.

An ICV standard (second source standard) was analyzed to verify the calibration curve. Due to limited suppliers and excessive cost of the ^{13}C -labeled PRCs, the second source standards used by both laboratories contained non-labelled target PCB congeners only. The %D values were within ± 20 . The ICALs were considered valid.

2.4 Calibration Verification (CCV)

The analytical method requires that (1) continuing calibration verifications be analyzed at the beginning of each 12-hour analysis period prior to the analysis of method blank and samples, and (2) the %D be within $\pm 20\%$. All CCVs met the laboratory control criteria for Laboratory 58. One Laboratory 34 CCV did not meet the laboratory control criteria; affected data are qualified as follows:

Laboratory	CCV ID	Analyte	%D	Bias	Affected Sample	Data Qualifier
Laboratory 34	Sample No. 451 6/10/20, 21:43	PCB-206	31.7%	High	P-B S1 P-B S2 P-B S4 P-B S5 P-B S6	J+
Laboratory 34	Sample No. 451 6/10/20, 21:43	PCB-209	27.2%	High	P-B S1 P-B S2 P-B S3 P-B S4 P-B S5 P-B S6	J+

Note: J+ signifies that the data is potentially biased high.

2.5 Method Blanks

Method blanks were prepared and analyzed as required. Target PCB congeners and PCB PRCs were not detected at or above the method detection limits (MDLs).

2.6 Surrogate Spikes

Surrogate spikes were added to all samples as required by the method. All surrogate spike %R values were within the control limits specified in the laboratory SOPs.

2.7 Matrix Spike (MS) and MS Duplicate (MSD)

MS and MSD analyses were not applicable for the calibration standard analysis.

2.8 Laboratory Control Sample (LCS)

LCS was not prepared/analyzed by Laboratory 58. LCS was prepared and analyzed by Laboratory 34. The %R values met the laboratory control limits.

2.9 Internal Standards

The method requires that (1) internal standard retention time be within ± 30 seconds from that of the associated 12-hour calibration standard, and (2) the area counts of all internal standards be within -50% to $+100\%$ of the associated 12-hour calibration standard. Laboratory 34 chose to use those of the mid-point ICAL standard for internal standard recovery control criteria. Internal standard recovery met the method or laboratory requirements.

2.10 Target Compound Identification

All chromatograms were properly displayed and scaled. No target compounds were detected in any of the field samples. No anomalies were found in relation to target compound identification.

2.11 Reporting Limits and Target Compound Quantitation

Re-calculation was performed on 10% of the instrument calibration and reported QC and sample analyses. No anomalies were found via the verification calculation. MRLs were supported with adequate initial calibration concentrations. In cases where target compound concentrations exceeded ICAL calibration ranges, extracts were diluted and re-analyzed for definitive quantitation.

Response peak integrations were primarily performed automatically with computer software. In cases where peak shifting, signal interferences, and/or peak tailing occurred, manual integrations were performed. Manual integrations criteria and approaches were consistent justifiable across the analyses; no anomalies were identified in relation to compound identification and quantitation.

2.12 Overall Assessment of PCB Congeners Data Usability

PCB Congeners data are of known quality and acceptable for use, with the acknowledgement of SOP deviations and anomalies stated above.

3. PAHs by Isotope Dilution GC/MS (EPA Method SW8270D Modified and EPA Method 1625 Modified)

Laboratory 52 and Laboratory 84 chose to use EPA Method SW8270D modified with EPA Method 1625 for this study. Note that neither EPA Method 8270D, EPA Method 1625 nor laboratory SOPs specified evaluation criteria for carbon-labeled PAHs. However, unless noted otherwise, criteria set

forth for non-labeled PAHs in the methods and SOPs were applied for PAH PRC data quality and method compliance evaluation.

3.1 Sample Management and Holding Times

No anomalies were noted by the laboratories in relation to sample packaging, transportation, handling, preservation, and integrity upon sample receipt in the laboratories.

EPA Method 8270D does not specify holding time requirements for LDPE samples (submerged in loading solution). Holding time requirements for solid samples (one year from collection to extraction, 40 days from extraction to analysis) were applied as a guideline for sample collection (the time the LDPE strips were retrieved from the sediment) and extract holding time evaluation. Samples were extracted and analyzed within the holding times by both laboratories.

3.2 GC/MS Instrument Performance Check

The method requires that DFTPP tuning be performed within each 12-hour interval. All required ion abundance ratios should meet the requirements in the method. Each of the laboratories specified GC/MS tuning procedures and requirements in their SOPs. However, tuning reports were not included in their data package in this task. This information will be required for all data packages in future sample analyses for this study.

3.3 Initial Calibration (ICAL)

Laboratory 84 chose to fully follow the method requirements to establish ICAL for regular target PAH and 13C6-Labeled PAH PRCs. Laboratory 52 followed the method requirements for regular target PAHs only. The method ICAL criteria require that (1) if linear average RFs is chosen as the quantitation option, at least five standards at different concentrations should be analyzed and the %RSD of RFs be $\leq 20\%$ for the analyte, (2) if least-square linear regression is chosen for quantitation, the correlation coefficient (r) be > 0.995 , and (3) if six-point non-linear (quadratic) curve is chosen for quantitation, the coefficient of determination (r^2) be > 0.99 . An ICV standard (second source standard) was analyzed to verify the calibration curve. The %D values were within $\pm 20\%$. The ICALs were considered valid.

Laboratory 52 followed their SOP to establish ICAL for the 13C6-Labeled PAH PRCs. A mid-point calibration standard was analyzed at the beginning and the end of the analytical sequence. The response factor RPD values for the target compounds and surrogate compounds should be within 20%, and RT within 3 seconds between the two analyses. The ICAL met the laboratory SOP requirements.

3.4 Calibration Verification (CCV)

The analytical method requires that (1) continuing calibration verifications be analyzed at the beginning of each 12-hour analysis period prior to the analysis of method blank and samples, and (2) the %D be within $\pm 20\%$. All CCVs met the laboratory control criteria.

3.5 Method Blanks

A method blank was prepared and analyzed by both laboratories. Target PAHs and PAH PRCs were not detected at or above the MDLs.

3.6 Surrogate Spikes

Surrogate spikes were added to all samples as required by the method. All surrogate spike %R values were within the control limits specified in the laboratory SOPs.

3.7 Laboratory Control Sample (LCS) and LCS Duplicate (LCSD)

Since no matrix-specific (i.e., LDPE in this case) LCS was available to be processed along with the samples, the laboratories analyzed/reported laboratory-made standards as LCS. Due to the limited supplier and the excessive cost of the ¹³C-labelled PRCs, the LCS analyzed/reported by Laboratory 84 did not contain the target PRCs. However, the %R values in LCS were all within the laboratory control criteria.

RPD values for most of the analytes of the laboratory control sample (LCS) and laboratory control sample duplicate (LCSD) for preparation batch 140-38862 and analytical batch 140-39026 were outside control limits. The RPD values were calculated using the amount detected in the sample, which varies based on the initial weight of the sample. The RPD values were within laboratory control limits using the percent recovery values. No data qualifying action is required in this case.

OPR was prepared and analyzed in lieu of LCS by Laboratory 52. See discussion below.

3.8 Ongoing Precision and Recovery (OPR)

OPR was prepared and analyzed for PRC PCBs at the adequate frequency by Laboratory 52. The %R values met the laboratory control criteria.

3.9 Labeled Compound Recovery

Labeled internal standards were added to all samples as required by the analytical method and laboratory SOPs. The labeled internal standards percent recoveries all met the method and laboratory SOP requirements, except that the acenaphthalene-d8 %R value (121%) in Laboratory 84 sample PE Active - PAH 3 and the benzo(a)pyrene-d12 %R value in sample PE Static - PAH 3 were slightly greater than the upper control limit (30-120%). This minor anomaly had no significant effects on data usability; no data qualifying action was taken in this case.

3.10 Target Compound Identification

All chromatograms were properly displayed and scaled. No target compounds were detected in any of the field samples. No anomalies were found in relation to target compound identification.

3.11 Reporting Limits and Target Compound Quantitation

Re-calculation was performed on 10% of the instrument calibration and reported QC and sample analyses. No anomalies were found via the verification calculation. MRLs were supported with adequate initial calibration concentrations. In cases where target compound concentrations exceeded ICAL calibration ranges.

Response peak integrations were primarily performed automatically with computer software. In cases where peak shifting, signal interferences, and/or peak tailing occurred, manual integrations were performed. Manual integrations criteria and approaches were consistent justifiable across the analyses; no anomalies were identified in relation to compound identification and quantitation.

3.12 Overall Assessment of PAHs Data Usability

PAHs data are of known quality and acceptable for use, with the acknowledgement of SOP deviations and anomalies stated above.

4. PAHs by GC/MS - SIM (EPA Method SW8270D-SIM)

Laboratory 58 and Laboratory 34 chose to use this methodology for PAHs analysis. Neither EPA Method 8270D nor laboratory SOPs specified evaluation criteria for ¹³C₆-labelled PAHs. However, unless noted otherwise, criteria set forth for non-labeled PAHs in the method and SOPs were applied for carbon-labeled PAHs data quality and method compliance evaluation.

4.1 Sample Management and Holding Times

No anomalies were noted by the laboratories in relation to sample packaging, transportation, handling, preservation, and integrity upon sample receipt in the laboratories.

EPA Method 8270D does not specify holding time requirements for PE samples (submerged in loading solution). Holding time requirements for solid samples (one year from collection to extraction, 40 days from extraction to analysis) were applied as a guideline for sample collection (the time the LDPE strips were retrieved from the sediment) and extract holding time evaluation. Samples were extracted and analyzed within the holding times by both laboratories.

4.2 GC/MS Instrument Performance Check

The laboratories performed GC/MS tuning analysis as required by the analytical method and their SOPs. DFTPP tuning was performed within each 12-hour interval. All required ion abundance ratios met the method requirements.

4.3 Initial Calibration (ICAL)

The EPA Method 8270D criteria require that (1) if linear average RFs is chosen as the quantitation option, at least five standards at different concentrations should be analyzed and the %RSD of RFs

be $\leq 20\%$ for the analyte, (2) if least-square linear regression is chosen for quantitation, the correlation coefficient (r) be >0.995 , and (3) if six-point non-linear (quadratic) curve is chosen for quantitation, the coefficient of determination (r^2) be >0.99 . Laboratory 34's criteria vary slightly from the method requirements. All ICALs met the method and laboratory criteria.

An ICV standard (second source standard) was analyzed to verify the calibration curve. Due to limited suppliers and excessive cost of the carbon labeled PRCs, the second source standards used by both laboratories contained non-labelled target PAHs only. The %D values were within ± 20 . The ICALs were considered valid.

4.4 Calibration Verification (CCV)

The analytical method requires that (1) continuing calibration verifications be analyzed at the beginning of each 12-hour analysis period prior to the analysis of method blank and samples, and (2) the %D be within $\pm 20\%$ (25% for Laboratory 34).

The dibenzo(a,h)anthracene-d14 (a surrogate spike) %D values exceeded 20% in CCVs for Laboratory 58, indicating a biased high recovery. This likely was the result of high levels of PAHs in samples. The recovery of this surrogate spike in samples was within control limits in dilution analyses. Data usability has not significantly affected. No data qualifying action was taken in this case. See discussion in Section 4.6 as well.

4.5 Method Blanks

Method blanks were prepared and analyzed as required. Target regular PAHs and PAH PRCs were not detected at or above the MDLs.

4.6 Surrogate Spikes

Surrogate spikes were added to all samples as required by the method. All surrogate spike %R values were within the control limits specified in laboratory SOPs, except that the recovery of dibenzo(a,h)anthracene-d14 in samples and laboratory QC analyses exceeded the upper control limits for Laboratory 58. The recovery was within the laboratory control limits in dilution analyses, indicating the biased-high recovery was a result of matrix effects and not the deficiency related to sample extraction. No data qualifying action was taken in these cases.

4.7 Matrix Spike (MS) and MS Duplicate (MSD)

MS and MSD analyses were not applicable for this calibration standard analysis

4.8 Laboratory Control Sample (LCS)

LCS was not prepared by Laboratory 58. LCS was prepared and analyzed by Laboratory 34. The %R values met the laboratory control limits.

4.9 Internal Standards

The method requires that (1) internal standard retention time be within ± 30 seconds from that of the associated 12-hour calibration standard, and (2) the area counts of all internal standards be within -50% to $+100\%$ of the associated 12-hour calibration standard. Laboratory 34 chose to use those of the mid-point ICAL standard for internal standard recovery control criteria. Internal standard recovery met the method or laboratory requirements.

4.10 Target Compound Identification

All chromatograms were properly displayed and scaled. No target compounds were detected in any of the field samples. No anomalies were found in relation to target compound identification.

4.11 Reporting Limits and Target Compound Quantitation

Re-calculation was performed on 10% of the instrument calibration and reported QC and sample analyses. No anomalies were found via the verification calculation. MRLs were supported with adequate initial calibration concentrations. Response peak integrations were primarily performed automatically with computer software. In cases where peak shifting, signal interferences, and/or peak tailing occurred, manual integrations were performed. Manual integrations criteria and approaches were consistent justifiable across the analyses; no anomalies were identified in relation to compound identification and quantitation.

4.12 Overall Assessment of PAHs Data Usability

PAHs data are of known quality and acceptable for use with the acknowledgement of SOP deviations and anomalies stated above.

SUMMARY

Table 1. Data Affected by QC Anomalies

Laboratory	Sample ID	Analyte	Data Qualifier	Reason	Report Section
Laboratory 52	Active Test 3	PCB-209	U	The result was less than five times the level found in the method blank	1.5
Laboratory 34	P-B S1 P-B S2 P-B S4 P-B S5 P-B S6	PCB-206	J+	The continuing calibration verification recovery biased high.	2.4
Laboratory 34	P-B S1 P-B S2 P-B S3 P-B S4 P-B S5 P-B S6	PCB-209	J+	The continuing calibration verification recovery biased high	2.4

Table 2. Data Qualifier Definition

Qualifier	Sample ID
J+	The result is potentially biased high.
U	The result can be false positive and may be considered not detected at the reported value.

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APPENDIX A

QUALITY CONTROL CRITERIA FOR ANALYTICAL METHODS

Table A1 – PCB Congeners Analysis Quality Control Evaluation Criteria Summary

QC Parameters and Performance Frequency	Laboratory and Referenced Analytical Method			
	Laboratory 58 (EPA 8270D)	Laboratory 52 (EPA 1668C)	Laboratory 34 (EPA 8270D Modified)	Laboratory 84 (EPA 1668C)
Tuning (Resolution Check) At the beginning and the end of each 12-hour period of analysis.	Same as Method	Same as Method	Prior to initial calibration. Prior to CCV if system idle for >24 hrs. Criteria same as 8270D.	Same as Method
GC Column Performance Check Prior to ICAL or calibration verification.	N/A	Same as Method	N/A	Same as Method
Initial Calibration (ICAL) Prior to sample analysis; as needed if failure of calibration verification; or a new lot is used as standard source.	Same as Method	- Same as Method - Standards' result values are within 15% of true values.	Same as 8270D.	Same as Method
Calibration Verification (CCV), Ongoing Precision Recovery (OPR), or Verification (VER) At the beginning of each 12-hour period.	Same as Method	- Same as Methods. - SOP Tables 4a and 4b.	At the beginning and end of 10 injections or each 24 hour period (whichever is more frequent)	Same as Method
Method Blank One per preparatory batch, run after calibration standards and before samples.	No analytes detected $\geq \frac{1}{2}$ limit of quantitation or $\geq 5\%$ of the associated regulatory limit for the analyte or $\geq 10\%$ of the sample result for the analyte, whichever is greater, per method.	Analyte amounts in blank samples for PCB congeners 77, 81, 114, 123, 126 and 169 must be ≤ 2 pg/congener/sample, amounts of PCB congeners 156, 157, 167 and 189 must be ≤ 10 pg/congener/sample, and the maximal amount of PCB 11 must be ≤ 150 pg/sample. Amounts of all other individual PCB congeners or coelutions must be ≤ 50 pg/congener/sample in blank samples. The sum of all 209 congeners should be ≤ 300 pg/sample. Higher levels are acceptable where sample concentrations exceed 10 times blank levels.	Analyte concentration in PB should be < MDL and must be < 5xMDL No analytes detected > $\frac{1}{2}$ RL. For common laboratory contaminants, no analytes detected > RL.	Target analytes must be less than estimated maximum levels (EMLs) in SOP Table 4

Instrument Blank At the beginning of each 12-hour period.	Same as Method Blank.	Same as Method Blank.	Same as Method Blank.	Target analytes must be less than EMLs in SOP Table 4
Laboratory Control Sample (LCS) One per preparatory batch.	%R value should be within 70-130% of the true value	SOP Tables 4a and 4b.	70 to 130% recovery vs. SIS 40 to 120% recovery vs. IS	Within control limits for OPR (SOP Tables 10A and 10B).
Matrix Spike (MS) (OPTIONAL)	%R value should be within 70-130% of the true value	N/A	70 to 130% recovery vs. SIS 40 to 120% recovery vs. IS Spiked target analyte concentration must be > 5 x the level in the background sample.	NA
Sample Duplicate or MS Duplicate (MSD)	RPD ≤ 30%	RPD ≤ 20% (applicable to concentrations ≥10 times the DL)	RPD ≤ 30%	N/A
Extraction Standards and Cleanup Standards Every field sample, standard, and QC sample.	- Same as Method for Internal standard recovery - Surrogate Spike recovery is within 70 - 130%.	Same as Method SOP Tables 4a and 4b.	Surrogate spike recovery 40 - 120%	Same as Method
Compound Identification	Same as Method	Same as Method	Same as 8270D	Same as Method

Notes:

N/A: Not applicable

EPA 8270D - USEPA. 1998. *Test Methods for Evaluating Solid Waste (SW 846). Third Edition and Revised Update IIIA. Method 8000 and Method 8270D. Office of Solid Waste and Emergency Response, Washington, D.C. April 1998 and Updates.*

EPA 1668C - USEPA Method 1668C - *Chlorinated Biphenyl Congeners in Water, Soil, Sediment, Biosolids, and Tissue by HRGC/HRMS. April 2010.*

Table A2 – PAHs Analysis Quality Control Evaluation Criteria Summary

QC Parameter & Performance Frequency	Laboratory and Referenced Method			
	Laboratory 58 EPA 8270D-SIM	Laboratory 52 EPA 8720C-SIM EPA 1625 (HRGC/MS)	Laboratory 34 (EPA 8270D Modified)	Laboratory 84 EPA 8720C-SIM EPA 1625 (GC/MS)
Relative Retention Time (RRT) Evaluation Each Sample	RRT of each target analyte in each calibration standard within ± 0.05 RRT units.	- RT within ± 3 seconds of the predicted retention time determined from the calibration standard and adjusted relative to the peak retention time reference (i.e. labelled surrogate). - A second requirement is that an authentic elute after its labelled analog.	RT window for an analyte is ± 15 s from the determined RT of the analyte in the ICAL.	N/A
Initial Calibration (ICAL) Prior to sample analysis; as needed if failure of calibration verification; or a new lot is used as standard source.	- A minimum of five points. - Analytes' RRFs must meet method limits across calibration range. - Analytes %RSDs must be less than or equal to 20%, or the analyte must employ a linear or non-linear calibration model with a coefficient of determination (r^2) greater than 0.99. - Up to 10% of the total analytes may fail 1 and 2 above. - Verify ICAL with one second-source standard at mid- point concentration. Value for all analytes within $\pm 30\%$ of expected value.	- Calibration standard solutions are presented in SOP Table 6. - Linearity is demonstrated by a 5-point calibration over the working concentration range with a relative standard deviation of the RRFs $\leq 20\%$ for targets with a labelled analog present and all labelled compounds, $\leq 35\%$ for targets with no labelled analog present.	- A minimum of five points. - Analyte RF %RSDs must be less than or equal to 25% average RF. - Verify ICAL with one second-source standard. Value for all analytes within $\pm 25\%$ of expected value.	- SOP Table 3 lists ICAL concentrations. %RSD must be $\leq 30\%$ for analytes and internal standards. - Verify ICAL with one second-source standard at mid-point (CS4) concentration. Value for all analytes within $\pm 30\%$ of expected value.

QC Parameter & Performance Frequency	Laboratory and Referenced Method			
	Laboratory 58 EPA 8270D-SIM	Laboratory 52 EPA 8720C-SIM EPA 1625 (HRGC/MS)	Laboratory 34 (EPA 8270D Modified)	Laboratory 84 EPA 8270C-SIM EPA 1625 (GC/MS)
Calibration verification (CCV) Before sample analysis, and every 12 hours of analysis time	- Average RRFs for analytes must meet the method defined limits. %Difference/Drift for analytes $\leq 20\%$ - Up to 20% of the target analytes may fail the criteria in 1 and 2 so long as the sample analyses associated with the CCVS are J flagged.	- Opening Cal Ver: Concentrations of native compounds and labelled surrogates must be within $\pm 25\%$ of expected values for all targets. - Closing Cal Ver: Concentrations of native compounds must be within $\pm 25\%$ of expected values. - Concentrations of labelled surrogates must be within $\pm 25\%$ of expected values, with any two (2) values allowed to be within $\pm 40\%$. - Ion ratios for authentic and labelled dibenz[ah]anthracene, indeno[1,2,3-cd]pyrene and benzo[ghi]perylene must be within $\pm 35\%$ of the mid-point of the I-CAL. - All other native analytes and labelled surrogates must be within $\pm 20\%$ of the mid-point of the I-CAL.	- Average RRFs for analytes must meet the method defined limits. - CCV after every 10 injections of 24 hrs – whichever is shorter. - Individual % difference $\leq 25\%$ - Grand mean of % difference $\leq 15\%$. - IS area has not changed by more than a factor of two (-50% to +100% from the area found in level 3 of the ICAL.	%Difference/Drift for analytes must be $\leq 30\%$ (SOP Table 7). - The recovery standard response must be within 50- 200% of the response in the corresponding CS4 calibration level of the initial calibration. - New ICAL is needed if this criterion is not met.
Internal Standards Every field sample, standard, and QC sample	- Retention time ± 30 seconds from retention time of the midpoint standard in the ICAL or CCV. - EICP area within - 50% to +100% of ICAL midpoint standard	Within -50% to +100% of ICAL midpoint standard.	IS area has not changed by more than a factor of two (-50% to +100% from the area found in level 3 of the ICAL.	The recovery standard response must be within 50- 200% of the response in the corresponding CS4 calibration level of the initial calibration.
Method blank One per preparation batch of 20 or less samples	No analytes detected > $\frac{1}{2}$ RL. For common laboratory contaminants, no analytes detected $\geq$ RL.	SOP Table 8.	Analyte concentration in PB should be < MDL and must be < 5 MDL No analytes detected > $\frac{1}{2}$ RL. For common laboratory contaminants, no analytes detected > RL.	No analytes detected > RL ($\frac{1}{2}$ RL for DoD projects).
Laboratory control sample (LCS) One per preparation batch of 20 or less samples	See Laboratory QA Plan (LQAP). Reported along with LCS results	SOP Table 8.	70 to 130% recovery vs. SIS 40 to 120% recovery vs. IS	SOP Table 7
Matrix Spike (MS) and MS Duplicate (MSD)	- For matrix evaluation, see LQAP. MS recovery is advisory. - RPD $\leq 30\%$ (MS/MSD or sample duplicate). Limits are advisory.	SOP Table 8.	70 to 130% recovery vs. SIS 40 to 120% recovery vs. IS RPD $\leq 30\%$	N/A

QC Parameter & Performance Frequency	Laboratory and Referenced Method			
	Laboratory 58 EPA 8270D-SIM	Laboratory 52 EPA 8720C-SIM EPA 1625 (HRGC/MS)	Laboratory 34 (EPA 8270D Modified)	Laboratory 84 EPA 8270C-SIM EPA 1625 (GC/MS)
Surrogate Spikes Every field and QC sample	QC acceptance criteria for LCS specified by DoD, if available; otherwise method- specified criteria or laboratory's own in-house criteria (No more than 1 acid surrogate or 1 base surrogate is allowed out of control, all surrogate recoveries must be > 10%.)	SOP Table 8 for SPMD samples, including criteria for PRCs.	40 - 120% recovery	SOP Table 7
Laboratory Duplicates (Optional)	N/A	Duplicates must fall within $\pm 20\%$ of the mean (applicable to concentrations ≥ 10 times the DL). (Note that $\pm 20\%$ of the mean is equivalent to 40 relative percent difference)	$\leq 30\%$ RPD	N/A

QC Parameter & Performance Frequency	Laboratory and Referenced Method			
	Laboratory 58 EPA 8270D-SIM	Laboratory 52 EPA 8720C-SIM EPA 1625 (HRGC/MS)	Laboratory 34 (EPA 8270D Modified)	Laboratory 84 EPA 8270C-SIM EPA 1625 (GC/MS)
Compound Identification	Same as Method	- Peak responses must be at least three times the background noise level. - The retention time (RT) must be within three seconds of that predicted from the calibration run and the sample retention time reference (labelled compound). - Peak maxima for the quantification and confirmation ions must coincide within two seconds. - The relative ion abundance ratios must be within 20% of the opening calibration values.	- Primary SIM ion must be present. - Peak responses must be at least three times the background noise level. - RT must fall within established RT window.	- The internal standard quantitation ions must be present. - The relative intensities of confirmation ions should agree to within $\pm 30\%$ between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 20% and 80%). The absence of confirmation ions should be considered carefully when making decisions regarding qualitative identification. Confirmation ions may have lower response than quantitation ions and may not always be present at lower concentrations. Their absence in this case may not be cause for determining that the analyte is not present. The absence of confirmation ions at higher levels where they should have been detectable may be cause for determination that an analyte is not present. - The sample component retention time must compare to within ± 0.2 min. of the retention time of the internal standard component. For reference, the standard must be run within the same 12- hour period as the sample. - If a compound cannot be verified by all the above criteria, but in the technical judgment of the analyst the identification is correct, the analyst shall report that identification and proceed with quantitation.

Notes:

N/A - Not applicable.; DoD – U.S. Department of Defense

EPA 8270D - USEPA. 1998. *Test Methods for Evaluating Solid Waste (SW 846). Third Edition and Revised Update IIIA. Method 8000 and Method 8270D. Office of Solid Waste and Emergency Response, Washington, D.C. April 1998 and Updates.*

EPA 1625 – 40CFR, Appendix A to Part 136, Method 1625 Revision B, Semivolatile Organic Compounds by Isotope Dilution GC/MS

HRGC/MS – High resolution gas chromatography coping with mass spectrometry

GC/MS – Gas chromatography coping with mass spectrometry

RL – Reporting Limit

Data Validation Report

Standardizing Polymeric Sampling for Measuring Freely Dissolved Organic Contaminants in Sediment Porewater ER 201735

Task 3 – Solid Phase Microextraction (SPME) Fiber *ex-situ* Sediment Exposure

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ACRONYMS

%D	percent difference
%D_f	percent drift
%R	percent recovery
%RSD	percent relative standard deviation
CCV	continuing calibration verification
COC	chain-of-custody
CS1	the first calibration standard
CS3	the third calibration standard
EDD	electronic data deliverable
EDL	estimated detection limit
EMPC	estimated maximum possible concentration
EPA	U.S. Environmental Protection Agency
HRGC/ HRMS	high-resolution gas chromatography/high-resolution mass spectrometry
ICAL	initial calibration
ICV	initial calibration verification
IPR	initial precision and recovery
LCL	lower control limit
LCS	laboratory control sample
LCSD	laboratory control sample duplicate
LIMs	laboratory information management system
m/z	mass-to-charge ratio
MB	method blank
MDL	method detection limit
MS	matrix spike
MSD	matrix spike duplicate
ng/g	nanogram per gram
ng/L	nanogram per liter
ng/mL-PDMS	nanogram per milliliter of polydimethylsiloxane
OPR	ongoing precision and recovery
PCB	polychlorinated biphenyl
PDMS	polydimethylsiloxane
PFK	perfluorokerosene
PQL	practical quantitation limit
PRC	performance reference compound

QA/QC	quality assurance/quality control
QAPP	quality assurance project plan
RF	response factor
RPD	relative percent difference
RRT	relative retention time
SDG	sample delivery group
SICP	selected ion current profile
S/N	signal-to-noise ratio
SOP	standard operating procedure
SPME	solid phase microextraction
TTU	Texas Technology University
USACE	US Army Corps of Engineers

INTRODUCTION

This report presents the findings of the data validation performed on analytical data submitted by participating commercial laboratories for the study of *ex-situ* Sediment Exposure using Solid Phase Microextraction (SPME) Fiber Passive Sampler. This sediment exposure study is final laboratory effort as part of the effort for Task 3 identified in the Project Demonstration Plan (USACE *et. al.*, 2018).

Each of the participating laboratories performed the *ex-situ* sediment exposure in their facilities. The sediment supplied for this study was homogenized and aliquoted into twelve jars – six for static (passive) exposure and six for active exposure. Six SPME fibers were loaded with PRCs (following the procedures developed in Task 2), merged into jars individually and the jars sealed. Static exposure jars were placed upright and stored properly during the entire course of exposure. The active exposure jars underwent continuous vertical shaking plus periodical manual shaking in various directions to mimic dynamic real environmental conditions. The exposure time varied with laboratories, ranging from 30 to 40 days (Laboratory 83's exposure time extended to approximately 3 months due to restricted access to the facility by the COVID-19 pandemic.) Once retrieved from the sediment jars, LDPE strips were wiped-cleaned and underwent solvent extractions following the procedures developed in Task 2. A method blank SPME strip and, for selected laboratories, a laboratory control sample (LCS) and/or LCS duplicate (LCSD) spiked with known-concentration target analytes were extracted along with the sediment-exposed LDPE. The extracts were analyzed for target polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyl (PCB) congeners and performance reference compounds (PRCs), as defined in the Project Demonstration Plan (USACE *et. al.*, 2018).

Target polycyclic aromatic compounds (PAHs) include the 17 non-derivatives PAHs; target PCB congeners for this task are PCB-44, PCB-52, PCB-66, PCB-101, PCB-105, PCB-118, PCB-126, PCB-128, PCB-138, PCB-153, PCB-170, PCB-180, PCB-187, PCB-195, PCB-206, and PCB-209.

Participating commercial laboratories and respective analytical methodologies applied to this study are summarized as follows:

Participating Commercial Laboratory	Analytical Method	
	PCB Congeners	PAHs
Laboratory 19	SW846 Method 8270D Modified	SW846 Method 8270D Modified
Laboratory 98	EPA Method 1668C	SW846 Method 8270D Modified EPA Method 1625
Laboratory 48	EPA Method 1668C	SW846 Method 8270D Modified EPA Method 1625
Laboratory 83	SW846 Method 8270D Modified	SW846 Method 8270D Modified

Notes:

1. Method 1668C: *Chlorinated Biphenyl Congeners in Water, Soil, Sediment, Biosolids, and Tissue* by HRGC/HRMS. April 2010.

2. Method 1625C: *Semi-volatile Organic Compounds by Isotope Dilution GCMS*. June 1989.
3. SW846 - Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Third Edition, December 1996.

Laboratories throughout this report are referred to using random number assignments to ensure the anonymity of participating commercial laboratories. Each participating laboratory was required to submit analytical deliverables for each analysis, including (1) a Level IV full data package containing reporting forms and all raw data supporting the reported sample and QC analyses results, and (2) an electronic data deliverable (EDD) in the Washington State Department of Ecology's Environmental Information Management System (EIMs) format. The laboratory could choose to submit the EDDs in Excel or csv. format. Each laboratory report and EDD were assigned a unique sample delivery group (SDG) number. Laboratory deliverables, after fully validated, were archive in the project file at the US Army Corps of Engineers Seattle District. SDG numbers assigned by each laboratory are summarized as follows:

Participating Commercial Laboratory	Sample Delivery Group or Laboratory Identification Number	
	PCB Congeners	PAHs
Laboratory 19	20D0006	20D0006
Laboratory 98	140-18674-1	140-18674-1
Laboratory 48	DPWG72500	DPWG72434
Laboratory 83	DP-20-0550	DP-20-0552

Final sample results were reported as ng/mL-PDMS, based on the conversion conventions provided by TTU. Values reported in the laboratory reports did not present this conversion, but in separate EDDs due to the limitations posed by the laboratories' information management systems (LIMs).

A Stage 4 validation (as defined by EPA 2009) was performed on all PCB congener and PAHs data. The validation followed guidance specified by EPA (2014, 2016 & 2017), with modifications to accommodate respective analytical methods and requirements specified in the Standard Operating Procedures (SOPs) provided by the participating commercial laboratories. The numerical quality assurance/quality control (QA/QC) criteria applied to the validation were in accordance with method requirements and the current performance-based control limits established by the laboratory (laboratory control limits). Instrument calibration, frequency of QC analyses, and analytical sequence requirements were evaluated against the respective analytical methods. Laboratory-specific QC Criteria are summarized in *Appendix A, Tables A1 and A2*.

Validation findings are discussed in each section pertinent to the QC parameter for each type of analysis. Qualified data with applied data qualifiers are summarized in the **Summary** section at the end of this report.

DATA VALIDATION FINDINGS

1. PCB Congeners by EPA Method 1668C: High-resolution Gas Chromatography and High-resolution Mass Spectrometry (HRGC/HRMS)

Two participating commercial laboratories – Laboratory 48 and Laboratory 98 chose to use EPA Method 1668C for the study. Note that neither EPA Method 1668C nor laboratory SOPs specified evaluation criteria for carbon-labeled PCBs (i.e., PRCs). However, unless noted otherwise, criteria set forth for non-labeled PCBs in the method and SOPs were applied for carbon-labeled PCB data quality and method compliance evaluation.

1.1 Sample Management and Holding time

No anomalies were noted by the laboratories in relation to sample packaging, transportation, handling, preservation, and integrity upon sample receipt in the laboratories.

EPA Method 1668C does not specify holding time requirements for SPME samples (submerged in loading solution). Holding time requirements for solid samples (one year from collection to extraction, 40 days from extraction to analysis) were applied as a guideline for sample collection (the time the SPME fibers were retrieved from the sediment) and extract holding time evaluation. Samples were extracted and analyzed within the holding times by both laboratories.

1.2 HRGC/HRMS Instrument Performance Check

The EPA Method 1668C criteria for instrument performance checks are as follows:

Mass Spectrometer Resolution: (1) The resolution check should be performed, using perfluorokerosene (PFK) or equivalent standard materials, prior to initial calibration and at the start and end of each 12-hour shift, (2) the resolution should be $\geq 8,000$ throughout the mass range and $\geq 10,000$ resolving power at m/z 330.9792 (or any other significant PFK fragments in the range of 300 to 350), and (3) the deviation between the exact m/z and the theoretical m/z must be less than 5 ppm for monitored isomers.

Column Performance: (1) A combined 209 congener standard should be analyzed prior to initial calibration and continuing calibration verification, (2) peak for congener 34 should be resolved from 23 and peak for congener 187 resolved from 182 peak with a valley of $\leq 40\%$, (3) congeners 156 and 157 should co-elute within 2 seconds at their peak maximum, and (4) the absolute retention time (RT) for congener 209 should be >55 minute for SPB-octyl or an alternate column.

In addition to the method requirements, laboratories imposed more criteria based on their specific instrumentation. HRGC/HRMS instrument performance checks met the method and SOP criteria for these laboratories.

1.3 Initial Calibration (ICAL)

Laboratory 98 chose to fully follow the EPA Method 1668C initial calibration (ICAL) for regular and the ^{13}C -labeled PCB PRCs. The EPA Method 1668C criteria for initial calibration are: (1) a

minimum of five standards should be employed for native congeners and labeled compounds, (2) the percent relative standard deviation (%RSD) of isomer response should be $\leq 20\%$, (3) the ion abundance ratios should be within the control limits listed in EPA Method 1668C, Table 8, (4) the signal-to-noise (S/N) ratio should be >10 for all native and labeled compounds in the first calibration standard (CS1), and (5) response factor (RF) should be determined using one-point calibration for congeners quantitated with internal standard method. Initial calibrations met the criteria. An initial calibration verification (second source) standard was analyzed to verify the calibration curve. The percent difference (%D) values were less than or equal to 30% and the initial calibration was considered valid.

Laboratory 48 followed the EPA Method 1668C requirements for regular PCB congeners and their SOP to establish ICAL for the ^{13}C -labeled PCB PRCs. For PCB PRCs, a mid-point calibration standard was analyzed at the beginning and the end of the analytical sequence. The response factor RPD values for the target compounds and surrogate compounds should be within 20%, and RT within 3 seconds between the two analyses. The ICAL met the laboratory SOP requirements.

1.4 Calibration Verification (CCV)

The EPA Method 1668C criteria require that: (1) continuing calibration verifications be performed at the beginning of each 12-hour shift using the mid-point calibration standard (CS3), (2) the %D value should be within the control limits listed in EPA Method 1668C, Table 6, and (3) the ion abundance ratios, retention times, relative retention times, and S/N ratio should meet the same criteria as for initial calibrations. Note that the method did not specify ion abundance ratios for ^{13}C -labeled PRCs; laboratory-specified criteria were applied for data quality determination. All CCVs met the laboratory control criteria, except that the relative retention times (RRTs) for selected compounds slightly went outside the RRT window in Laboratory 98's CCVs. The chromatograms and ion spectrums were examined; no anomalies were found as far as compound identification. The %D values were all well within the control limits. The RRT shifting had no significant effects on data quality. No data qualifying action was taken in these cases.

1.5 Method Blanks

A method blank was prepared and analyzed by both laboratories. PRCs were not detected at or above the method detection limits (MDLs). Selected target PCB congeners were detected in method blanks at levels less than the practical quantitation limits (PQLs) but greater than their MDLs for both laboratories. Sample results that were greater than five times the levels found in the method blanks were considered not affected and no actions were taken. Results were less than the method reporting limits (MRLs) and less than five times the level found in the method blanks were qualified (U) as non-detected at the reported values. Data qualified in this manner are summarized in SUMMARY, Table 1.

1.6 Initial Precision and Recovery Study (IPR)

IPR study results are normally maintained in the laboratory and were not included in data packages. This information will be required in data packages reported for the following phases of this study as needed.

1.7 Ongoing Precision and Recovery (OPR)

OPR was prepared and analyzed for PRC PCBs at the adequate frequency by Laboratory 48. The %R values met the laboratory control criteria.

1.8 Laboratory Control Sample (LCS) and LCS Duplicate (LCSD)

Since no matrix-specific (i.e., SPME in this case) LCS was available to be processed along with the samples, the laboratories analyzed/reported laboratory-made standards as LCS. Due to the limited supplier and the excessive cost of the ¹³C-labelled PRCs, the LCS analyzed/reported by Laboratory 98 did not contain the target PRCs. However, the %R values in LCS were all within the laboratory control criteria.

OPR was prepared and analyzed in lieu of LCS by Laboratory 48. See discussion above.

1.9 Labeled Compound Recovery

Labeled internal standards were added to all samples as required by the analytical method and laboratory SOPs. The labeled internal standards and cleanup standards percent recoveries all met the method and laboratory SOP requirements.

1.10 Target Compound Identification

Target compound identification was evaluated by examining if: (1) the signals for the two exact m/z's being monitored were present, and maximized within ± 2 seconds of one another (± 3 seconds for Laboratory 48), (2) the S/N ratio of each of the two exact m/z's must be greater than or equal to 2.5, (3) the ion abundance ratios were within the method control limits, and (4) the relative retention time (RRT) or retention time (RT) of the peaks were within the method control limits or laboratory control limits. No anomalies were found in relation to target compound identification, except that ion abundance ratios did not fully meet the method criteria for selected results. These results were reported as estimated maximum possible concentration (EMPC). The ion spectra were evaluated and determined that the anomaly in ion abundance ratios did not significantly affect data usability for these results. No data qualifying actions were taken.

1.11 Reporting Limits, Estimated Detection Limits (EDLs) and Compound Quantitation

Correct internal standards, quantitation ions, and average RFs were used to quantitate target compound detections. The MRLs were supported with adequate ICAL calibration concentrations. The project goal for quantitation limits were attained to in these cases.

A verification calculation was performed on 10% of the reported calibration, laboratory QC analyses, and sample results. No anomalies were found. The verification calculation worksheets were maintained in project files for requests.

Response peak integrations were primarily performed automatically with computer software. In cases where peak shifting, signal interferences, and/or peak tailing occurred, manual integrations were performed. Manual integrations criteria and approaches were consistent justifiable across the analyses; no anomalies were identified in relation to compound identification and quantitation.

1.12 Overall Assessment of PCB Congener Data Usability

PCB congener data were of known quality and acceptable for use as qualified, with the acknowledgement of deviations and anomalies discussion above.

2. PCB Congeners by GC/MS - SIM (EPA Method SW8270D-SIM)

Two laboratories, Laboratory 19 and Laboratory 83, chose to use EPA Method SW8270D-SIM for PCB congeners analysis. Note that neither EPA Method 8270D nor laboratory SOPs specified evaluation criteria for carbon-labeled PCBs. However, unless noted otherwise, criteria set forth for non-labeled PCBs in the method and SOPs were applied for ¹³C-labeled PCBs data quality and method compliance evaluation.

2.1 Sample Management and Holding Times

No anomalies were noted by the laboratories in relation to sample packaging, transportation, handling, preservation, and integrity upon sample receipt in the laboratories.

EPA Method 8270D does not specify holding time requirements for SPME samples (submerged in loading solution). Holding time requirements for solid samples (one year from collection to extraction, 40 days from extraction to analysis) were applied as a guideline for sample collection (the time the SPME fibers were retrieved from the sediment) and extract holding time evaluation. Samples were extracted and analyzed within the holding times by both laboratories.

2.2 GC/MS Instrument Performance Check

The laboratories performed GC/MS tuning analysis as required by the analytical method and their SOPs. DFTPP tuning was performed within each 12-hour interval. All required ion abundance ratios met the method requirements.

2.3 Initial Calibration (ICAL)

EPA Method 8270D criteria require that (1) if a linear average RFs is chosen as the quantitation option, at least five standards at different concentrations should be analyzed and the %RSD of RFs be $\leq 15\%$ ($\leq 25\%$ for Laboratory 83) for the analyte, (2) if least-square linear regression is chosen for quantitation, the correlation coefficient (r) be >0.995 , and (3) if six-point non-linear (quadratic) curve is chosen for quantitation, the coefficient of determination (r^2) be >0.99 . All ICALs met the method and laboratory criteria.

An ICV standard (second source standard) was analyzed to verify the calibration curve. Due to limited suppliers and excessive cost of the ^{13}C -labeled PRCs, the second source standards used by both laboratories contained non-labelled PCBs rather than the ^{13}C -labeled PCB PRCs. The %D values were within ± 20 . The ICALs were considered valid.

2.4 Calibration Verification (CCV)

The analytical method requires that (1) continuing calibration verifications be analyzed at the beginning of each 12-hour analysis period prior to the analysis of method blank and samples, and (2) the %D be within $\pm 20\%$ ($\pm 25\%$ for Laboratory 83). All CCVs met the method and laboratory criteria.

2.5 Method Blanks

Method blanks were prepared and analyzed as required. Target PCB congeners and PCB PRCs were not detected at or above the method detection limits (MDLs).

2.6 Surrogate Spikes

Surrogate spikes were added to all samples as required by the method. All surrogate spike %R values were within the control limits specified in the laboratory SOPs.

2.7 Matrix Spike (MS) and MS Duplicate (MSD)

MS and MSD analyses were not applicable for the calibration standard analysis.

2.8 Laboratory Control Sample (LCS)

LCS was not prepared/analyzed by Laboratory 19. LCS was prepared and analyzed by Laboratory 83. The %R values met the laboratory control limits.

2.9 Internal Standards

The method requires that (1) internal standard retention time be within ± 30 seconds from that of the associated 12-hour calibration standard, and (2) the area counts of all internal standards be within -50% to $+100\%$ of the associated 12-hour calibration standard. Laboratory 83 chose to use those of the mid-point ICAL standard for internal standard recovery control criteria. Internal standard recovery met the method or laboratory requirements.

2.10 Target Compound Identification

All chromatograms were properly displayed and scaled. No target compounds were detected in any of the field samples. No anomalies were found in relation to target compound identification.

2.11 Reporting Limits and Target Compound Quantitation

Re-calculation was performed on 10% of the instrument calibration and reported QC and sample analyses. No anomalies were found via the verification calculation. MRLs were supported with adequate initial calibration concentrations. In cases where target compound concentrations exceeded ICAL calibration ranges, extracts were diluted and re-analyzed for definitive quantitation.

Response peak integrations were primarily performed automatically with computer software. In cases where peak shifting, signal interferences, and/or peak tailing occurred, manual integrations were performed. Manual integrations criteria and approaches were consistent justifiable across the analyses; no anomalies were identified in relation to compound identification and quantitation.

2.12 Overall Assessment of PCB Congeners Data Usability

PCB Congeners data are of known quality and acceptable for use, with the acknowledgement of SOP deviations and anomalies stated above.

3. PAHs by Isotope Dilution GC/MS (EPA Method SW8270D Modified and EPA Method 1625 Modified)

Laboratory 48 and Laboratory 98 chose to use EPA Method SW8270D modified with EPA Method 1625 for this study. Note that neither EPA Method 8270D, EPA Method 1625 nor laboratory SOPs specified evaluation criteria for carbon-labeled PAHs. However, unless noted otherwise, criteria set forth for non-labeled PAHs in the methods and SOPs were applied for PAH PRC data quality and method compliance evaluation.

3.1 Sample Management and Holding Times

No anomalies were noted by the laboratories in relation to sample packaging, transportation, handling, preservation, and integrity upon sample receipt in the laboratories.

EPA Method 8270D does not specify holding time requirements for SPME samples (submerged in loading solution). Holding time requirements for solid samples (one year from collection to extraction, 40 days from extraction to analysis) were applied as a guideline for sample collection (the time the SPME strips were retrieved from the sediment) and extract holding time evaluation. Samples were extracted and analyzed within the holding times by both laboratories.

3.2 GC/MS Instrument Performance Check

The method requires that DFTPP tuning be performed within each 12-hour interval. All required ion abundance ratios should meet the requirements in the method. Each of the laboratories specified GC/MS tuning procedures and requirements in their SOPs. However, tuning reports were not included in their data package in this task. This information will be required for all data packages in future sample analyses for this study.

3.3 Initial Calibration (ICAL)

Laboratory 98 chose to fully follow the method requirements to establish ICAL for regular target PAH and $^{13}\text{C}_6$ -Labeled PAH PRCs. Laboratory 48 followed the method requirements for regular target PAHs only. The method ICAL criteria require that (1) if linear average RFs is chosen as the quantitation option, at least five standards at different concentrations should be analyzed and the %RSD of RFs be $\leq 20\%$ for the analyte, (2) if least-square linear regression is chosen for quantitation, the correlation coefficient (r) be >0.995 , and (3) if six-point non-linear (quadratic) curve is chosen for quantitation, the coefficient of determination (r^2) be >0.99 . An ICV standard (second source standard) was analyzed to verify the calibration curve. The %D values were within $\pm 20\%$. The ICALs were considered valid.

Laboratory 48 followed their SOP to establish ICAL for the $^{13}\text{C}_6$ -Labeled PAH PRCs. A mid-point calibration standard was analyzed at the beginning and the end of the analytical sequence. The response factor RPD values for the target compounds and surrogate compounds should be within 20%, and RT within 3 seconds between the two analyses. The ICAL met the laboratory SOP requirements.

3.4 Calibration Verification (CCV)

The analytical method requires that (1) continuing calibration verifications be analyzed at the beginning of each 12-hour analysis period prior to the analysis of method blank and samples, and (2) the %D be within $\pm 20\%$. All CCVs met the laboratory control criteria.

3.5 Method Blanks

A method blank was prepared and analyzed by both laboratories. Target PAHs and PAH PRCs were not detected at or above the MDLs.

3.6 Surrogate Spikes

Surrogate spikes were added to all samples as required by the method. All surrogate spike %R values were within the control limits specified in the laboratory SOPs.

3.7 Laboratory Control Sample (LCS) and LCS Duplicate (LCSD)

Since no matrix-specific (i.e., LDPE in this case) LCS was available to be processed along with the samples, the laboratories analyzed/reported laboratory-made standards as LCS. Due to the limited supplier and the excessive cost of the ^{13}C -labelled PRCs, the LCS analyzed/reported by Laboratory 98 did not contain the target PRCs. However, the %R values in LCS were all within the laboratory control criteria.

OPR was prepared and analyzed in lieu of LCS by Laboratory 48. See discussion below.

3.8 Ongoing Precision and Recovery (OPR)

OPR was prepared and analyzed for PRC PCBs at the adequate frequency by Laboratory 48. The %R values met the laboratory control criteria.

3.9 Labeled Compound Recovery

Labeled internal standards were added to all samples as required by the analytical method and laboratory SOPs. The labeled internal standards percent recoveries all met the method and laboratory SOP requirements.

3.10 Target Compound Identification

All chromatograms were properly displayed and scaled. No target compounds were detected in any of the field samples. No anomalies were found in relation to target compound identification.

3.11 Reporting Limits and Target Compound Quantitation

Re-calculation was performed on 10% of the instrument calibration and reported QC and sample analyses. No anomalies were found via the verification calculation. MRLs were supported with adequate initial calibration concentrations. In cases where target compound concentrations exceeded ICAL calibration ranges.

Response peak integrations were primarily performed automatically with computer software. In cases where peak shifting, signal interferences, and/or peak tailing occurred, manual integrations were performed. Manual integrations criteria and approaches were consistent justifiable across the analyses; no anomalies were identified in relation to compound identification and quantitation.

3.12 Overall Assessment of PAHs Data Usability

PAHs data are of known quality and acceptable for use, with the acknowledgement of SOP deviations and anomalies stated above.

4. PAHs by GC/MS - SIM (EPA Method SW8270D-SIM)

Laboratory 19 and Laboratory 83 chose to use this methodology for PAHs analysis. Neither EPA Method 8270D nor laboratory SOPs specified evaluation criteria for ¹³C₆-labelled PAHs. However, unless noted otherwise, criteria set forth for non-labeled PAHs in the method and SOPs were applied for carbon-labeled PAHs data quality and method compliance evaluation.

4.1 Sample Management and Holding Times

No anomalies were noted by the laboratories in relation to sample packaging, transportation, handling, preservation, and integrity upon sample receipt in the laboratories.

EPA Method 8270D does not specify holding time requirements for SPME samples (submerged in loading solution). Holding time requirements for solid samples (one year from collection to extraction, 40 days from extraction to analysis) were applied as a guideline for sample collection (the time the SPME fibers were retrieved from the sediment) and extract holding time evaluation. Samples were extracted and analyzed within the holding times by both laboratories.

4.2 GC/MS Instrument Performance Check

The laboratories performed GC/MS tuning analysis as required by the analytical method and their SOPs. DFTPP tuning was performed within each 12-hour interval. All required ion abundance ratios met the method requirements.

4.3 Initial Calibration (ICAL)

The EPA Method 8270D criteria require that (1) if linear average RFs is chosen as the quantitation option, at least five standards at different concentrations should be analyzed and the %RSD of RFs be $\leq 20\%$ for the analyte, (2) if least-square linear regression is chosen for quantitation, the correlation coefficient (r) be >0.995 , and (3) if six-point non-linear (quadratic) curve is chosen for quantitation, the coefficient of determination (r^2) be >0.99 . Laboratory 83's criteria vary slightly from the method requirements. All ICALs met the method and laboratory criteria.

An ICV standard (second source standard) was analyzed to verify the calibration curve. Due to limited suppliers and excessive cost of the carbon-labeled PRCs, the second source standards used by both laboratories contained non-labelled PCBs rather than the carbon-labeled PRCs. The %D values were within ± 20 . The ICALs were considered valid.

4.4 Calibration Verification (CCV)

The analytical method requires that (1) continuing calibration verifications be analyzed at the beginning of each 12-hour analysis period prior to the analysis of method blank and samples, and (2) the %D be within $\pm 20\%$ (25% for Laboratory 83).

The dibenzo(a,h)anthracene-d14 (a surrogate spike) %D values exceeded 20% in CCVs for Laboratory 19, indicating a biased high recovery. This likely was the result of high levels of PAHs in samples. The recovery of this surrogate spike in samples was within control limits in dilution analyses. Data usability has not significantly affected. No data qualifying action was taken in this case. See discussion in Section 4.6 as well.

4.5 Method Blanks

Method blanks were prepared and analyzed as required. Target regular PAHs and PAH PRCs were not detected at or above the MDLs.

4.6 Surrogate Spikes

Surrogate spikes were added to all samples as required by the method. All surrogate spike

%R values were within the control limits specified in laboratory SOPs, except that the recovery of dibenzo(a,h)anthracene-d14 in samples and laboratory QC analyses exceeded the upper control limits for Laboratory 19. The recovery was within the laboratory control limits in dilution analyses, indicating the biased-high recovery was a result of matrix effects and not the deficiency related to sample extraction. No data qualifying action was taken in these cases.

4.7 Matrix Spike (MS) and MS Duplicate (MSD)

MS and MSD analyses were not applicable for this calibration standard analysis

4.8 Laboratory Control Sample (LCS)

LCS was not prepared by Laboratory 19. LCS was prepared and analyzed by Laboratory 83. The %R values met the laboratory control limits.

4.9 Internal Standards

The method requires that (1) internal standard retention time be within ± 30 seconds from that of the associated 12-hour calibration standard, and (2) the area counts of all internal standards be within -50% to $+100\%$ of the associated 12-hour calibration standard. Laboratory 83 chose to use those of the mid-point ICAL standard for internal standard recovery control criteria. Internal standard recovery met the method or laboratory requirements.

4.10 Target Compound Identification

All chromatograms were properly displayed and scaled. No target compounds were detected in any of the field samples. No anomalies were found in relation to target compound identification.

4.11 Reporting Limits and Target Compound Quantitation

Re-calculation was performed on 10% of the instrument calibration and reported QC and sample analyses. No anomalies were found via the verification calculation. MRLs were supported with adequate initial calibration concentrations. Response peak integrations were primarily performed automatically with computer software. In cases where peak shifting, signal interferences, and/or peak tailing occurred, manual integrations were performed. Manual integrations criteria and approaches were consistent justifiable across the analyses; no anomalies were identified in relation to compound identification and quantitation.

4.12 Overall Assessment of PAHs Data Usability

PAHs data are of known quality and acceptable for use with the acknowledgement of SOP deviations and anomalies stated above.

SUMMARY

Table 1. Data Affected by QC Anomalies

Laboratory	Sample ID	Analyte	Reported Value (ng/g)	Lab Flag	Validator Qualifier	Reason Code	Report Section
Laboratory 48	WG72096-101 ^(A)	PCB-209	0.472	KJ		MB, EMPC	1.5
	Active Test 1	PCB-209	0.535	J	U	MB, EMPC	
	Active Test 2	PCB-209	0.523	K J	U	MB, EMPC	
	Active Test 3	PCB-209	0.615	J	U	MB, EMPC	
	Active Test 4	PCB-209	0.448	K J	U	MB, EMPC	
	Active Test 5	PCB-209	0.386	J	U	MB, EMPC	
	Active Test 6	PCB-209	0.791	J	U	MB, EMPC	
	Static Test 1	PCB-209	0.476	K J	U	MB, EMPC	
	Static Test 2	PCB-209	0.535	K J	U	MB, EMPC	
	Static Test 3	PCB-209	0.569	K J	U	MB, EMPC	
	Static Test 4	PCB-209	0.581	K J	U	MB, EMPC	
	Static Test 5	PCB-209	0.413	J	U	MB, EMPC	
	Static Test 6	PCB-209	0.635	J	U	MB, EMPC	
Laboratory 98	MB 140-38861/15-B ^(A)	PCB-128	0.0303	J			1.5
	PDMS Active - PCB 1	PCB-128	0.024	J C B	U	MB	
	PDMS Active - PCB 2	PCB-128	0.035	J C B	U	MB	
	PDMS Active - PCB 3	PCB-128	0.023	J C B q	U	MB, EMPC	
	PDMS Active - PCB 4	PCB-128	0.036	J C B	U	MB	
	PDMS Active - PCB 5	PCB-128	0.044	J C B	U	MB	
	PDMS Active - PCB 6	PCB-128	0.037	J C B	U	MB	
	PDMS Static - PCB 1	PCB-128	0.028	J C B	U	MB	
	PDMS Static - PCB 2	PCB-128	0.026	J C B q	U	MB, EMPC	
	PDMS Static - PCB 3	PCB-128	0.027	J C B	U	MB	
	PDMS Static - PCB 4	PCB-128	0.026	J C B	U	MB	
	PDMS Static - PCB 5	PCB-128	0.026	J C B	U	MB	
	PDMS Static - PCB 6	PCB-128	0.02	J C B q	U	MB, EMPC	
Laboratory 98	MB 140-38861/15-B ^(A)	PCB-170	0.0418	J			1.5
	PDMS Active - PCB 1	PCB-170	0.045	J B q	U	MB, EMPC	
	PDMS Active - PCB 2	PCB-170	0.078	J B	U	MB	
	PDMS Active - PCB 3	PCB-170	0.055	J B	U	MB	
	PDMS Active - PCB 4	PCB-170	0.025	J B q	U	MB, EMPC	
	PDMS Active - PCB 5	PCB-170	0.061	J B q	U	MB, EMPC	
	PDMS Active - PCB 6	PCB-170	0.069	J B q	U	MB, EMPC	
	PDMS Static - PCB 1	PCB-170	0.050	J B	U	MB	
	PDMS Static - PCB 2	PCB-170	0.033	J B q	U	MB, EMPC	
	PDMS Static - PCB 3	PCB-170	0.031	J B q	U	MB, EMPC	
	PDMS Static - PCB 4	PCB-170	0.038	J B q	U	MB, EMPC	
	PDMS Static - PCB 5	PCB-170	0.044	J B	U	MB	
	PDMS Static - PCB 6	PCB-170	0.042	J B q	U	MB, EMPC	

Laboratory	Sample ID	Analyte	Reported Value (ng/g)	Lab Flag	Validator Qualifier	Reason Code	Report Section
Laboratory 98	MB 140-38861/15-B ^(A)	PCB-180	0.0507	J	U		1.5
	PDMS Active - PCB 1	PCB-180	0.1	J C B	U	MB	
	PDMS Active - PCB 2	PCB-180	0.17	J C B	U	MB	
	PDMS Active - PCB 3	PCB-180	0.14	J C B	U	MB	
	PDMS Active - PCB 4	PCB-180	0.13	J C B	U	MB	
	PDMS Active - PCB 5	PCB-180	0.14	J C B	U	MB	
	PDMS Active - PCB 6	PCB-180	0.16	J C B	U	MB	
	PDMS Static - PCB 1	PCB-180	0.11	J C B	U	MB	
	PDMS Static - PCB 2	PCB-180	0.086	J C B	U	MB	
	PDMS Static - PCB 3	PCB-180	0.086	J C B	U	MB	
	PDMS Static - PCB 4	PCB-180	0.09	J C B	U	MB	
	PDMS Static - PCB 5	PCB-180	0.1	J C B	U	MB	
	PDMS Static - PCB 6	PCB-180	0.11	J C B	U	MB	
Laboratory 98	MB 140-38861/15-B ^(A)	PCB-195	0.0501	J			1.5
	PDMS Active - PCB 1	PCB-195	0.0059	J B q	U	MB, EMPC	
	PDMS Active - PCB 2	PCB-195	0.017	J B q	U	MB, EMPC	
	PDMS Active - PCB 3	PCB-195	0.01	J B q	U	MB, EMPC	
	PDMS Active - PCB 4	PCB-195	0.0088	J B q	U	MB, EMPC	
	PDMS Active - PCB 5	PCB-195	0.013	J B q	U	MB, EMPC	
	PDMS Active - PCB 6	PCB-195	0.011	J B q	U	MB, EMPC	
	PDMS Static - PCB 1	PCB-195	0.006	J B q	U	MB, EMPC	
	PDMS Static - PCB 2	PCB-195	0.0049	J B q	U	MB, EMPC	
	PDMS Static - PCB 3	PCB-195	0.0062	J B	U	MB	
	PDMS Static - PCB 4	PCB-195	0.0047	J B q	U	MB, EMPC	
	PDMS Static - PCB 5	PCB-195	0.0038	J B q	U	MB, EMPC	
	PDMS Static - PCB 6	PCB-195	0.0078	J B q	U	MB, EMPC	
Laboratory 98	MB 140-38861/15-B ^(A)	PCB-206	0.0449	J q			1.5
	PDMS Active - PCB 2	PCB-206	0.015	J B q	U	MB, EMPC	
	PDMS Active - PCB 6	PCB-206	0.019	J B	U	MB	
Laboratory 98	MB 140-38861/15-B ^(A)	PCB-209	0.0389	J B			1.5
	PDMS Active - PCB 2	PCB-209	0.0076	J B q	U	MB	
	PDMS Static - PCB 1	PCB-209	0.0014		U	MB, EMPC	

Notes:

^(A) – his sample is a laboratory method blank.

B – This compound was detected in the method blank as well.

C – Co-elution with another congener(s) was observed.

EMPC - Estimated Maximum Possible Concentration

J – The value is greater than the method detection limit (MDL) but less than the practical quantitation limit (PQL) and is an estimated value.

K – The detection did not meet the ion abundance ration criteria and is considered as an EMPC.

MB – The result was less than five times the level found in the method blank.

q – Same as K.

U – The result may be false positive and can be treated as a non-detect at the reported value.

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APPENDIX A

QUALITY CONTROL CRITERIA FOR ANALYTICAL METHODS

Table A1 – PCB Congeners Analysis Quality Control Evaluation Criteria Summary

QC Parameters and Performance Frequency	Laboratory and Referenced Analytical Method			
	Laboratory 19 (EPA 8270D)	Laboratory 48 (EPA 1668C)	Laboratory 83 (EPA 8270D Modified)	Laboratory 98 (EPA 1668C)
Tuning (Resolution Check) At the beginning and the end of each 12-hour period of analysis.	Same as Method	Same as Method	Prior to initial calibration. Prior to CCV if system idle for >24 hrs. Criteria same as 8270D.	Same as Method
GC Column Performance Check Prior to ICAL or calibration verification.	N/A	Same as Method	N/A	Same as Method
Initial Calibration (ICAL) Prior to sample analysis; as needed if failure of calibration verification; or a new lot is used as standard source.	Same as Method	- Same as Method - Standards' result values are within 15% of true values.	Same as 8270D.	Same as Method
Calibration Verification (CCV), Ongoing Precision Recovery (OPR), or Verification (VER) At the beginning of each 12-hour period.	Same as Method	- Same as Methods. - SOP Tables 4a and 4b.	At the beginning and end of 10 injections or each 24 hour period (whichever is more frequent)	Same as Method
Method Blank One per preparatory batch, run after calibration standards and before samples.	No analytes detected $\geq \frac{1}{2}$ limit of quantitation or $\geq 5\%$ of the associated regulatory limit for the analyte or $\geq 10\%$ of the sample result for the analyte, whichever is greater, per method.	Analyte amounts in blank samples for PCB congeners 77, 81, 114, 123, 126 and 169 must be ≤ 2 pg/congener/sample, amounts of PCB congeners 156, 157, 167 and 189 must be ≤ 10 pg/congener/sample, and the maximal amount of PCB 11 must be ≤ 150 pg/sample. Amounts of all other individual PCB congeners or coelutions must be ≤ 50 pg/congener/sample in blank samples. The sum of all 209 congeners should be ≤ 300 pg/sample. Higher levels are acceptable where sample concentrations exceed 10 times blank levels.	Analyte concentration in PB should be < MDL and must be < 5xMDL No analytes detected > $\frac{1}{2}$ RL. For common laboratory contaminants, no analytes detected > RL.	Target analytes must be less than estimated maximum levels (EMLs) in SOP Table 4

Instrument Blank At the beginning of each 12-hour period.	Same as Method Blank.	Same as Method Blank.	Same as Method Blank.	Target analytes must be less than EMLs in SOP Table 4
Laboratory Control Sample (LCS) One per preparatory batch.	%R value should be within 70-130% of the true value	SOP Tables 4a and 4b.	70 to 130% recovery vs. SIS 40 to 120% recovery vs. IS	Within control limits for OPR (SOP Tables 10A and 10B).
Matrix Spike (MS) (OPTIONAL)	%R value should be within 70-130% of the true value	N/A	70 to 130% recovery vs. SIS 40 to 120% recovery vs. IS Spiked target analyte concentration must be > 5 x the level in the background sample.	NA
Sample Duplicate or MS Duplicate (MSD)	RPD $\leq$ 30%	RPD $\leq$ 20% (applicable to concentrations $\geq$ 10 times the DL)	RPD $\leq$ 30%	N/A
Extraction Standards and Cleanup Standards Every field sample, standard, and QC sample.	- Same as Method for Internal standard recovery - Surrogate Spike recovery is within 70 - 130%.	Same as Method SOP Tables 4a and 4b.	Surrogate spike recovery 40 - 120%	Same as Method
Compound Identification	Same as Method	Same as Method	Same as 8270D	Same as Method

Notes:

N/A: Not applicable

EPA 8270D - USEPA. 1998. *Test Methods for Evaluating Solid Waste (SW 846). Third Edition and Revised Update IIIA. Method 8000 and Method 8270D. Office of Solid Waste and Emergency Response, Washington, D.C. April 1998 and Updates.*

EPA 1668C - USEPA Method 1668C - *Chlorinated Biphenyl Congeners in Water, Soil, Sediment, Biosolids, and Tissue by HRGC/HRMS. April 2010.*

Table A2 – PAHs Analysis Quality Control Evaluation Criteria Summary

QC Parameter & Performance Frequency	Laboratory and Referenced Method			
	Laboratory 19 EPA 8270D-SIM	Laboratory 48 EPA 8720C-SIM EPA 1625 (HRGC/MS)	Laboratory 83 (EPA 8270D Modified)	Laboratory 98 EPA 8270C-SIM EPA 1625 (GC/MS)
Relative Retention Time (RRT) Evaluation Each Sample	RRT of each target analyte in each calibration standard within ± 0.05 RRT units.	- RT within ± 3 seconds of the predicted retention time determined from the calibration standard and adjusted relative to the peak retention time reference (i.e. labelled surrogate). - A second requirement is that an authentic elute after its labelled analog.	RT window for an analyte is ± 15 s from the determined RT of the analyte in the ICAL.	N/A
Initial Calibration (ICAL) Prior to sample analysis; as needed if failure of calibration verification; or a new lot is used as standard source.	- A minimum of five points. - Analytes' RRFs must meet method limits across calibration range. - Analytes %RSDs must be less than or equal to 20%, or the analyte must employ a linear or non-linear calibration model with a coefficient of determination (r^2) greater than 0.99. - Up to 10% of the total analytes may fail 1 and 2 above. - Verify ICAL with one second-source standard at mid- point concentration. Value for all analytes within $\pm 30\%$ of expected value.	- Calibration standard solutions are presented in SOP Table 6. - Linearity is demonstrated by a 5-point calibration over the working concentration range with a relative standard deviation of the RRFs $\leq 20\%$ for targets with a labelled analog present and all labelled compounds, $\leq 35\%$ for targets with no labelled analog present.	- A minimum of five points. - Analyte RF %RSDs must be less than or equal to 25% average RF. - Verify ICAL with one second-source standard. Value for all analytes within $\pm 25\%$ of expected value.	- SOP Table 3 lists ICAL concentrations. %RSD must be $\leq 30\%$ for analytes and internal standards. - Verify ICAL with one second-source standard at mid-point (CS4) concentration. Value for all analytes within $\pm 30\%$ of expected value.

QC Parameter & Performance Frequency	Laboratory and Referenced Method			
	Laboratory 19 EPA 8270D-SIM	Laboratory 48 EPA 8720C-SIM EPA 1625 (HRGC/MS)	Laboratory 83 (EPA 8270D Modified)	Laboratory 98 EPA 8270C-SIM EPA 1625 (GC/MS)
Calibration verification (CCV) Before sample analysis, and every 12 hours of analysis time	- Average RRFs for analytes must meet the method defined limits. %Difference/Drift for analytes $\leq 20\%$ - Up to 20% of the target analytes may fail the criteria in 1 and 2 so long as the sample analyses associated with the CCVS are J flagged.	- Opening Cal Ver: Concentrations of native compounds and labelled surrogates must be within $\pm 25\%$ of expected values for all targets. - Closing Cal Ver: Concentrations of native compounds must be within $\pm 25\%$ of expected values. - Concentrations of labelled surrogates must be within $\pm 25\%$ of expected values, with any two (2) values allowed to be within $\pm 40\%$. - Ion ratios for authentic and labelled dibenz[ah]anthracene, indeno[1,2,3-cd]pyrene and benzo[ghi]perylene must be within $\pm 35\%$ of the mid-point of the I-CAL. - All other native analytes and labelled surrogates must be within $\pm 20\%$ of the mid-point of the I-CAL.	- Average RRFs for analytes must meet the method defined limits. - CCV after every 10 injections of 24 hrs – whichever is shorter. - Individual % difference $\leq 25\%$ - Grand mean of % difference $\leq 15\%$. - IS area has not changed by more than a factor of two (-50% to +100% from the area found in level 3 of the ICAL.	%Difference/Drift for analytes must be $\leq 30\%$ (SOP Table 7). - The recovery standard response must be within 50- 200% of the response in the corresponding CS4 calibration level of the initial calibration. - New ICAL is needed if this criterion is not met.
Internal Standards Every field sample, standard, and QC sample	- Retention time ± 30 seconds from retention time of the midpoint standard in the ICAL or CCV. - EICP area within - 50% to +100% of ICAL midpoint standard	Within -50% to +100% of ICAL midpoint standard.	IS area has not changed by more than a factor of two (-50% to +100% from the area found in level 3 of the ICAL.	The recovery standard response must be within 50- 200% of the response in the corresponding CS4 calibration level of the initial calibration.
Method blank One per preparation batch of 20 or less samples	No analytes detected > $\frac{1}{2}$ RL. For common laboratory contaminants, no analytes detected $\geq$ RL.	SOP Table 8.	Analyte concentration in PB should be < MDL and must be < 5 MDL No analytes detected > $\frac{1}{2}$ RL. For common laboratory contaminants, no analytes detected > RL.	No analytes detected > RL ($\frac{1}{2}$ RL for DoD projects).
Laboratory control sample (LCS) One per preparation batch of 20 or less samples	See Laboratory QA Plan (LQAP). Reported along with LCS results	SOP Table 8.	70 to 130% recovery vs. SIS 40 to 120% recovery vs. IS	SOP Table 7
Matrix Spike (MS) and MS Duplicate (MSD)	- For matrix evaluation, see LQAP. MS recovery is advisory. - RPD $\leq 30\%$ (MS/ MSD or sample duplicate). Limits are advisory.	SOP Table 8.	70 to 130% recovery vs. SIS 40 to 120% recovery vs. IS RPD $\leq 30\%$	N/A

QC Parameter & Performance Frequency	Laboratory and Referenced Method			
	Laboratory 19 EPA 8270D-SIM	Laboratory 48 EPA 8720C-SIM EPA 1625 (HRGC/MS)	Laboratory 83 (EPA 8270D Modified)	Laboratory 98 EPA 8270C-SIM EPA 1625 (GC/MS)
Surrogate Spikes Every field and QC sample	QC acceptance criteria for LCS specified by DoD, if available; otherwise method- specified criteria or laboratory's own in-house criteria (No more than 1 acid surrogate or 1 base surrogate is allowed out of control, all surrogate recoveries must be > 10%.)	SOP Table 8 for SPMD samples, including criteria for PRCs.	40 - 120% recovery	SOP Table 7
Laboratory Duplicates (Optional)	N/A	Duplicates must fall within $\pm 20\%$ of the mean (applicable to concentrations ≥ 10 times the DL). (Note that $\pm 20\%$ of the mean is equivalent to 40 relative percent difference)	$\leq 30\%$ RPD	N/A

QC Parameter & Performance Frequency	Laboratory and Referenced Method			
	Laboratory 19 EPA 8270D-SIM	Laboratory 48 EPA 8720C-SIM EPA 1625 (HRGC/MS)	Laboratory 83 (EPA 8270D Modified)	Laboratory 98 EPA 8270C-SIM EPA 1625 (GC/MS)
Compound Identification	Same as Method	- Peak responses must be at least three times the background noise level. - The retention time (RT) must be within three seconds of that predicted from the calibration run and the sample retention time reference (labelled compound). - Peak maxima for the quantification and confirmation ions must coincide within two seconds. - The relative ion abundance ratios must be within 20% of the opening calibration values.	- Primary SIM ion must be present. - Peak responses must be at least three times the background noise level. - RT must fall within established RT window.	- The internal standard quantitation ions must be present. - The relative intensities of confirmation ions should agree to within $\pm 30\%$ between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 20% and 80%). The absence of confirmation ions should be considered carefully when making decisions regarding qualitative identification. Confirmation ions may have lower response than quantitation ions and may not always be present at lower concentrations. Their absence in this case may not be cause for determining that the analyte is not present. The absence of confirmation ions at higher levels where they should have been detectable may be cause for determination that an analyte is not present. - The sample component retention time must compare to within ± 0.2 min. of the retention time of the internal standard component. For reference, the standard must be run within the same 12- hour period as the sample. - If a compound cannot be verified by all the above criteria, but in the technical judgment of the analyst the identification is correct, the analyst shall report that identification and proceed with quantitation.

Notes:

N/A - Not applicable.; DoD – U.S. Department of Defense

EPA 8270D - USEPA. 1998. *Test Methods for Evaluating Solid Waste (SW 846). Third Edition and Revised Update IIIA. Method 8000 and Method 8270D. Office of Solid Waste and Emergency Response, Washington, D.C. April 1998 and Updates.*

EPA 1625 – 40CFR, Appendix A to Part 136, Method 1625 Revision B, Semivolatile Organic Compounds by Isotope Dilution GC/MS

HRGC/MS – High resolution gas chromatography coping with mass spectrometry

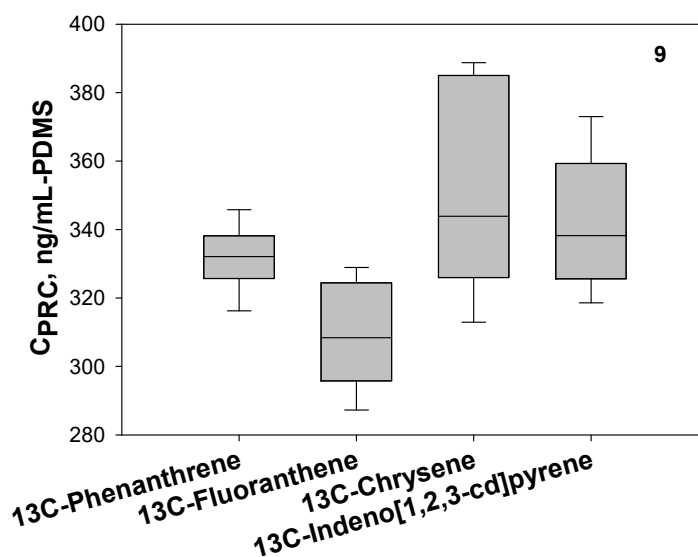
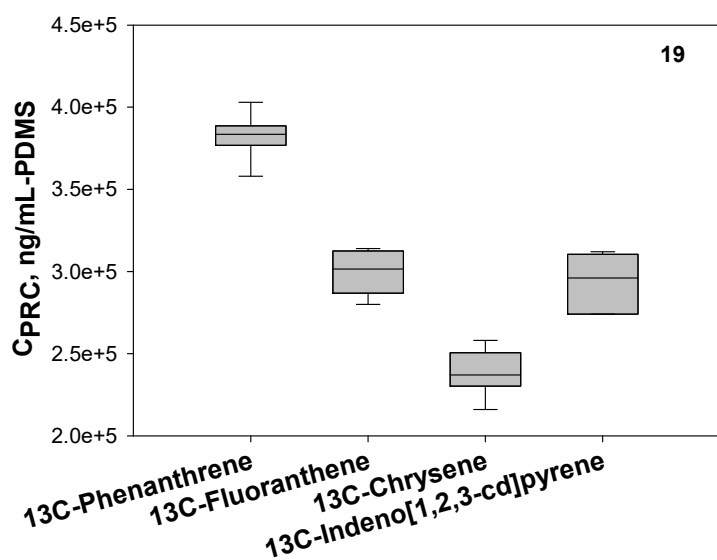
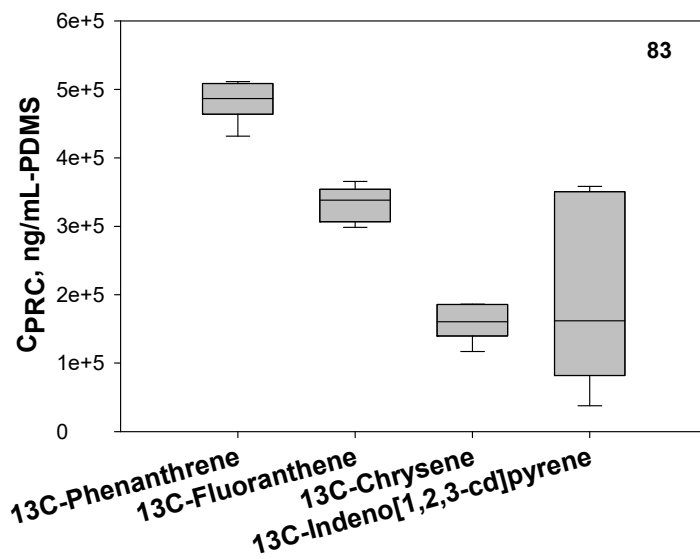
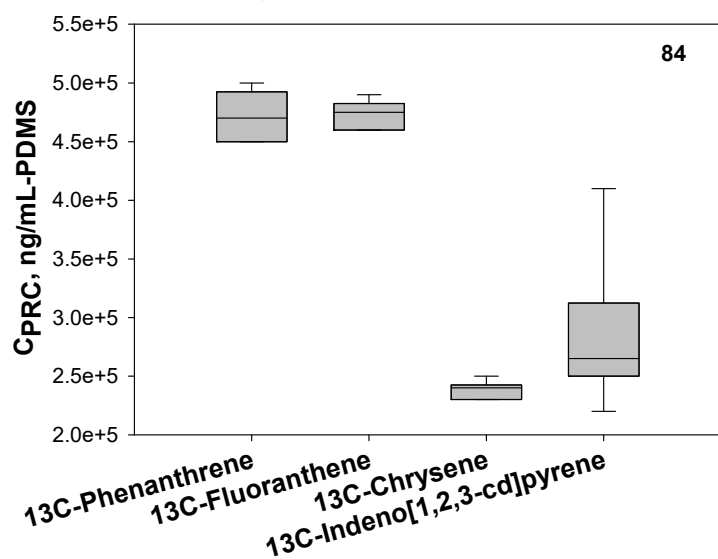
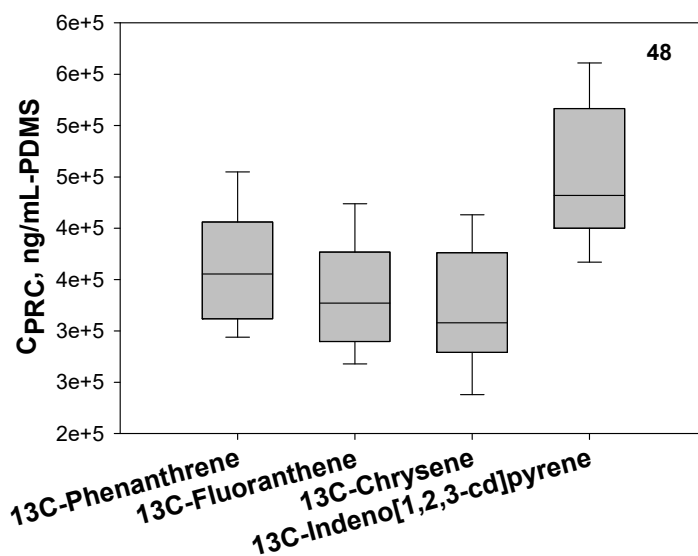
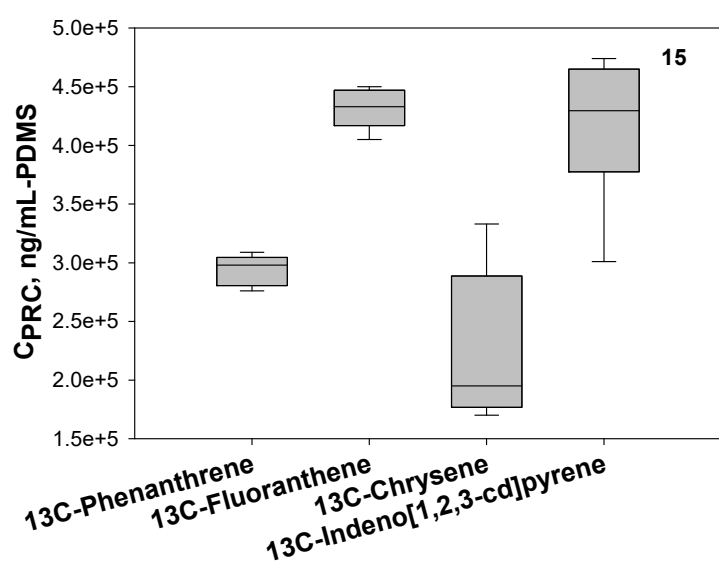
GC/MS – Gas chromatography coping with mass spectrometry

RL – Reporting Limit

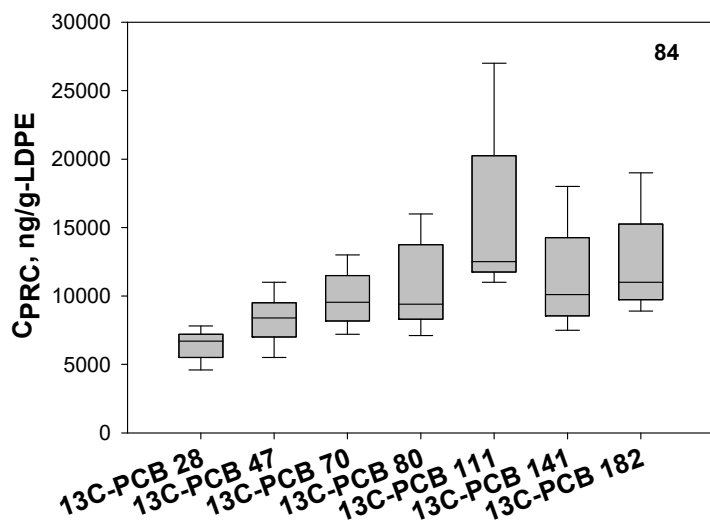
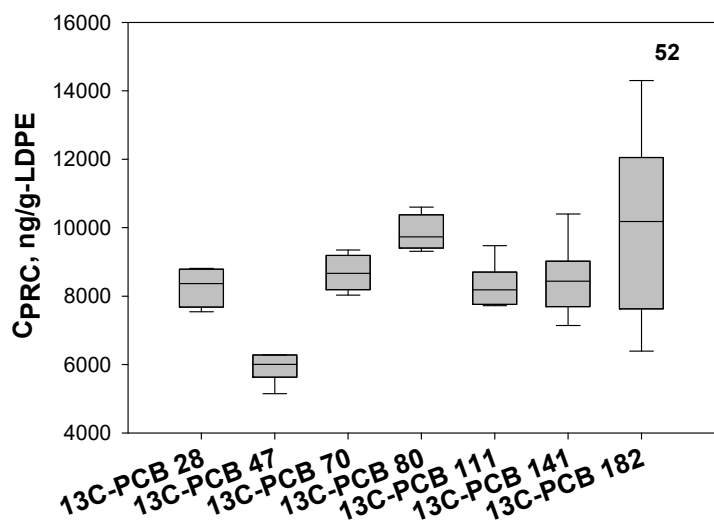
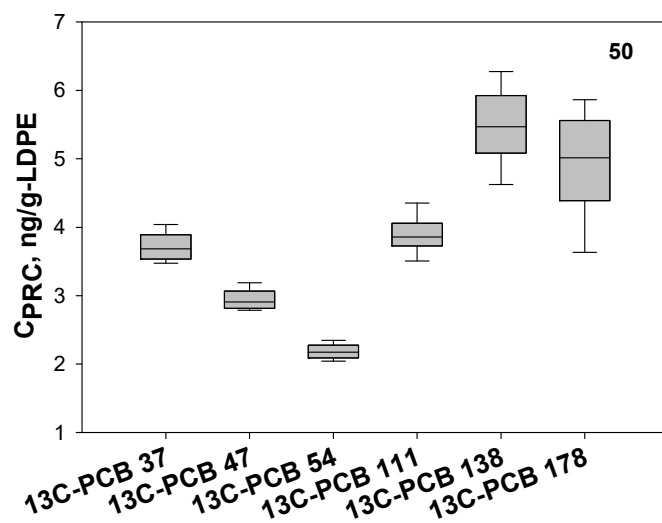
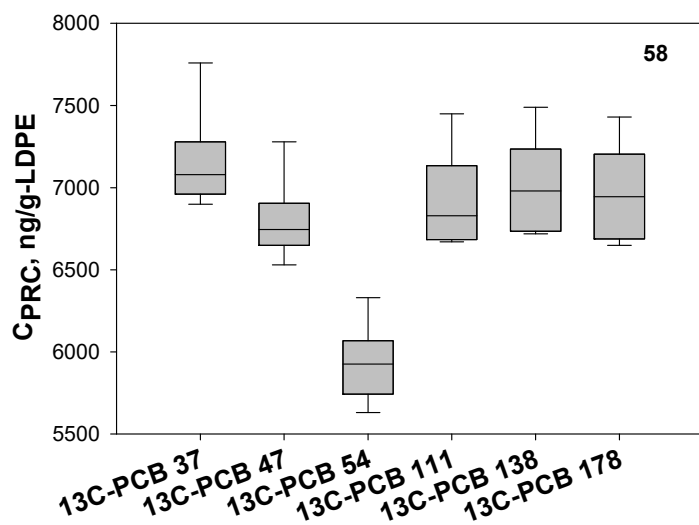
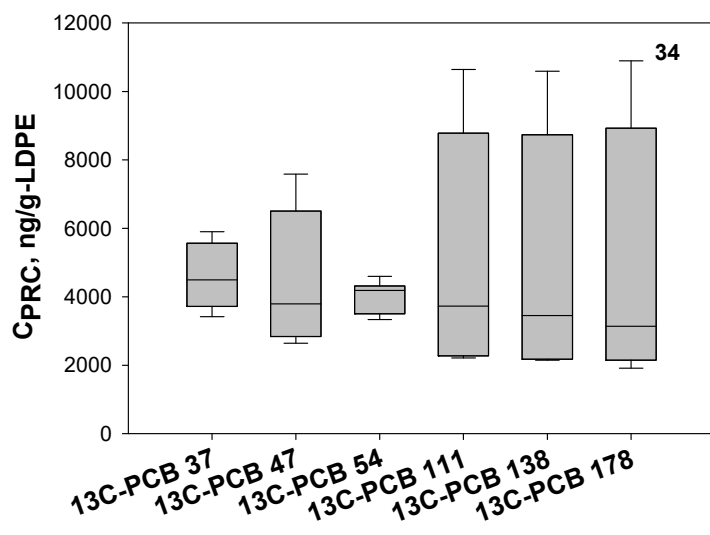
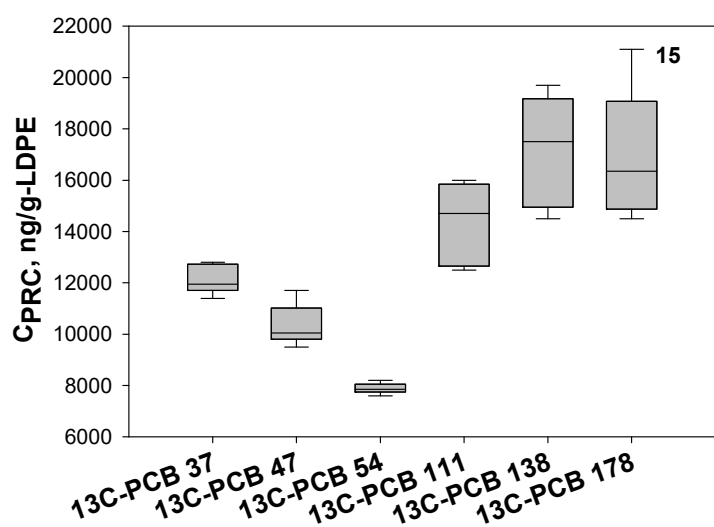
APPENDIX G-4
Task 3 Supporting Figures

Task 3, Final PRC Loaded Ct=0 Results by Polymer and Compound

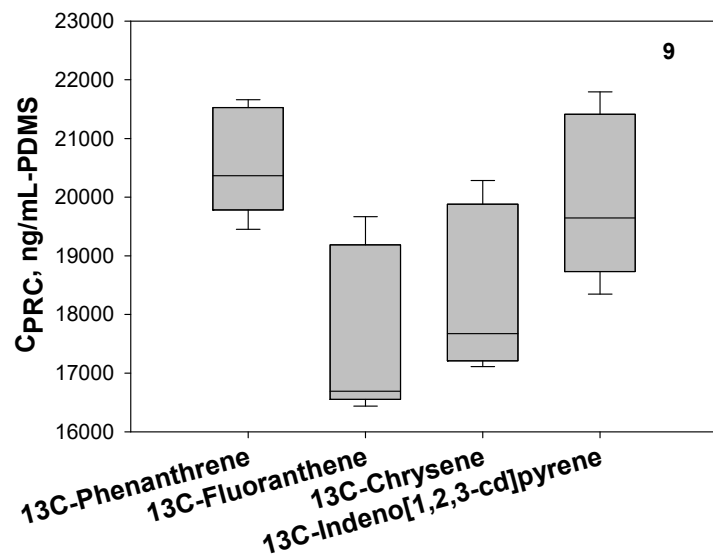
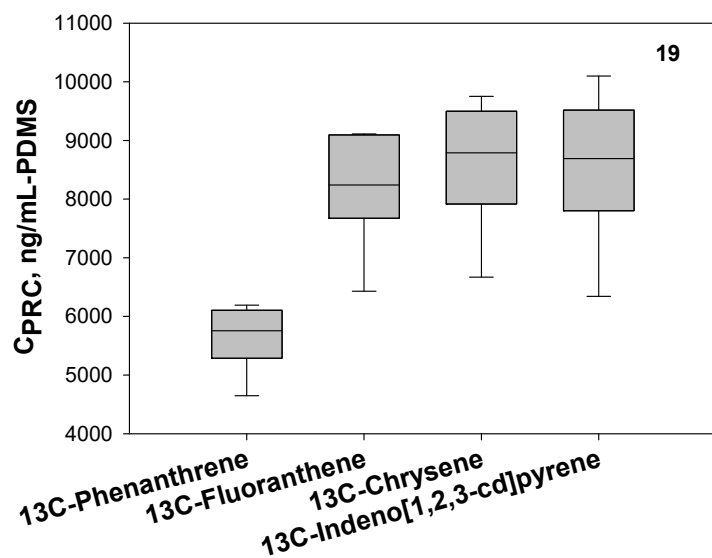
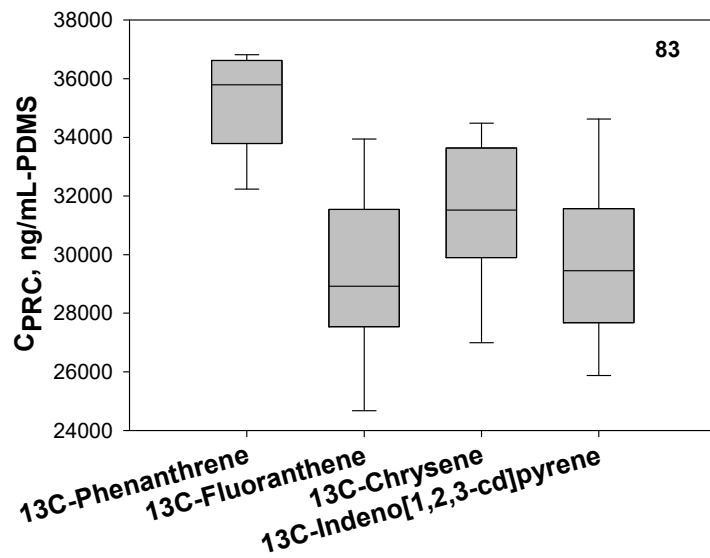
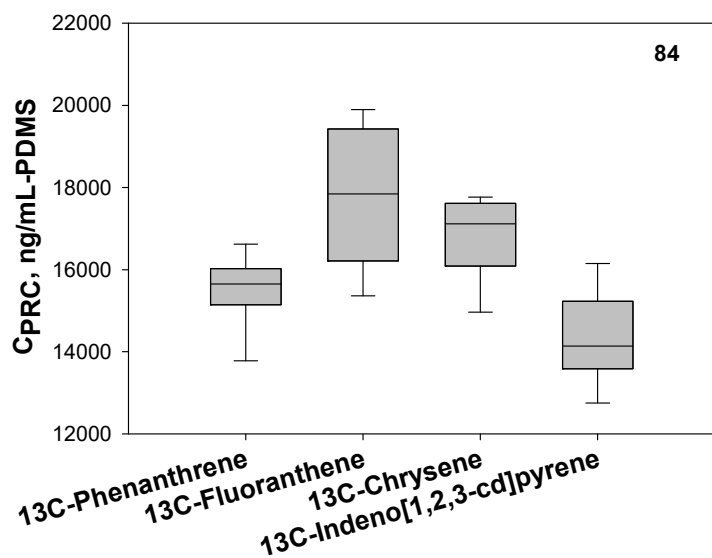
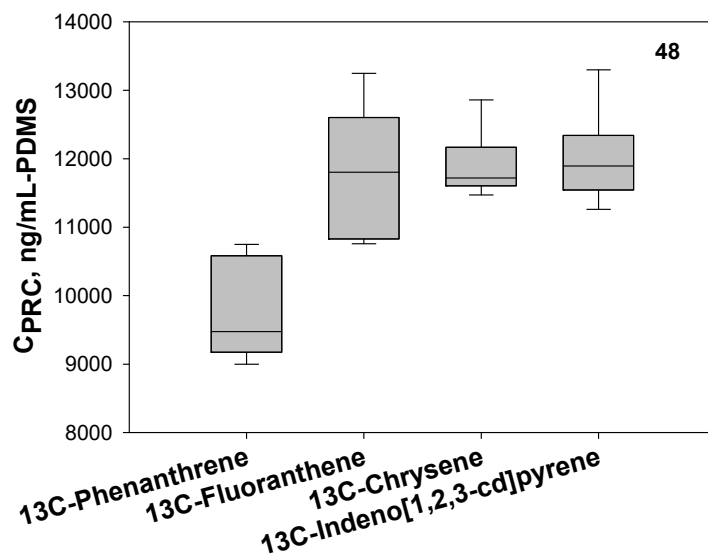
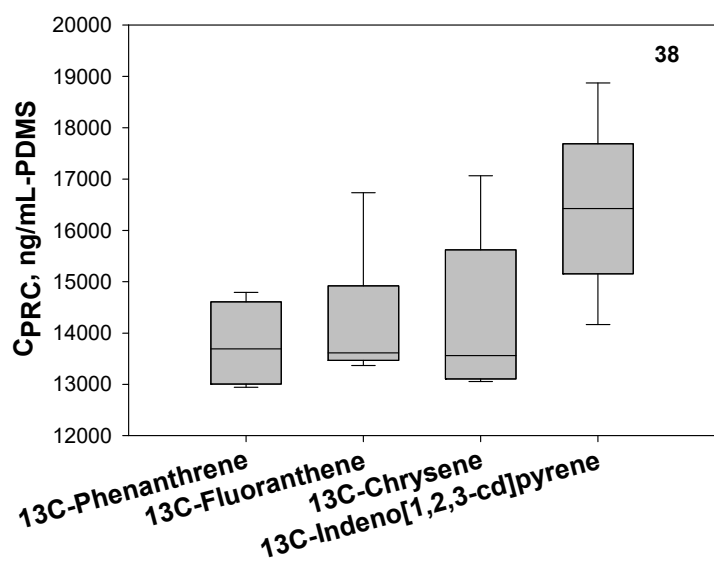
LDPE PAH PRCs, PRC $C_{t=0}$ Final



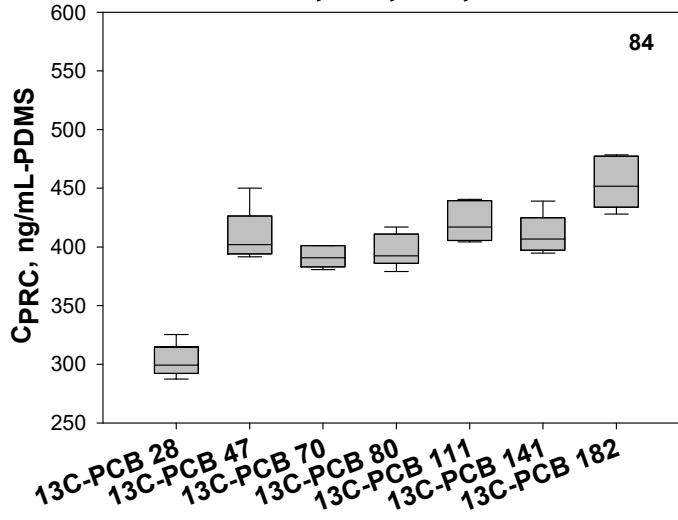
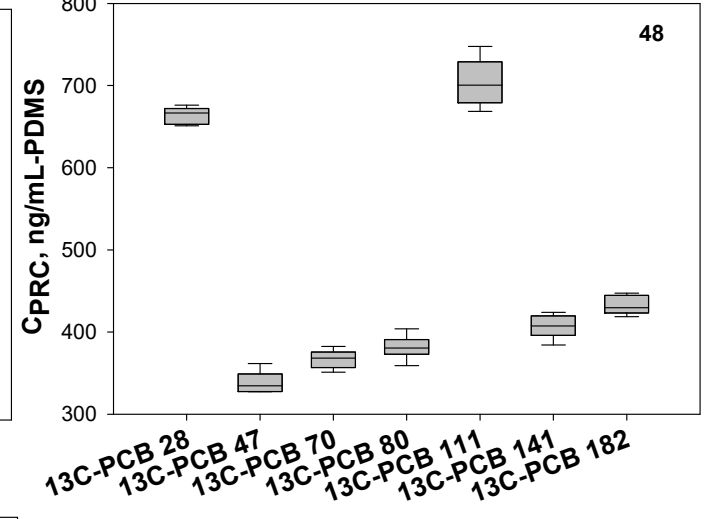
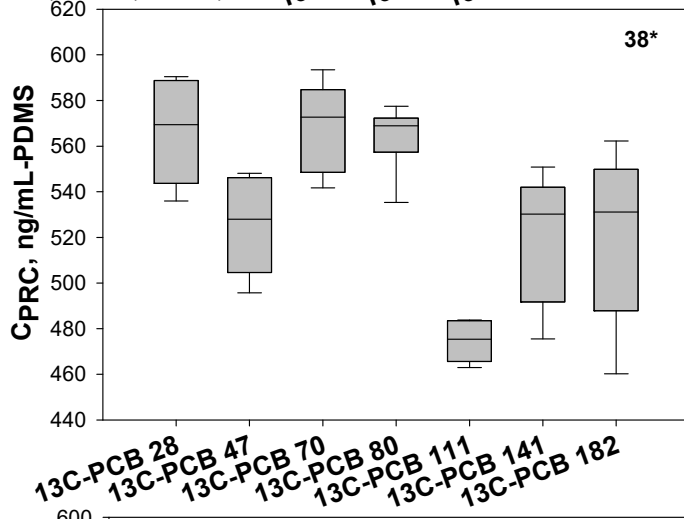
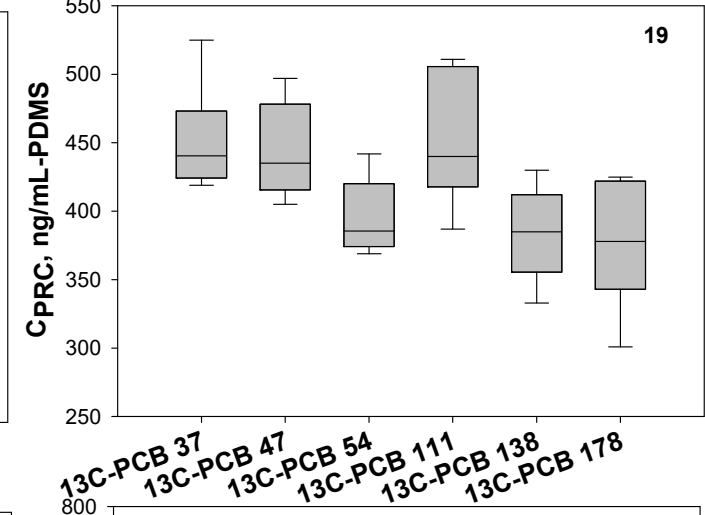
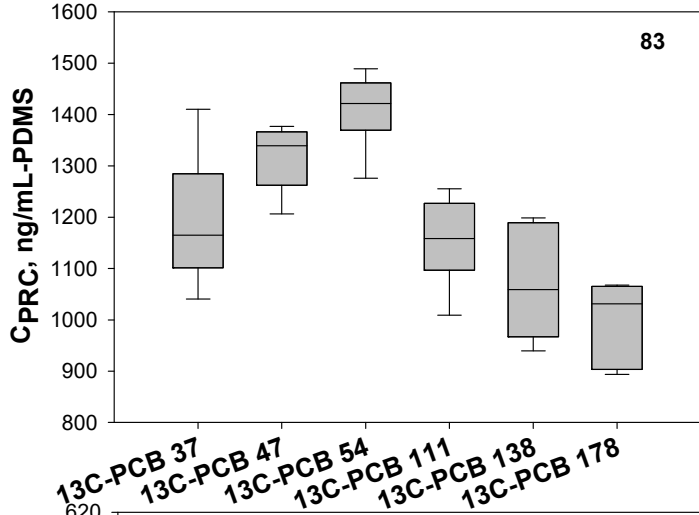
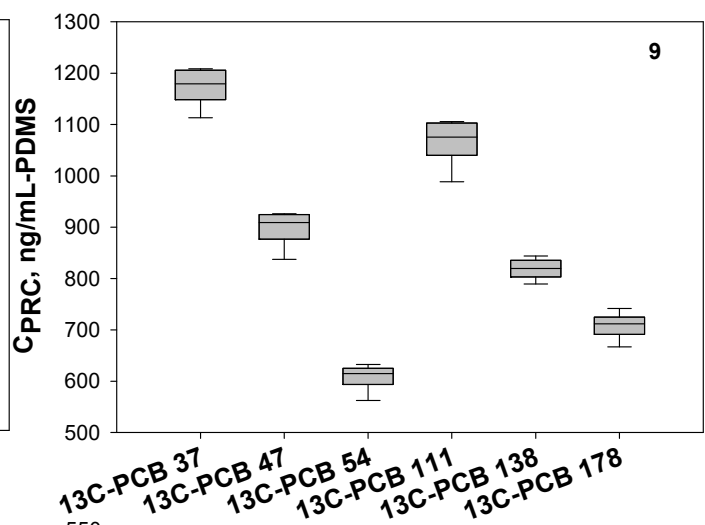
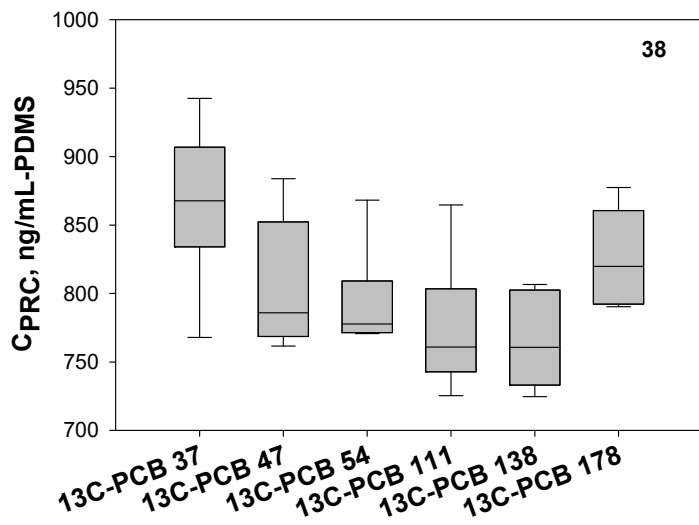
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PDMS PAH PRCs, PRC C_{t=0} Final

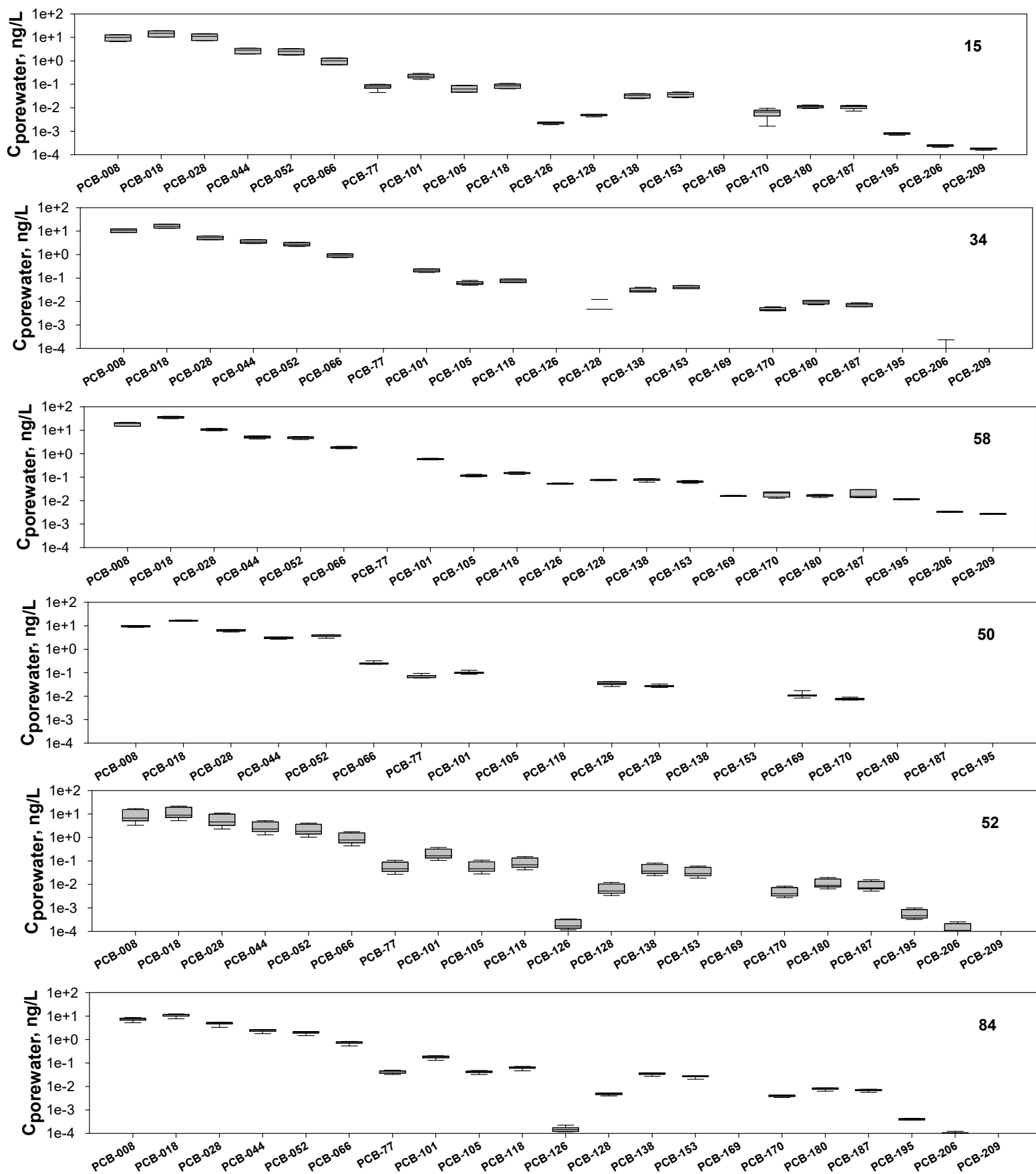


PDMS LR- & HR-PCB PRCs, PRC C_t=0 Final

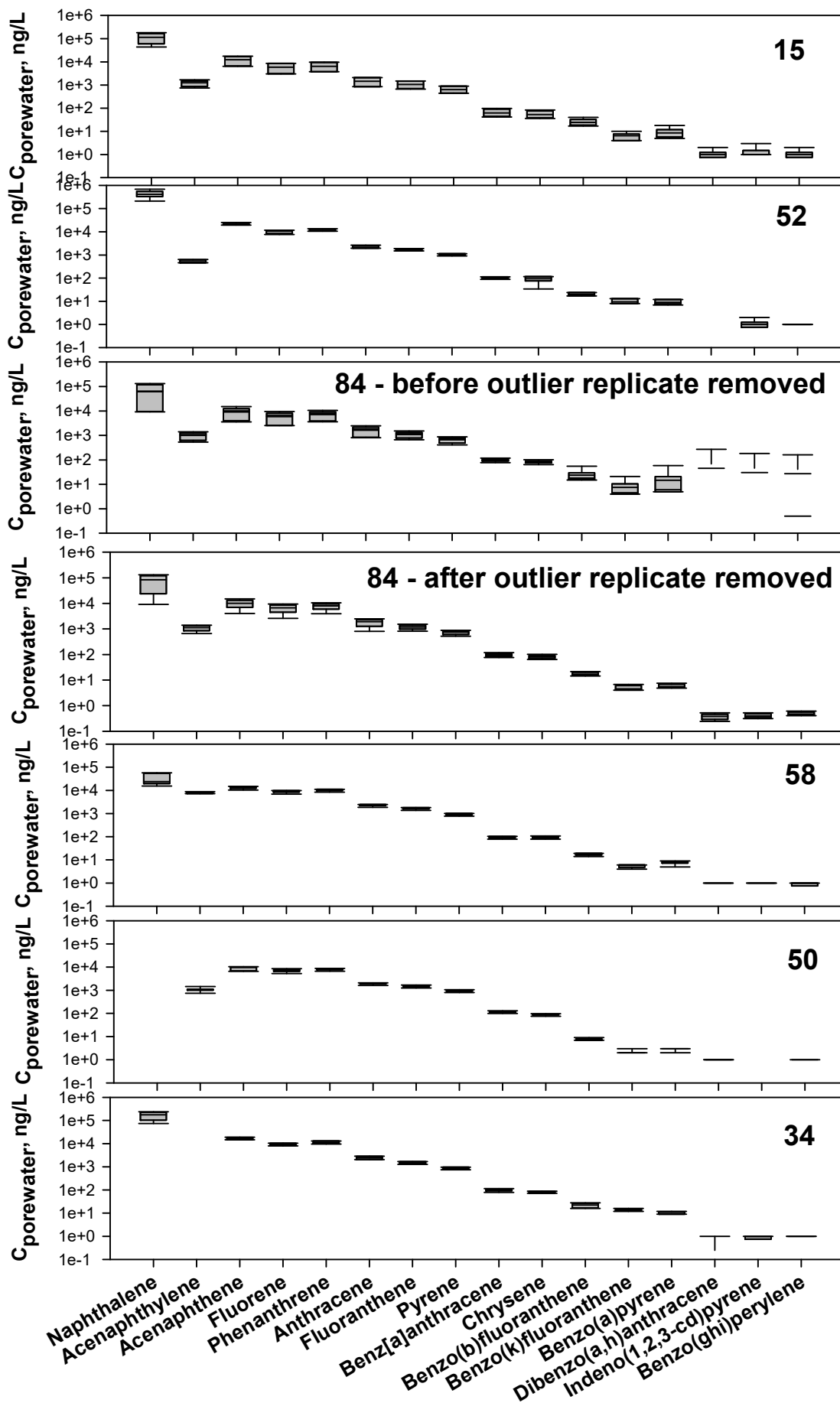


Task 3, Task 3 Porewater Results by Laboratory and Compound Grouping

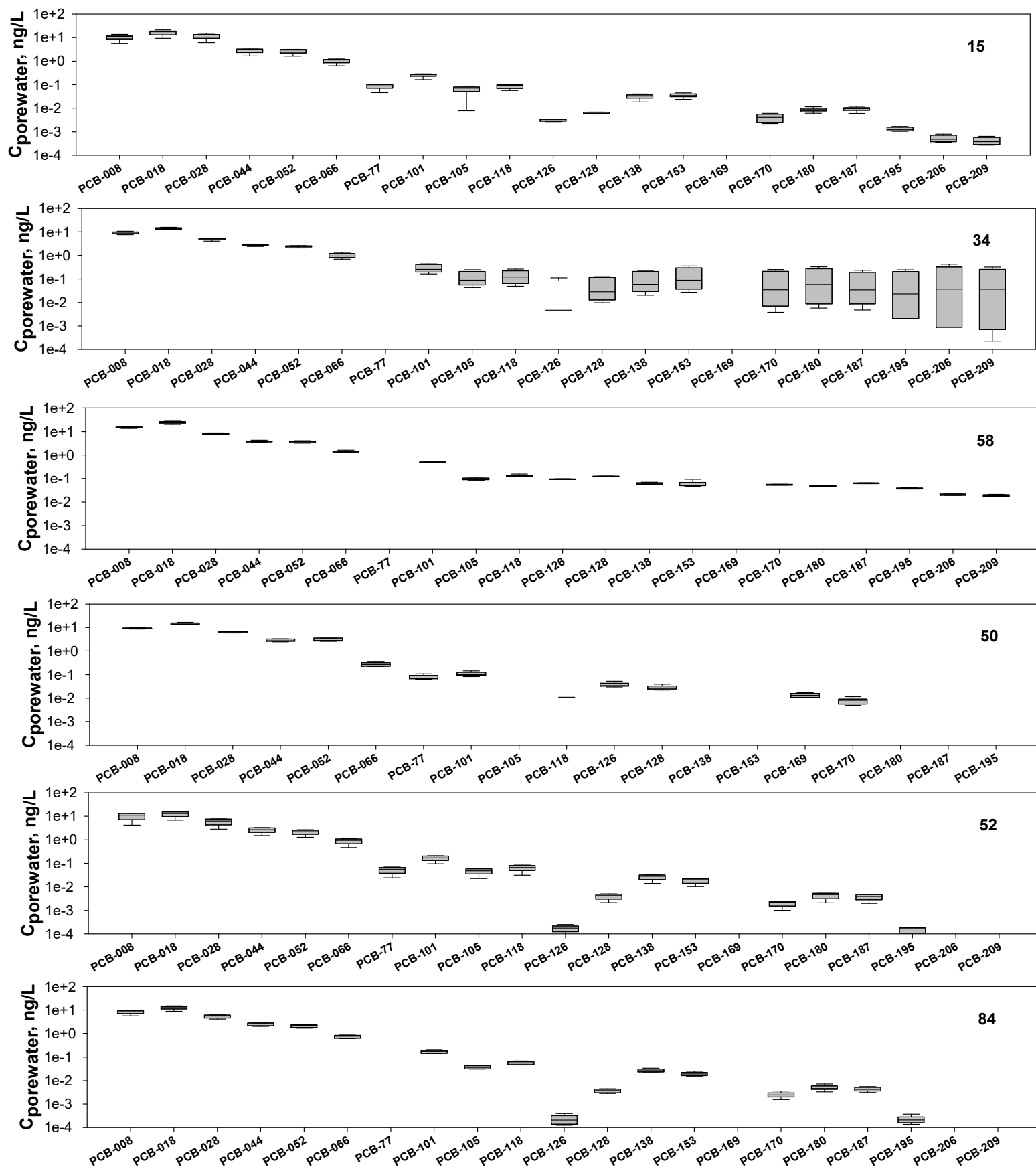
ACTIVE LDPE LR- & HR-PCBs - Task 3 Porewater



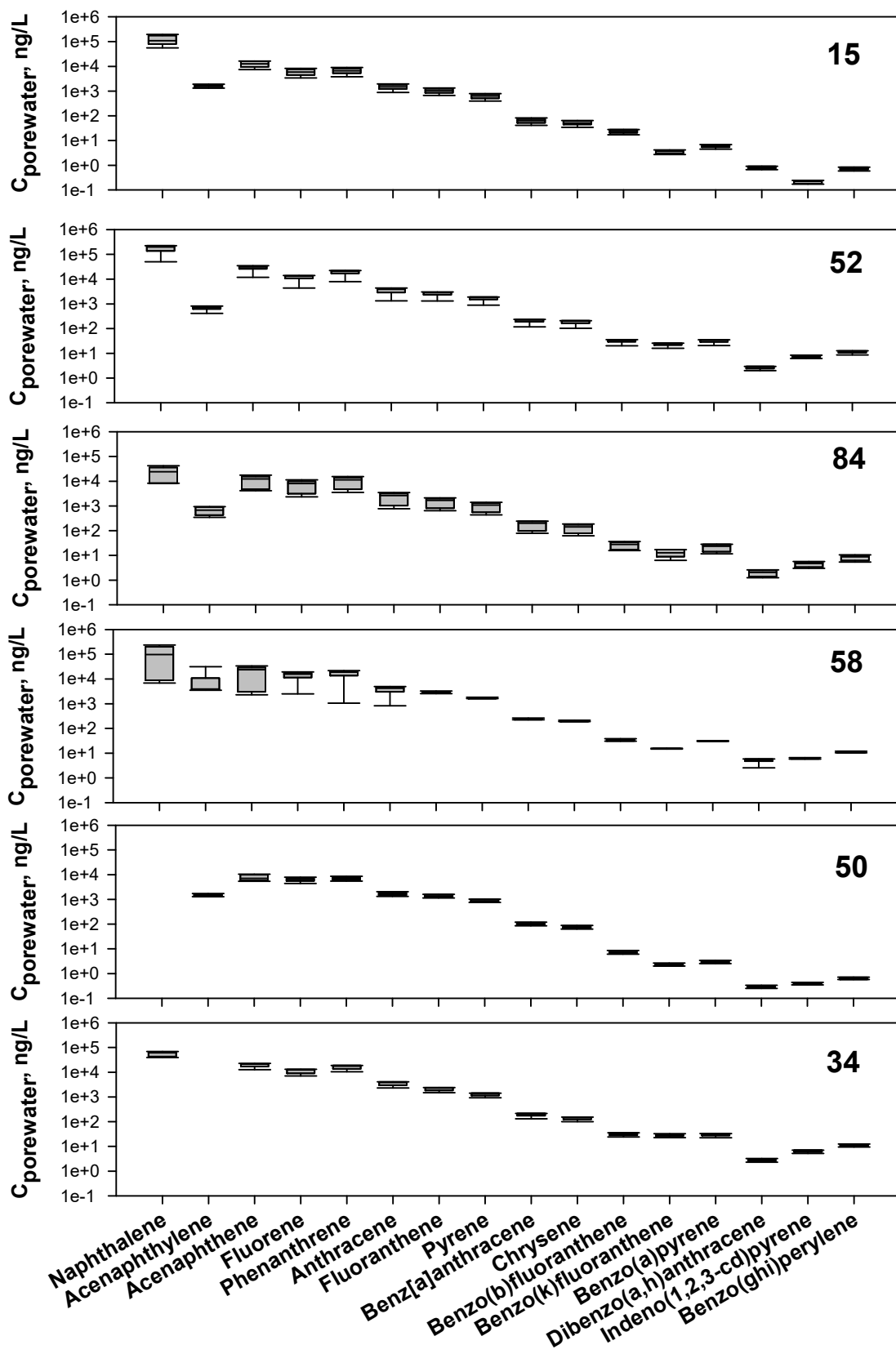
ACTIVE LDPE PAHs - Task 3 Porewater



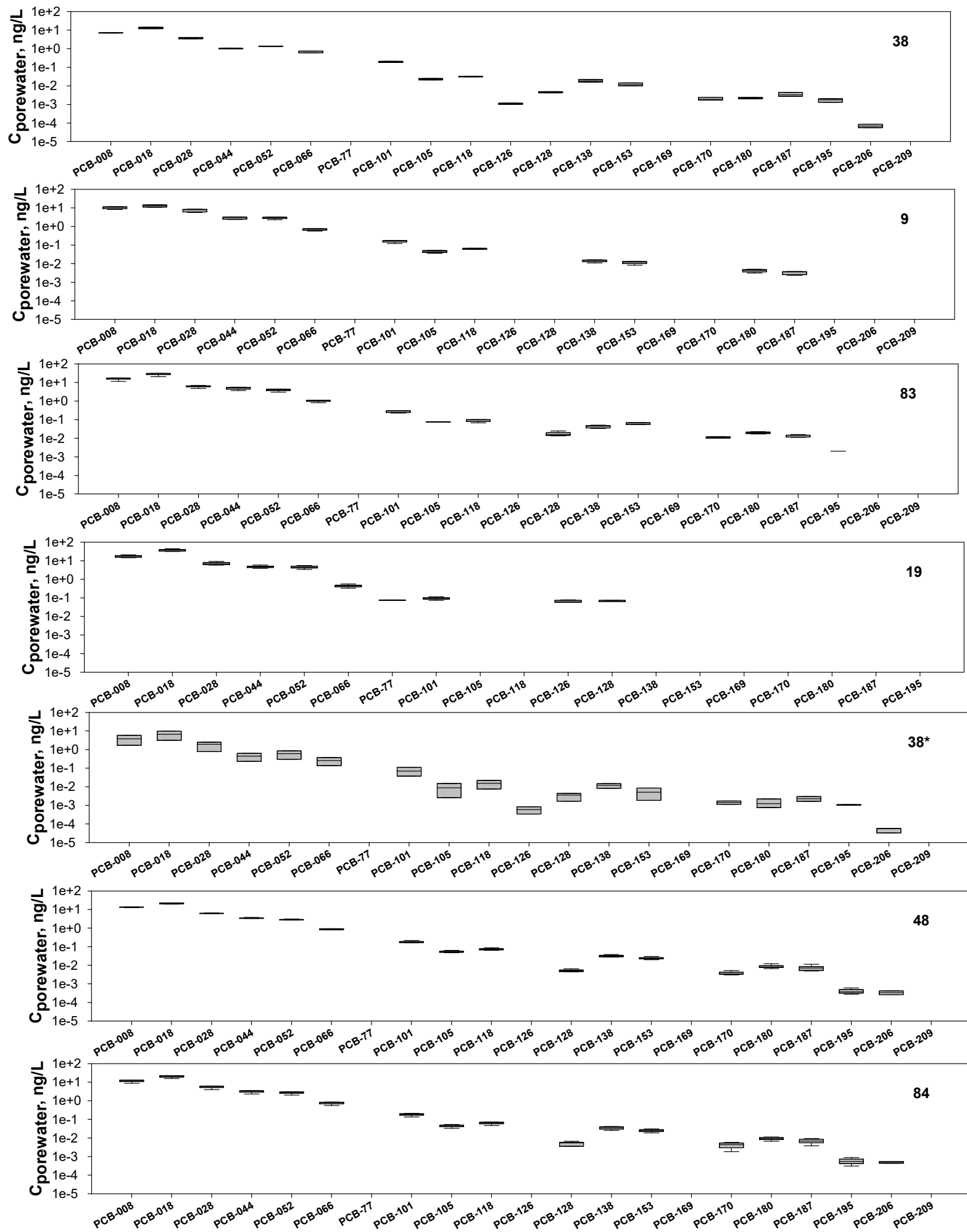
STATIC LDPE LR- & HR-PCBs - Task 3 Porewater



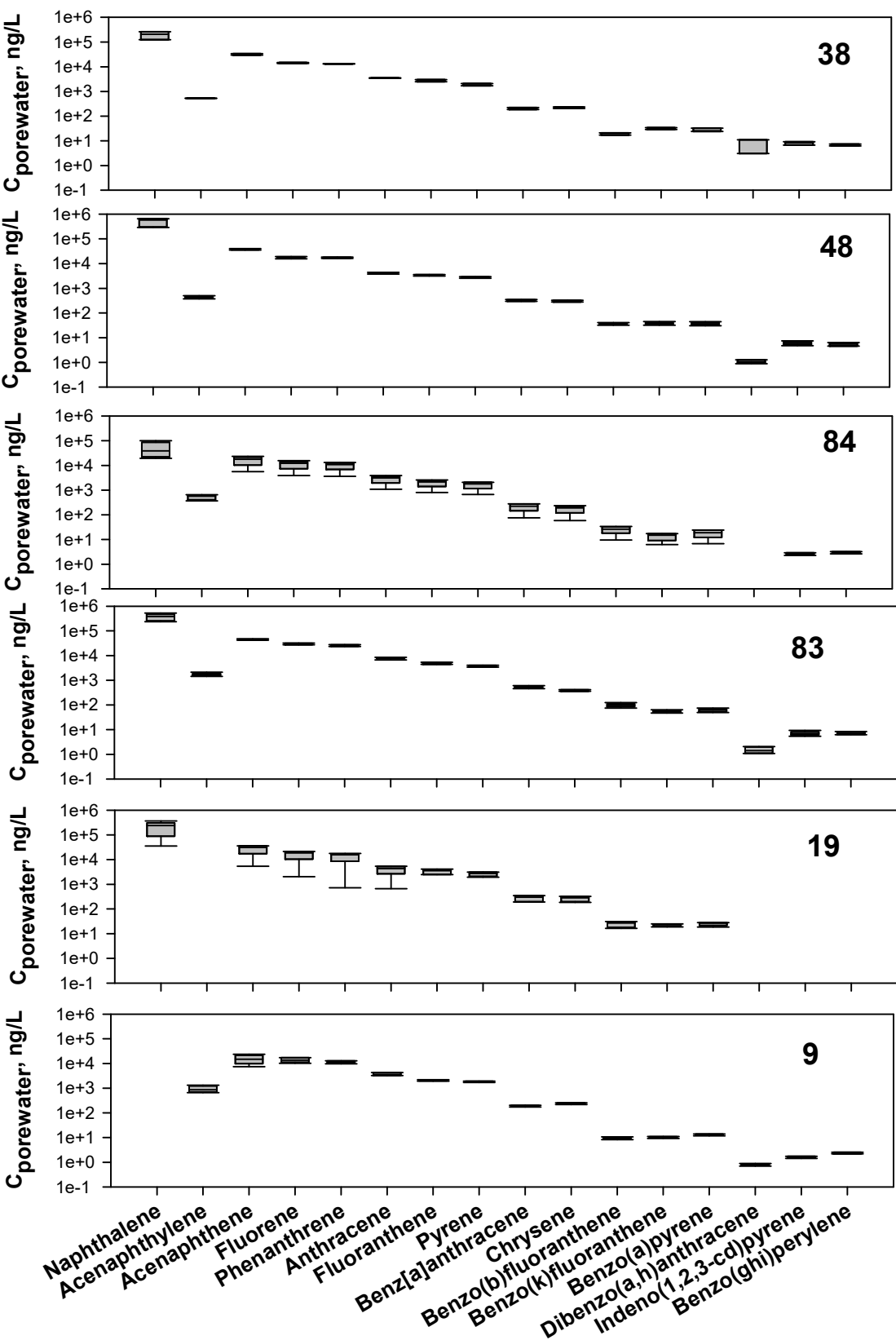
STATIC LDPE PAHs - Task 3 Porewater



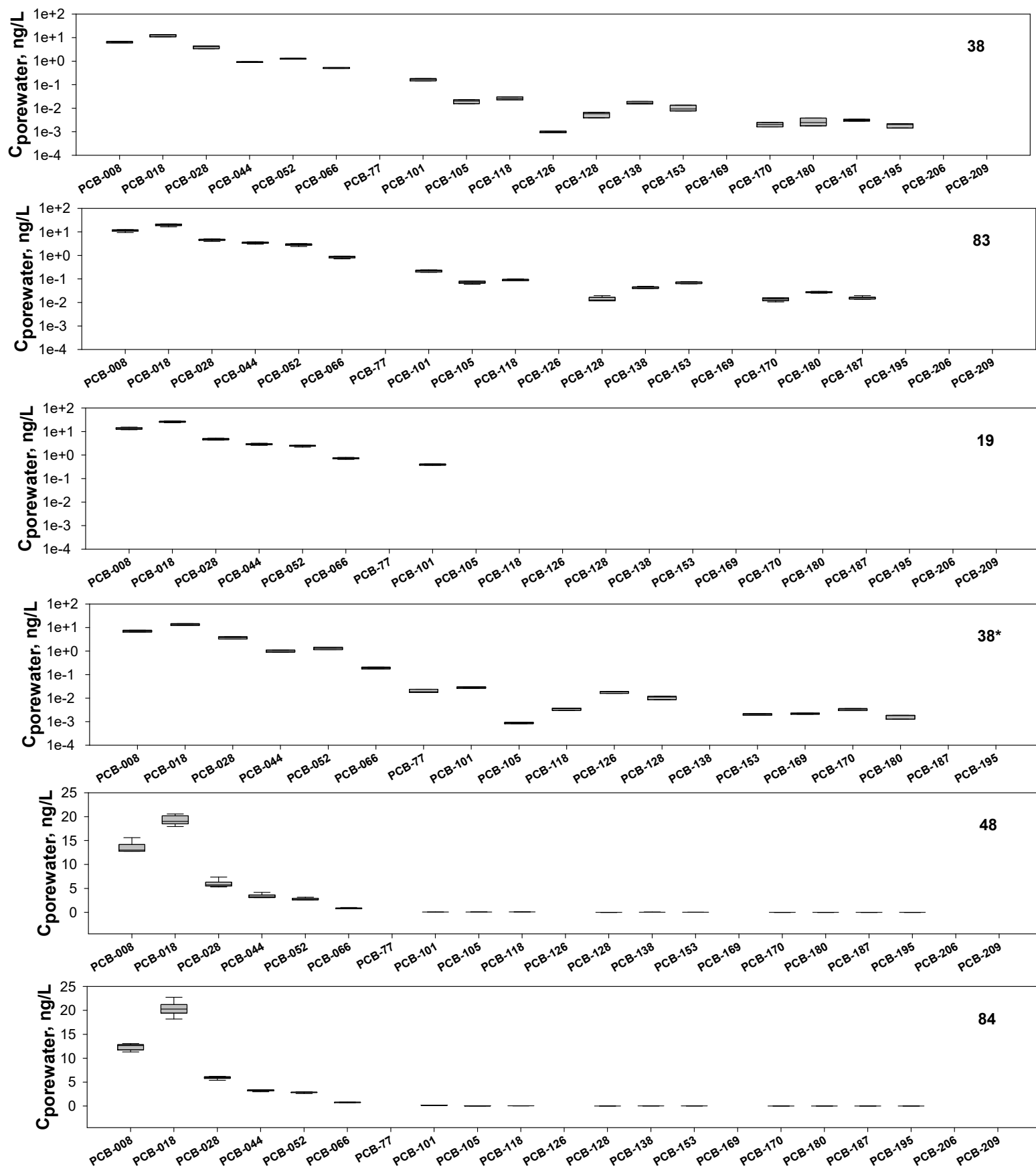
ACTIVE PDMS LR- & HR- PCBs - Task 3 Porewater



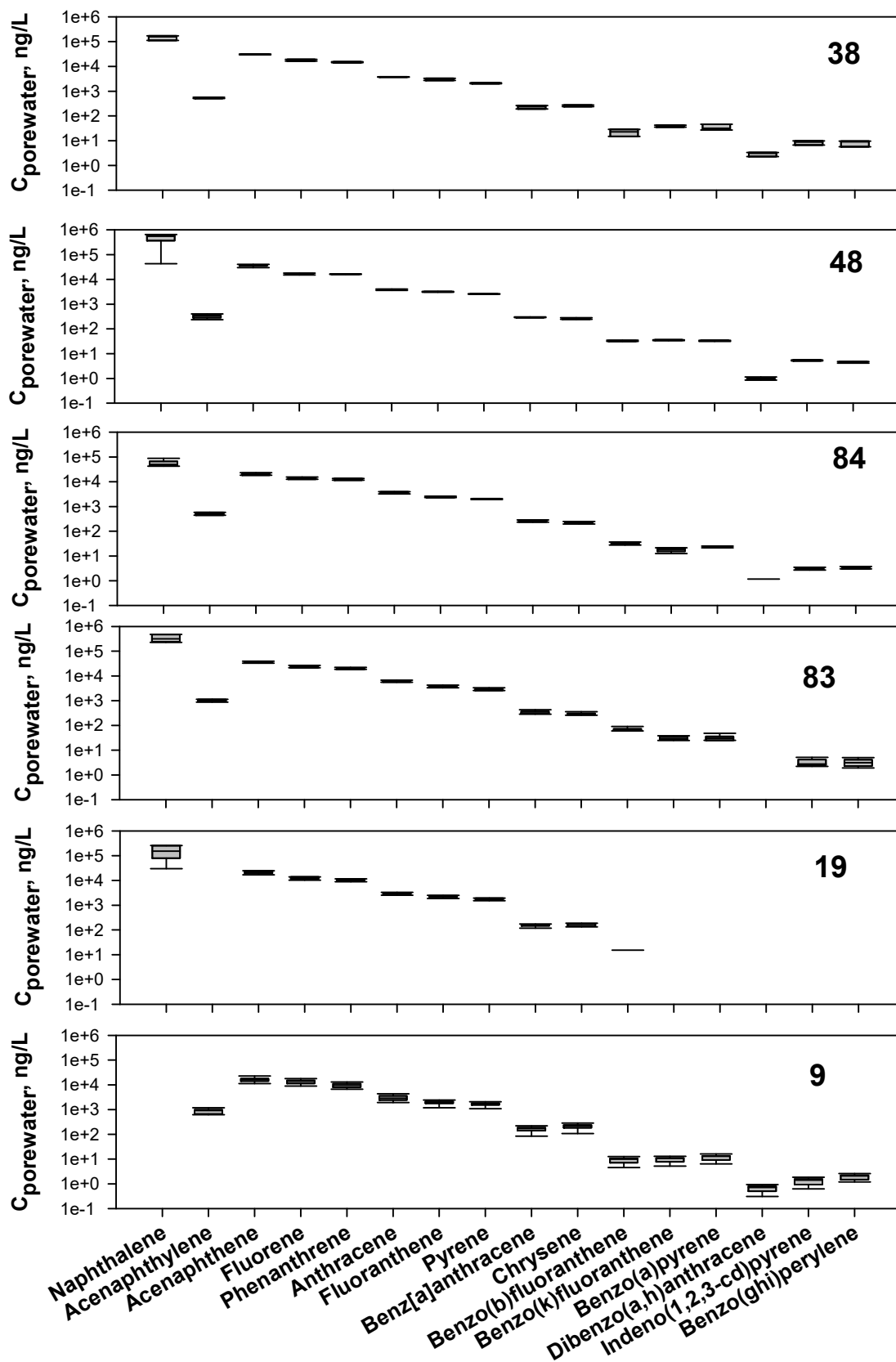
ACTIVE PDMS PAHs - Task 3 Porewater



PDMS Static LR- & HR-PCBs - Task 3 Porewater



STATIC PDMS PAHs - Task 3 Porewater



APPENDIX G-5
Porewater Results by Laboratory

Laboratory ID:	15	15	15	15	15	15	15	15	52	52	52	52	52	52	52	52
Groundwater PAH Low-Res (ng/L)	Rep_1	Rep_2	Rep_3	Rep_4	Rep_5	Rep_6	Average	Std Dev	Rep_1	Rep_2	Rep_3	Rep_4	Rep_5	Rep_6	Average	Std Dev
Naphthalene	43348.608	66271.323	134160.444	183081.502	159331.147	94316.745	113418.295	54568.592	211018.894	393345.317	429535.156	375140.508	510821.369	688742.986	434767.371	158524.276
Acenaphthylene	739.355	1070.180	1674.676	1430.709	1438.472	911.214	1210.768	359.767	601.954	458.672	522.386	460.618	638.817	501.266	530.619	74.567
Acenaphthene	6419.310	6707.186	16757.191	17659.976	16058.408	8643.235	12040.884	5320.765	21401.778	19757.947	20160.301	19518.318	21508.291	25003.015	21224.942	2028.965
Fluorene	3127.622	3033.563	8586.149	8610.824	7915.391	3913.115	5864.444	2773.749	10504.953	7708.340	8104.940	8077.833	8842.310	11653.768	9148.691	1582.371
Phenanthrene	3762.771	3764.648	9676.029	9346.521	8498.362	4416.580	6577.485	2879.669	13186.714	10643.538	11165.365	10689.377	11855.268	13480.910	11836.862	1242.335
Anthracene	853.373	849.318	2089.538	2099.601	1941.620	970.678	1467.355	635.202	2544.981	1981.604	2044.482	1952.303	2252.563	2634.924	2235.143	295.554
Fluoranthene	675.393	705.769	1507.669	1465.333	1308.179	803.882	1077.704	390.746	1878.470	1497.394	1577.461	1522.438	1717.158	1881.351	1679.045	173.201
Pyrene	436.776	445.227	898.524	894.200	789.351	479.568	657.274	226.690	1123.496	916.170	981.290	953.263	1065.052	1137.147	1029.403	92.376
Benz[a]anthracene	41.688	44.794	90.189	97.259	77.763	47.112	66.468	24.887	112.500	89.894	92.049	91.588	106.623	113.042	100.949	10.963
Chrysene	36.422	39.913	73.563	82.923	64.037	40.844	56.284	19.846	33.629	90.257	94.215	95.120	114.769	117.041	90.838	30.207
Benzo(b)fluoranthene	16.755	19.131	30.043	40.078	28.804	20.316	25.854	8.800	20.895	16.613	18.151	17.881	23.698	24.297	20.256	3.223
Benzo(k)fluoranthene	3.713	4.111	6.621	10.147	6.823	5.563	6.163	2.328	10.216	8.499	8.236	9.246	13.397	12.601	10.366	2.167
Benzo[e]pyrene	11.660	13.602	21.500	25.477	21.429	15.191	18.143	5.426	17.347	13.861	13.974	14.433	17.201	18.879	15.949	2.129
Benzo(a)pyrene	5.159	6.497	10.132	17.898	9.890	7.041	9.436	4.582	9.669	7.322	7.586	7.994	12.287	12.214	9.512	2.273
Perylene	3.404	4.028	5.606	8.582	6.170	6.161	5.658	1.834	4.664	3.756	3.716	3.812	4.834	5.198	4.330	0.647
Dibenzo(a,h)anthracene	0.499	0.770	0.815	2.261	0.879	0.758	0.997	0.632	0.216	0.173	0.136	0.184	0.306	0.280	0.216	0.065
Indeno(1,2,3-cd)pyrene	0.632	0.774	0.789	3.388	1.280	1.046	1.318	1.040	1.112	0.838	0.450	0.815	1.489	1.618	1.054	0.442
Benzo(ghi)perylene	0.461	0.643	0.762	1.867	0.817	0.699	0.875	0.501	0.814	0.544	0.537	0.601	0.984	1.011	0.748	0.218

Laboratory ID:	84	84	84	84	84	84	84	84	58	58	58	58	58	58	58	58	50	50	50
Groundwater PAH Low-Res (ng/L)	Rep_1	Rep_2	Rep_3	Rep_4	Rep_5	Rep_6	Average	Std Dev	Rep_1	Rep_2	Rep_3	Rep_4	Rep_5	Rep_6	Average	Std Dev	Rep_1	Rep_2	Rep_3
Naphthalene	131521.023	9757.545	38879.823	110663.158	84047.932	9148.081	64002.927	52384.079	57461.626	26000.440	53611.684	21026.774	15542.620	21669.402	32552.091	18152.154	ND	ND	ND
Acenaphthylene	1257.493	532.710	1042.437	1393.276	1112.268	658.227	999.402	337.799	ND	ND	ND	ND	ND	ND	ND	ND	1096.473	1008.600	1034.284
Acenaphthene	11522.243	3598.609	9937.572	15111.526	10186.127	4092.339	9074.736	4454.774	13482.332	10255.369	14817.540	14665.354	12909.499	13028.649	13193.124	1650.923	9833.833	9770.529	10467.117
Fluorene	7666.228	2547.875	6535.675	9524.156	6711.065	2558.623	5923.937	2818.300	8781.635	6953.792	9609.760	9867.471	9032.660	8930.823	8862.690	1024.860	7643.143	7663.247	7596.934
Phenanthrene	8720.110	3619.701	7984.176	10548.361	7978.483	3947.029	7132.977	2761.037	10160.371	8332.023	10982.705	10997.427	10845.205	10701.110	10336.474	1029.084	7948.833	8187.812	8455.816
Anthracene	2082.698	843.526	1719.439	2463.289	1908.149	802.209	1636.552	676.490	2290.928	1872.669	2463.289	2468.132	2433.053	2359.509	2314.597	226.976	1861.339	1956.509	1990.268
Fluoranthene	1252.423	658.306	1179.197	1509.343	1147.909	816.568	1093.958	308.081	1672.497	1379.163	1799.597	1764.377	1785.520	1750.360	1691.919	159.509	1258.354	1419.012	1531.055
Pyrene	757.830	407.892	745.371	876.645	680.277	516.436	664.075	172.206	911.409	776.676	1000.148	985.916	1009.064	1002.671	947.647	91.175	796.073	891.754	947.190
Benz[a]anthracene	97.406	107.552	92.943	118.094	96.912	76.694	98.267	13.969	94.170	77.767	102.768	97.487	102.162	96.723	95.180	9.146	98.620	110.804	117.200
Chrysene	83.808	83.727	81.135	101.313	79.045	63.926	82.159	11.960	94.597	78.406	103.211	100.433	107.765	102.024	97.739	10.390	75.470	85.123	89.221
Benzo(b)fluoranthene	19.352	55.373	16.988	21.362	16.072	14.526	23.946	15.586	17.027	14.202	18.327	18.821	19.207	18.782	17.728	1.886	6.591	6.881	7.180
Benzo(k)fluoranthene	4.035	20.734	5.472	6.738	4.495	4.116	7.598	6.515	5.673	3.727	5.781	5.846	6.436	5.382	5.474	0.923	1.921	2.118	2.142
Benzo[e]pyrene	10.179	47.866	9.542	11.894	9.813	9.190	16.414	15.437	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzo(a)pyrene	5.543	57.830	6.260	7.616	5.235	4.859	14.557	21.222	8.785	5.312	8.359	7.599	7.522	7.659	7.539	1.200	2.399	2.696	2.718
Perylene	3.635	17.406	3.743	4.202	3.505	3.322	5.969	5.611	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dibenzo(a,h)anthracene	0.245	271.224	0.381	0.523	0.337	0.406	45.519	110.572	ND	ND	ND	ND	ND	ND	ND	ND	0.935	1.096	1.332
Indeno(1,2,3-cd)pyrene	0.315	182.466	0.394	0.523	0.368	0.432	30.750	74.325	0.799	0.505	0.729	0.819	0.893	0.730	0.746	0.133	0.345	0.396	0.439
Benzo(ghi)perylene	0.411	161.110	0.475	0.618	0.439	0.522	27.263	65.571	0.819	0.498	0.707	0.742	0.904	0.633	0.717	0.142	0.449	0.507	0.538

LDPE_Static_PAHs

Laboratory ID:	50	50	50	50	50	50	34	34	34	34	34	34	34	34
Porewater PAH Low-Res (ng/L)	Rep_4	Rep_5	Rep_6	Rep_7	Average	Std Dev	Rep_1	Rep_2	Rep_3	Rep_4	Rep_5	Rep_6	Average	Std Dev
Naphthalene	ND	ND	ND	ND	ND	ND	217508.397	188404.501	238592.136	159966.862	113827.490	73400.657	165283.341	62856.378
Acenaphthylene	1081.292	1457.313	748.182	1007.456	1061.943	209.328	ND	ND	ND	ND	ND	ND	ND	ND
Acenaphthene	6811.838	10024.062	6537.501	9233.496	8954.054	1601.136	15425.409	15317.006	19036.744	18351.352	14626.399	16285.865	16507.129	1787.329
Fluorene	6530.691	8531.660	5237.363	7109.861	7187.557	1052.680	8589.835	8589.365	10512.064	10215.656	8026.033	9670.865	9267.303	1007.073
Phenanthrene	8120.940	8779.615	6667.331	7715.020	7982.195	673.682	10246.323	10473.730	12936.045	13032.219	9564.900	11977.649	11371.811	1477.093
Anthracene	1936.304	2096.367	1611.355	1912.010	1909.165	150.325	2105.181	2262.689	2675.746	2871.234	2041.753	2763.140	2453.291	359.734
Fluoranthene	1567.830	1688.103	1434.077	1589.308	1498.249	140.357	1361.513	1394.176	1659.600	1680.793	1266.569	1558.284	1486.822	170.518
Pyrene	974.002	1054.191	916.759	1001.063	940.147	83.225	794.623	813.889	960.702	967.961	739.844	891.184	861.367	93.376
Benz[a]anthracene	121.338	131.314	111.628	120.667	115.939	10.283	97.825	95.680	104.211	111.206	78.004	113.601	100.088	12.926
Chrysene	91.314	98.247	86.889	92.314	88.368	7.091	78.454	72.791	85.621	84.775	71.862	88.189	80.282	6.951
Benzo(b)fluoranthene	7.887	8.511	6.920	7.023	7.285	0.674	24.334	17.022	26.316	21.114	16.233	27.984	22.167	4.869
Benzo(k)fluoranthene	2.370	2.549	2.036	2.127	2.180	0.212	14.601	12.623	15.344	12.667	12.290	16.032	13.926	1.604
Benzo[e]pyrene	ND	ND	ND	ND	ND	ND	16.770	14.163	16.864	16.469	15.360	17.874	16.250	1.302
Benzo(a)pyrene	3.016	3.270	2.575	2.732	2.772	0.288	11.141	8.898	9.692	9.482	8.659	12.127	10.000	1.357
Perylene	ND	ND	ND	ND	ND	ND	5.487	6.084	6.919	5.551	5.290	6.630	5.993	0.666
Dibenzo(a,h)anthracene	1.059	1.401	1.272	1.215	1.187	0.165	0.252	0.188	0.560	0.143	0.319	0.257	0.286	0.147
Indeno(1,2,3-cd)pyrene	0.453	0.566	0.411	0.419	0.433	0.068	0.767	0.516	0.842	0.447	0.636	1.145	0.726	0.253
Benzo(ghi)perylene	0.617	0.752	0.512	0.542	0.560	0.099	0.949	0.697	0.790	0.589	0.817	1.234	0.846	0.225

Laboratory ID:	15	15	15	15	15	15	15	15	34	34	34	34	34	34	34	34	58	58
Porewater PCB Low-Res (ng/L)	Rep_1	Rep_2	Rep_3	Rep_4	Rep_5	Rep_6	Average	Std Dev	Rep_1	Rep_2	Rep_3	Rep_4	Rep_5	Rep_6	Average	Std Dev	Rep_1	Rep_2
PCB-008	10.832	11.585	9.972	5.761	13.700	12.047	10.650	2.702	8.428	9.638	7.625	8.903	10.740	9.149	9.081	1.062	14.848	15.945
PCB-018	18.375	17.852	14.405	9.291	21.295	17.601	16.470	4.145	13.194	14.763	12.396	13.282	15.835	14.410	13.980	1.253	23.789	27.893
PCB-028	13.032	12.905	10.429	6.260	15.317	13.045	11.831	3.138	4.757	5.118	4.066	4.920	5.231	5.018	4.852	0.418	8.232	8.915
PCB-044	3.219	3.141	2.573	1.691	3.647	3.156	2.904	0.686	2.821	2.894	2.389	2.843	3.050	2.818	2.802	0.220	3.868	4.336
PCB-052	3.111	3.048	2.456	1.673	3.240	2.936	2.744	0.590	2.605	2.410	2.070	2.536	2.531	2.407	2.427	0.191	3.633	4.096
PCB-066	1.145	1.139	0.934	0.645	1.262	1.187	1.052	0.227	1.343	0.849	0.693	1.176	0.877	1.016	0.993	0.237	1.431	1.642
PCB-101	0.270	0.271	0.252	0.164	0.291	0.265	0.252	0.045	0.439	0.220	0.165	0.404	0.208	0.292	0.288	0.112	0.471	0.550
PCB-105	0.069	0.074	0.066	0.008	0.087	0.077	0.064	0.028	0.247	0.061	0.044	0.197	0.062	0.116	0.121	0.083	0.093	0.114
PCB-118	0.099	0.086	0.075	0.057	0.100	0.105	0.087	0.019	0.260	0.070	0.050	0.209	0.075	0.169	0.139	0.086	0.133	0.157
PCB-138	0.030	0.034	0.032	0.018	0.041	0.036	0.032	0.008	0.216	0.033	0.021	0.206	0.032	0.087	0.099	0.090	0.065	0.071
PCB-153	0.036	0.033	0.033	0.024	0.040	0.045	0.035	0.007	0.353	0.041	0.027	0.273	0.042	0.135	0.145	0.138	0.051	0.061
PCB-170	0.006	0.005	0.003	0.002	0.005	0.003	0.004	0.002	0.252	0.009	0.004	0.199	0.008	0.061	0.089	0.109	ND	ND
PCB-180	0.010	0.008	0.009	0.006	0.009	0.012	0.009	0.002	0.327	0.011	0.006	0.254	0.010	0.107	0.119	0.140	ND	ND
PCB-187	0.010	0.010	0.009	0.006	0.010	0.012	0.009	0.002	0.235	0.011	0.005	0.176	0.010	0.058	0.082	0.099	ND	ND

LDPE_Static_PCBs_LR															
Laboratory ID:	58	58	58	58	58	58	50	50	50	50	50	50	50	50	50
Porewater PCB Low-Res (ng/L)	Rep_3	Rep_4	Rep_5	Rep_6	Average	Std Dev	Rep_1	Rep_2	Rep_3	Rep_4	Rep_5	Rep_6	Rep_7	Average	Std Dev
PCB-008	14.540	15.502	13.427	14.495	14.793	0.878	8.493	9.197	8.862	9.457	9.407	9.418	9.793	9.232	0.431
PCB-018	23.150	26.201	20.000	22.049	23.847	2.844	15.552	13.694	13.401	15.236	14.135	14.096	16.548	14.666	1.141
PCB-028	8.048	7.993	7.914	7.802	8.151	0.401	6.606	6.477	5.776	6.411	5.954	6.409	6.772	6.344	0.354
PCB-044	3.811	3.709	3.542	3.714	3.830	0.272	3.255	2.733	2.428	2.946	2.579	2.672	3.274	2.841	0.329
PCB-052	3.464	3.376	3.229	3.405	3.534	0.305	3.558	2.815	2.563	3.141	2.642	2.726	3.558	3.001	0.422
PCB-066	1.412	1.371	1.351	1.428	1.439	0.104	1.376	1.077	0.974	1.149	0.999	1.096	1.333	1.143	0.156
PCB-101	0.502	0.472	0.472	0.484	0.492	0.031	0.356	0.265	0.228	0.275	0.219	0.259	0.320	0.274	0.049
PCB-105	0.102	0.092	0.084	0.095	0.097	0.010	0.109	0.072	0.063	0.073	0.066	0.070	0.092	0.078	0.016
PCB-118	0.133	0.125	0.126	0.134	0.135	0.012	0.145	0.101	0.092	0.106	0.083	0.096	0.126	0.107	0.022
PCB-138	0.060	0.059	0.057	0.059	0.062	0.005	0.052	0.043	0.032	0.034	0.030	0.034	0.042	0.038	0.008
PCB-153	0.053	0.046	ND	0.051	0.052	0.006	0.039	0.029	0.025	0.027	0.022	0.024	0.033	0.028	0.006
PCB-170	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
PCB-180	ND	ND	ND	ND	ND	ND	0.016	0.013	0.011	0.014	0.011	0.010	0.017	0.013	0.003
PCB-187	ND	ND	ND	ND	ND	ND	0.011	0.008	0.006	0.009	0.006	0.005	0.009	0.008	0.002

Laboratory ID:	52	52	52	52	52	52	52	52	84	84	84	84	84	84	84	84
Porewater PCB High Res (ng/L)	Rep_1	Rep_2	Rep_3	Rep_4	Rep_5	Rep_6	Average	Std Dev	Rep_1	Rep_2	Rep_3	Rep_4	Rep_5	Rep_6	Average	Std Dev
PCB-008	4.158	8.152	9.053	13.475	12.917	13.040	10.133	3.692	7.383	9.108	7.889	8.776	9.548	5.663	8.061	1.418
PCB-018	6.805	10.449	10.833	15.761	14.976	14.955	12.297	3.520	11.676	13.720	11.859	13.234	14.789	8.802	12.347	2.093
PCB-028	2.836	5.346	4.862	7.695	7.320	7.550	5.935	1.935	4.611	6.137	5.321	5.712	6.059	4.060	5.317	0.831
PCB-044	1.502	2.257	2.290	3.328	3.108	3.142	2.605	0.707	2.175	2.789	2.459	2.789	2.674	1.974	2.477	0.340
PCB-052	1.285	1.884	1.849	2.693	2.491	2.507	2.118	0.537	1.837	2.378	2.152	2.375	2.314	1.671	2.121	0.301
PCB-066	0.465	0.836	0.738	1.118	1.055	1.069	0.880	0.252	0.632	0.816	0.720	0.855	0.806	0.602	0.738	0.104
PCB-101	0.095	0.148	0.144	0.212	0.200	0.189	0.165	0.044	0.141	0.177	0.168	0.203	0.184	0.146	0.170	0.023
PCB-105	0.022	0.039	0.040	0.061	0.057	0.055	0.046	0.015	0.031	0.035	0.038	0.045	0.042	0.031	0.037	0.006
PCB-118	0.031	0.055	0.055	0.084	0.079	0.075	0.063	0.020	0.046	0.058	0.053	0.069	0.061	0.049	0.056	0.008
PCB-138	0.014	0.025	0.022	0.032	0.031	0.030	0.026	0.007	0.022	0.027	0.026	0.034	0.030	0.024	0.027	0.004
PCB-153	0.010	0.019	0.015	0.023	0.022	0.021	0.018	0.005	0.015	0.019	0.019	0.025	0.021	0.017	0.019	0.003
PCB-170	0.001	0.002	0.002	0.002	0.002	0.002	0.002	0.001	0.002	0.003	0.002	0.004	0.003	0.002	0.002	0.001
PCB-180	0.002	0.005	0.003	0.005	0.005	0.005	0.004	0.001	0.003	0.005	0.005	0.007	0.006	0.005	0.005	0.001
PCB-187	0.002	0.004	0.003	0.005	0.005	0.004	0.004	0.001	0.003	0.004	0.004	0.006	0.005	0.004	0.004	0.001

LDPE_Shaking_PAHs															
Laboratory ID:	15	15	15	15	15	15	15	15	52	52	52	52	52	52	52
Porewater PAH Low-Res (ng/L)	Rep_1	Rep_2	Rep_3	Rep_4	Rep_5	Rep_6	Average	Std Dev	Rep_1	Rep_2	Rep_3	Rep_4	Rep_5	Rep_6	Average
Naphthalene	87040.086	56131.440	195790.958	131307.500	170002.756	87501.842	121295.764	54007.425	50581.670	223760.589	190196.501	225527.120	166642.754	206684.123	177232.126
Acenaphthylene	1635.973	1318.753	1897.509	1761.313	1623.263	1408.620	1607.572	215.291	412.365	705.913	737.365	800.268	695.429	807.257	693.100
Acenaphthene	11762.638	7501.269	15946.846	13411.309	16469.794	10108.460	12533.386	3455.844	11952.397	31577.939	30692.576	32168.181	30987.697	34824.269	28700.510
Fluorene	5510.619	3395.379	7549.372	6264.259	8272.213	4854.897	5974.457	1786.854	4318.683	13490.541	12827.773	13020.189	13255.365	14067.791	11830.057
Phenanthrene	6185.137	3832.207	8004.614	6999.952	9060.892	5717.246	6633.341	1832.717	7925.374	20702.646	20246.641	21341.054	21249.853	22344.266	18968.305
Anthracene	1364.277	879.244	1769.088	1626.715	1954.178	1332.838	1487.723	380.931	1323.859	3929.099	3419.378	3964.496	3808.748	4325.549	3461.855
Fluoranthene	1002.423	667.407	1225.851	1077.920	1334.167	902.255	1035.004	237.307	1312.370	2791.899	2685.202	2898.595	2898.595	3005.292	2598.659
Pyrene	610.437	396.967	734.483	650.383	788.760	550.168	621.866	139.428	885.027	1829.314	1726.254	1880.844	1867.962	1893.727	1680.522
Benz[a]anthracene	60.780	41.007	73.597	66.721	81.520	56.159	63.297	14.171	117.777	222.921	212.147	231.466	231.095	234.067	208.245
Chrysene	49.461	33.972	59.585	50.860	65.327	48.994	51.367	10.719	102.907	197.470	186.654	209.213	209.831	208.286	185.727
Benzo(b)fluoranthene	23.611	17.093	27.328	23.284	27.740	21.615	23.445	3.931	20.206	33.271	32.313	34.751	33.097	35.884	31.587
Benzo(k)fluoranthene	3.528	2.744	3.888	3.798	4.170	3.134	3.544	0.526	15.912	24.698	23.591	25.736	25.805	25.390	23.522
Benzo[e]pyrene	17.300	13.468	18.176	18.305	19.030	17.324	17.267	1.972	17.602	26.996	25.992	29.184	29.549	29.184	26.418
Benzo(a)pyrene	5.894	4.507	6.398	5.935	6.818	5.709	5.877	0.783	20.646	33.252	32.093	35.352	35.063	35.352	31.960
Perylene	5.810	3.711	5.187	5.545	5.667	5.470	5.232	0.774	6.781	10.436	9.486	10.063	10.652	10.856	9.712
Dibenzo(a,h)anthracene	0.806	0.662	0.891	0.808	0.915	0.772	0.809	0.090	2.000	2.782	2.586	2.882	2.937	2.912	2.683
Indeno(1,2,3-cd)pyrene	0.221	0.180	0.234	0.223	0.245	0.172	0.212	0.030	6.198	7.526	7.811	8.412	7.748	7.716	7.568
Benzo(ghi)perylene	0.699	0.586	0.838	0.791	0.818	0.712	0.741	0.094	8.656	11.895	11.365	12.366	12.483	12.601	11.561

LDPE_Shaking_PAHs																
Laboratory ID:	52	84	84	84	84	84	84	84	84	58	58	58	58	58	58	58
Porewater PAH Low-Res (ng/L)	Std Dev	Rep_1	Rep_2	Rep_3	Rep_4	Rep_5	Rep_6	Average	Std Dev	Rep_1	Rep_2	Rep_3	Rep_4	Rep_5	Rep_6	Average
Naphthalene	65856.317	34152.932	23553.746	42396.743	8243.811	25320.277	8243.811	23651.887	13705.855	ND	191374.188	237303.993	89504.236	106580.702	9539.267	126860.477
Acenaphthylene	145.229	943.547	559.139	803.763	349.462	908.601	454.301	669.802	249.484	ND	31241.906	ND	ND	ND	ND	31241.906
Acenaphthene	8336.709	17707.255	10329.232	15051.167	4131.693	14460.925	5017.056	11116.221	5598.489	2272.431	ND	33348.664	25882.105	27652.830	21661.876	22163.581
Fluorene	3704.828	11331.199	6627.682	9620.829	2351.758	9620.829	3420.739	7162.173	3657.728	ND	15436.086	19391.316	15991.956	16996.799	14324.346	16428.101
Phenanthrene	5455.656	15504.184	9120.108	13680.163	3556.842	13680.163	5107.261	10108.120	4970.724	ND	18057.815	21797.059	19152.228	19881.836	17966.614	19371.110
Anthracene	1087.207	3468.934	2194.632	3114.961	778.740	3114.961	1132.713	2300.824	1129.834	ND	3723.795	4955.620	4375.105	4495.456	4084.847	4326.965
Fluoranthene	639.475	2133.935	1387.058	1956.107	640.181	1956.107	871.357	1490.791	626.845	2578.505	2845.247	3236.469	2880.813	2969.727	2791.899	2883.776
Pyrene	394.401	1417.075	914.657	1249.602	438.005	1288.250	592.595	983.364	401.692	1700.489	1623.194	1816.432	1648.959	1687.607	1610.312	1681.166
Benz[a]anthracene	45.041	245.213	167.191	230.352	78.022	234.067	104.030	176.479	72.072	227.751	225.150	264.533	234.439	244.470	229.980	237.721
Chrysene	41.568	185.418	120.522	163.786	61.806	169.966	83.438	130.823	50.426	199.633	188.508	215.394	192.834	199.015	189.435	197.470
Benzo(b)fluoranthene	5.721	33.097	23.516	32.226	15.677	36.580	17.419	26.419	8.791	34.664	30.397	38.148	31.529	33.793	31.442	33.329
Benzo(k)fluoranthene	3.819	17.296	11.761	17.296	6.365	13.837	9.686	12.707	4.327	14.598	15.359	15.013	14.805	15.705	14.874	15.059
Benzo[e]pyrene	4.546	21.888	15.504	20.064	9.120	21.888	10.944	16.568	5.605	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Benzo(a)pyrene	5.698	27.529	20.284	26.804	11.591	28.253	15.213	21.612	7.060	32.093	29.919	32.382	30.354	30.499	31.006	31.042
Perylene	1.515	10.219	7.574	9.979	4.809	10.460	5.891	8.155	2.431	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Dibenzo(a,h)anthracene	0.358	2.606	1.804	2.305	1.253	2.456	1.453	1.980	0.559	5.814	ND	ND	ND	ND	ND	5.814
Indeno(1,2,3-cd)pyrene	0.735	5.376	4.111	5.376	3.004	5.692	3.479	4.506	1.130	5.977	5.755	6.514	6.451	6.230	5.977	6.151
Benzo(ghi)perylene	1.495	10.010	7.655	10.010	5.417	10.599	6.477	8.362	2.152	11.954	10.305	12.012	10.894	10.599	10.599	11.060

LDPE_Shaking_PAHs																	
Laboratory ID:	58	50	50	50	50	50	50	50	50	34	34	34	34	34	34	34	34
Porewater PAH Low-Res (ng/L)	Std Dev	Rep_1	Rep_2	Rep_3	Rep_4	Rep_5	Rep_6	Average	Std Dev	Rep_1	Rep_2	Rep_3	Rep_4	Rep_5	Rep_6	Average	Std Dev
Naphthalene	89345.976	ND	ND	ND	ND	ND	ND	ND	ND	66182.087	65248.246	68234.007	57645.050	39261.575	44192.233	56793.867	12307.713
Acenaphthylene	NA	1293.999	1567.377	1412.948	1731.410	1514.319	1306.389	1471.074	167.794	ND	ND	ND	ND	ND	ND	ND	ND
Acenaphthene	11884.601	5375.663	6771.692	7295.037	10394.707	9895.370	5937.618	7611.681	2076.949	22530.549	18429.924	21092.475	21487.568	12669.075	21024.276	19538.978	3627.438
Fluorene	1917.300	4390.348	6205.034	5995.363	7947.734	6696.397	6195.611	6238.414	1149.686	13257.392	9760.849	12716.667	12220.989	7031.189	12550.962	11256.341	2401.323
Phenanthrene	1572.525	5458.867	7635.630	6498.385	8688.208	6806.388	7135.093	7037.095	1088.876	18723.425	14627.220	18016.454	17320.563	10428.061	18564.775	16280.083	3233.124
Anthracene	460.529	1315.119	1828.837	1563.973	2040.736	1637.091	1720.205	1684.327	245.857	4076.953	3169.626	3886.118	3882.855	2334.586	4043.818	3565.659	687.858
Fluoranthene	216.751	1136.176	1506.536	1274.990	1604.552	1292.992	1409.208	1370.742	170.189	2364.337	1965.055	2325.767	2214.389	1487.448	2378.889	2122.647	347.005
Pyrene	75.007	752.201	973.649	831.746	1026.324	827.083	892.926	883.988	101.699	1406.188	1204.036	1404.413	1342.263	924.583	1420.853	1283.722	193.456
Benz[a]anthracene	14.782	85.803	112.353	95.121	119.472	94.317	103.520	101.764	12.515	211.668	189.892	215.160	207.320	130.632	212.995	194.611	32.644
Chrysene	9.947	62.729	83.260	71.283	88.244	70.969	77.291	75.629	9.243	152.950	133.216	144.219	148.141	100.117	151.748	138.399	20.055
Benzo(b)fluoranthene	2.850	6.083	7.798	7.038	8.577	6.841	7.296	7.272	0.852	29.493	29.937	35.824	34.791	24.146	33.014	31.201	4.286
Benzo(k)fluoranthene	0.405	1.999	2.456	2.096	2.658	2.026	2.232	2.244	0.263	30.112	28.229	28.063	29.523	22.647	32.806	28.563	3.367
Benzo[e]pyrene	0.000	ND	ND	ND	ND	ND	ND	ND	ND	26.819	24.767	26.079	26.074	18.420	26.631	24.798	3.206
Benzo(a)pyrene	0.993	2.549	3.224	2.848	3.390	2.682	2.958	2.942	0.320	30.011	29.018	31.319	31.304	22.418	32.942	29.502	3.716
Perylene	0.000	ND	ND	ND	ND	ND	ND	ND	ND	10.096	11.372	12.351	13.049	8.201	12.905	11.329	1.886
Dibenzo(a,h)anthracene	NA	0.251	0.303	0.293	0.340	0.278	0.303	0.295	0.030	3.046	2.599	3.265	2.590	2.287	2.863	2.775	0.353
Indeno(1,2,3-cd)pyrene	0.298	0.350	0.431	0.379	0.441	0.371	0.386	0.393	0.035	6.982	6.128	7.086	6.428	5.223	7.047	6.482	0.728
Benzo(ghi)perylene	0.739	0.572	0.704	0.610	0.708	0.585	0.613	0.632	0.059	10.819	11.618	12.342	11.575	9.509	12.428	11.382	1.089

LDPE_Shaking_PCBs_LR

Laboratory ID:	15	15	15	15	15	15	15
Porewater PCB low res (ng/L)	Rep_1	Rep_2	Rep_3	Rep_4	Rep_5	Rep_6	Rep_7
PCB-008	4.780	9.977	13.048	12.778	6.606	9.986	7.066
PCB-018	4.950	14.851	19.333	18.618	10.176	15.268	10.548
PCB-028	5.383	11.020	14.424	14.128	7.509	11.196	7.231
PCB-044	5.460	2.827	3.366	3.516	2.010	2.967	1.966
PCB-052	5.550	2.549	3.360	3.200	1.839	2.595	1.754
PCB-066	5.910	1.002	1.327	1.301	0.691	1.027	0.678
PCB-101	6.090	0.236	0.293	0.259	0.195	0.209	0.165
PCB-105	6.360	0.059	0.091	0.087	0.046	0.068	0.047
PCB-118	6.450	0.089	0.099	0.109	0.065	0.084	0.068
PCB-138	6.540	0.032	0.041	0.038	0.025	0.037	0.027
PCB-153	6.633	0.037	0.044	0.047	0.029	0.038	0.027
PCB-170	6.980	0.007	0.010	0.006	0.002	0.005	0.007
PCB-180	7.070	0.011	0.013	0.012	0.009	0.012	0.010
PCB-187	6.880	0.010	0.013	0.012	0.007	0.012	0.010

LDPE_Shaking_PCBs_LR

Laboratory ID:	15	15	34	34	34	34	34
Porewater PCB low res (ng/L)	Average	Std Dev	Rep_1	Rep_2	Rep_3	Rep_4	Rep_5
PCB-008	9.910	2.724	12.612	12.520	8.749	12.704	8.659
PCB-018	14.799	3.868	19.996	19.770	13.199	18.013	13.849
PCB-028	10.918	3.095	6.153	6.299	4.335	6.105	4.436
PCB-044	2.775	0.660	4.259	4.312	2.967	3.675	3.190
PCB-052	2.549	0.666	3.251	3.322	2.225	3.095	2.426
PCB-066	1.004	0.282	1.084	1.109	0.745	1.032	0.837
PCB-101	0.226	0.046	0.247	0.253	0.175	0.239	0.198
PCB-105	0.066	0.019	0.069	0.079	0.050	0.064	0.058
PCB-118	0.086	0.017	0.091	0.085	0.069	0.089	0.065
PCB-138	0.033	0.006	0.041	0.033	0.026	0.036	0.027
PCB-153	0.037	0.008	0.049	0.047	0.036	0.045	0.035
PCB-170	0.006	0.003	0.005	0.006	0.005	0.004	0.004
PCB-180	0.011	0.001	0.011	0.011	0.007	0.010	0.009
PCB-187	0.011	0.002	0.009	0.008	0.006	0.008	0.006

LDPE_Shaking_PCBs_LR

Laboratory ID:	34	34	34	58	58	58
Porewater PCB low res (ng/L)	Rep_6	Average	Std Dev	Rep_1	Rep_2	Rep_3
PCB-008	9.205	10.741	2.058	14.737	19.251	22.073
PCB-018	13.710	16.423	3.190	36.017	34.222	39.607
PCB-028	4.532	5.310	0.963	10.805	10.184	12.089
PCB-044	3.063	3.578	0.600	5.097	4.889	5.825
PCB-052	2.461	2.797	0.479	4.819	4.622	5.496
PCB-066	0.793	0.933	0.160	1.833	1.772	2.079
PCB-101	0.191	0.217	0.033	0.595	0.563	0.645
PCB-105	0.055	0.063	0.011	0.116	0.109	0.134
PCB-118	0.064	0.077	0.012	0.156	0.145	0.168
PCB-138	0.026	0.031	0.006	0.081	0.078	0.088
PCB-153	0.035	0.041	0.007	0.063	0.061	0.073
PCB-170	0.004	0.005	0.001	0.013	ND	0.015
PCB-180	0.008	0.010	0.002	0.017	0.016	0.019
PCB-187	0.006	0.007	0.001	0.014	0.015	0.016

LDPE_Shaking_PCBs_LR

Laboratory ID:	58	58	58	58	58	50	50
Porewater PCB low res (ng/L)	Rep_4	Rep_5	Rep_6	Average	Std Dev	Rep_1	Rep_2
PCB-008	20.081	20.413	14.920	18.579	3.047	10.139	8.401
PCB-018	38.149	37.475	31.192	36.110	3.034	16.578	15.858
PCB-028	11.468	10.391	9.522	10.743	0.924	6.442	5.897
PCB-044	5.582	5.166	4.265	5.137	0.547	2.996	2.866
PCB-052	5.158	5.017	4.030	4.857	0.503	4.077	3.648
PCB-066	1.968	1.870	1.636	1.860	0.154	1.105	1.091
PCB-101	0.616	0.584	0.553	0.593	0.034	0.246	0.236
PCB-105	0.120	0.113	0.104	0.116	0.011	0.068	0.073
PCB-118	0.159	0.155	0.132	0.153	0.013	0.104	0.093
PCB-138	0.082	0.076	0.062	0.078	0.009	0.032	0.032
PCB-153	0.068	0.065	0.055	0.064	0.006	0.028	0.028
PCB-170	ND	ND	ND	0.014	0.001	ND	ND
PCB-180	0.018	0.016	0.014	0.016	0.002	0.010	0.011
PCB-187	ND	0.013	ND	0.015	0.001	0.008	0.007

LDPE_Shaking_PCBs_LR

Laboratory ID:	50	50	50	50	50	50
Porewater PCB low res (ng/L)	Rep_3	Rep_4	Rep_5	Rep_6	Average	Std Dev
PCB-008	9.756	9.037	9.094	10.075	9.417	0.686
PCB-018	16.858	15.226	15.755	17.667	16.324	0.883
PCB-028	6.340	5.455	6.081	6.995	6.202	0.524
PCB-044	2.991	2.640	2.918	3.270	2.947	0.205
PCB-052	3.795	2.918	3.696	4.163	3.716	0.442
PCB-066	1.142	1.013	1.090	1.217	1.110	0.067
PCB-101	0.242	0.231	0.227	0.256	0.240	0.011
PCB-105	0.062	0.059	0.073	0.075	0.068	0.007
PCB-118	0.098	0.086	0.099	0.103	0.097	0.007
PCB-138	0.035	0.026	0.037	0.041	0.034	0.005
PCB-153	0.028	0.023	0.025	0.028	0.027	0.002
PCB-170	ND	ND	ND	ND	ND	ND
PCB-180	0.011	0.008	0.011	0.011	0.010	0.001
PCB-187	0.007	0.007	0.008	0.008	0.007	0.000

Laboratory ID:	52	52	52	52	52	52	52	52	84	84	84	84	84	84	84	84
Porewater High Res PCBs (ng/L)	Rep_1	Rep_2	Rep_3	Rep_4	Rep_5	Rep_6	Average	Std Dev	Rep_1	Rep_2	Rep_3	Rep_4	Rep_5	Rep_6	Average	Std Dev
PCB-008	7.418	5.742	3.269	16.928	14.638	5.825	8.970	5.489	7.136	7.302	5.145	8.630	7.800	7.634	7.275	1.166
PCB-018	9.649	8.191	5.217	21.318	18.850	7.742	11.828	6.599	10.771	11.220	7.630	12.342	11.220	11.220	10.734	1.608
PCB-028	4.554	3.589	2.277	10.888	9.439	4.554	5.884	3.449	4.968	4.968	3.271	5.382	5.382	4.968	4.823	0.787
PCB-044	2.299	1.890	1.297	5.236	4.369	2.257	2.891	1.548	2.392	2.427	1.768	2.635	2.601	2.531	2.392	0.320
PCB-052	1.863	1.508	1.029	4.087	3.467	1.753	2.284	1.207	2.057	2.001	1.466	2.198	2.170	2.142	2.006	0.275
PCB-066	0.812	0.640	0.436	1.735	1.476	0.742	0.973	0.512	0.738	0.750	0.529	0.824	0.787	0.787	0.736	0.106
PCB-101	0.163	0.142	0.105	0.371	0.298	0.166	0.208	0.103	0.179	0.187	0.130	0.203	0.187	0.195	0.180	0.026
PCB-105	0.048	0.039	0.027	0.107	0.086	0.045	0.059	0.031	0.041	0.044	0.032	0.048	0.044	0.044	0.042	0.005
PCB-118	0.068	0.057	0.042	0.153	0.125	0.067	0.086	0.043	0.064	0.064	0.046	0.071	0.067	0.067	0.063	0.009
PCB-138	0.036	0.031	0.024	0.080	0.066	0.038	0.046	0.022	0.037	0.035	0.027	0.037	0.037	0.035	0.035	0.004
PCB-153	0.027	0.025	0.018	0.060	0.051	0.030	0.035	0.016	0.028	0.028	0.020	0.028	0.028	0.028	0.027	0.003
PCB-170	0.004	0.003	0.003	0.008	0.007	0.004	0.005	0.002	0.004	0.004	0.003	0.004	0.004	0.004	0.004	0.000
PCB-180	0.009	0.008	0.006	0.019	0.016	0.009	0.011	0.005	0.008	0.008	0.006	0.009	0.008	0.009	0.008	0.001
PCB-187	0.007	0.007	0.005	0.016	0.013	0.007	0.009	0.004	0.007	0.007	0.006	0.008	0.007	0.007	0.007	0.001

PDMS_Shaking_PAHs

Laboratory ID:	38	38	38	38	38	48	48	48	48	48	48	48	48	98	98
Porewater PAH Low-Res. (ng/L)	Rep_1	Rep_2	Rep_3	Average	Std Dev	Rep_1	Rep_2	Rep_3	Rep_4	Rep_5	Rep_6	Average	Std Dev	Rep_1	Rep_2
Naphthalene	207486.229	263802.322	124010.703	198433.085	70334.158	309091.391	512912.526	661858.740	290053.154	649539.881	654019.466	512912.526	174340.203	ND	30578.176
Acenaphthylene	522.613	535.175	530.316	529.368	6.335	397.033	373.480	500.497	437.409	400.397	479.467	431.380	50.235	ND	583.859
Acenaphthene	29831.710	34274.653	30102.647	31403.003	2490.608	35737.981	36233.284	38862.197	38481.195	40386.205	38481.195	38030.343	1739.710	5656.146	20903.150
Fluorene	13654.935	14678.719	14825.902	14386.519	637.830	16957.344	17653.806	19349.540	18380.549	15806.667	17865.773	17668.946	1211.958	3901.869	13656.542
Phenanthrene	13406.925	13433.908	13002.439	13281.090	241.696	16993.690	16232.778	17754.601	18388.694	16740.053	17120.509	17205.054	763.724	3670.362	12367.524
Anthracene	3572.699	3374.139	3386.469	3444.435	111.250	3954.705	3734.999	4064.558	4421.580	3858.584	4201.874	4039.383	247.233	1083.527	3553.970
Fluoranthene	3006.770	2500.914	2663.265	2723.650	258.277	3339.785	3169.333	3547.522	3574.156	3281.192	3270.539	3363.754	162.431	801.495	2404.484
Pyrene	2099.887	1698.134	1803.069	1867.030	208.374	2677.480	2569.700	2864.677	2961.112	2637.772	2728.534	2739.879	146.920	668.043	2055.518
Benz[a]anthracene	224.999	206.951	186.442	206.131	19.292	311.920	294.347	342.673	351.459	300.937	311.920	318.876	23.014	75.983	278.604
Chrysene	238.874	221.284	205.284	221.814	16.801	296.145	277.890	328.599	320.486	279.918	290.060	298.850	21.145	58.279	233.118
Benzo(b)fluoranthene	20.947	17.091	17.207	18.415	2.194	36.582	34.542	37.942	40.798	32.230	36.174	36.378	2.920	9.623	33.963
Benzo(k)fluoranthene	33.931	31.201	29.140	31.424	2.403	36.294	32.192	45.039	39.776	35.056	38.461	37.803	4.427	6.248	17.451
Benzo(a)pyrene	32.743	25.551	24.127	27.474	4.619	36.560	34.094	44.467	42.364	30.394	36.851	37.455	5.207	6.855	24.194
Dibenzo(a,h)anthracene	3.093	3.074	11.068	5.745	4.610	1.014	0.968	1.269	1.260	0.893	1.108	1.085	0.155	ND	ND
Indeno(1,2,3-cd)pyrene	9.184	8.121	6.790	8.032	1.200	5.847	4.749	7.527	6.719	5.330	6.073	6.041	0.988	ND	2.906
Benzo(ghi)perylene	7.387	6.725	6.293	6.801	0.551	4.932	4.577	6.350	5.738	4.545	5.222	5.227	0.707	ND	3.256

PDMS_Shaking_PAHs

Laboratory ID:	98	98	98	98	98	98	83	83	83	83	83	83	83
Porewater PAH Low-Res. (ng/L)	Rep_3	Rep_4	Rep_5	Rep_6	Average	Std Dev	Rep_1	Rep_2	Rep_3	Rep_4	Rep_5	Rep_6	Average
Naphthalene	46766.622	19426.135	ND	100728.108	49374.760	36028.694	257697.089	384679.801	522105.869	233618.125	450868.213	387827.841	372799.490
Acenaphthylene	570.281	448.078	366.609	651.749	524.115	114.653	1789.944	1733.802	2113.587	1436.579	1723.894	1608.308	1734.352
Acenaphthene	19673.553	15984.762	11804.132	23362.344	16230.681	6572.999	42079.074	41568.174	47785.623	43889.634	45314.777	42497.355	43855.773
Fluorene	12681.074	11705.607	8486.565	15607.476	11006.522	4202.630	27172.049	28210.305	31951.813	30660.496	30632.116	28520.127	29524.484
Phenanthrene	11569.619	10372.762	7979.048	13165.429	9854.124	3528.418	25081.100	24001.889	27740.722	26794.972	25456.520	23438.280	25418.914
Anthracene	3467.288	2860.512	2253.737	3900.699	2853.289	1044.661	7825.923	7802.961	8537.751	8251.767	8202.712	6686.165	7884.547
Fluoranthene	2244.185	2083.886	1602.989	2564.783	1950.303	652.451	4770.349	4442.589	5306.266	5108.076	4795.650	4458.306	4813.539
Pyrene	1884.224	1661.543	1301.828	2055.518	1604.446	539.795	3712.944	3480.577	4069.075	3943.261	3651.881	3396.975	3709.119
Benz[a]anthracene	234.281	215.285	170.962	272.272	207.898	75.710	531.481	504.990	603.128	562.940	529.976	461.038	532.259
Chrysene	203.978	180.666	139.871	215.634	171.925	64.345	381.333	356.547	412.764	403.487	389.918	360.701	384.125
Benzo(b)fluoranthene	26.415	26.415	20.755	32.076	24.874	8.818	92.155	75.602	125.662	99.453	106.573	88.729	98.029
Benzo(k)fluoranthene	17.020	13.789	10.126	16.158	13.465	4.453	58.230	49.330	63.977	57.874	50.601	47.092	54.517
Benzo(a)pyrene	19.557	18.549	14.113	24.194	17.911	6.614	55.372	65.362	74.876	63.792	63.459	49.331	62.032
Dibenzo(a,h)anthracene	ND	ND	ND	ND	ND	ND	1.681	2.072	1.093	1.151	0.000	0.000	0.999
Indeno(1,2,3-cd)pyrene	2.466	2.290	ND	2.818	2.620	0.291	6.875	5.451	9.270	6.421	7.763	6.999	7.130
Benzo(ghi)perylene	3.080	2.640	ND	3.080	3.014	0.263	6.297	6.380	8.341	7.722	7.206	6.710	7.109

PDMS_Shaking_PAHs

Laboratory ID:	83	19	19	19	19	19	19	19	19	9	9	9	9
Porewater PAH Low-Res. (ng/L)	Std Dev	Rep_1	Rep_2	Rep_3	Rep_4	Rep_5	Rep_6	Average	Std Dev	Rep_1	Rep_2	Rep_3	Rep_4
Naphthalene	110791.812	ND	368446.220	139987.166	240777.925	243017.719	35724.725	205590.751	124818.985	ND	ND	ND	ND
Acenaphthylene	224.310	ND	ND	ND	ND	ND	ND	ND	ND	908.573	711.474	821.308	1222.247
Acenaphthene	2358.331	5372.996	36324.483	33108.253	36324.483	29324.452	21416.310	26978.496	11962.507	15855.414	10566.046	13730.027	21044.792
Fluorene	1826.420	2033.752	20816.754	20217.711	21355.893	16982.877	13149.000	15759.331	7395.655	14227.029	11470.223	13018.758	17054.597
Phenanthrene	1632.834	718.647	16902.191	16902.191	17631.782	14348.623	11077.623	12930.176	6453.283	11374.173	10051.918	10461.976	12859.029
Anthracene	649.456	656.953	5221.260	4732.180	5432.754	3965.514	3317.813	3887.746	1769.026	3759.868	3343.797	3437.863	4287.433
Fluoranthene	345.112	2451.713	3990.709	3908.176	4107.226	3218.783	2529.391	3367.666	747.144	2099.797	2029.786	2017.012	2051.156
Pyrene	259.749	2148.714	3015.465	3036.226	3114.078	2491.262	1935.918	2623.611	506.028	1884.867	1768.944	1758.855	1810.412
Benz[a]anthracene	48.550	198.249	331.686	346.936	345.030	272.593	190.243	280.790	72.348	202.680	183.475	184.049	188.557
Chrysene	22.564	201.663	312.139	317.400	320.907	252.517	185.881	265.084	60.862	255.841	233.335	234.036	241.907
Benzo(b)fluoranthene	17.103	18.315	29.924	30.995	30.262	24.120	16.455	25.012	6.424	10.643	9.665	9.261	9.921
Benzo(k)fluoranthene	6.510	ND	23.702	24.732	23.959	18.807	ND	22.800	2.698	11.097	10.198	10.045	10.620
Benzo(a)pyrene	8.796	18.435	27.653	28.075	26.990	24.339	ND	25.098	3.998	13.486	13.733	12.385	13.982
Dibenzo(a,h)anthracene	0.854	ND	ND	ND	ND	ND	ND	ND	ND	0.859	0.773	0.768	0.862
Indeno(1,2,3-cd)pyrene	1.295	ND	ND	ND	ND	ND	ND	ND	ND	1.733	1.651	1.486	1.721
Benzo(ghi)perylene	0.807	ND	ND	ND	ND	ND	ND	ND	ND	2.251	2.386	2.203	2.533

Laboratory ID:	9	9	9	9
Porewater PAH Low-Res. (ng/L)	Rep_5	Rep_6	Average	Std Dev
Naphthalene	ND	ND	ND	ND
Acenaphthylene	1316.849	663.305	940.626	270.383
Acenaphthene	23573.339	7480.257	15374.979	6127.790
Fluorene	17264.917	10145.893	13863.569	2903.338
Phenanthrene	12415.715	9746.061	11151.479	1282.440
Anthracene	4164.404	3250.147	3707.252	438.630
Fluoranthene	2184.228	1928.072	2051.675	85.843
Pyrene	1914.864	1717.341	1809.214	76.792
Benz[a]anthracene	196.697	172.036	187.916	10.792
Chrysene	249.590	216.974	238.614	13.749
Benzo(b)fluoranthene	9.204	8.279	9.496	0.793
Benzo(k)fluoranthene	10.429	9.175	10.261	0.646
Benzo(a)pyrene	13.460	11.684	13.122	0.891
Dibenzo(a,h)anthracene	0.886	0.701	0.808	0.072
Indeno(1,2,3-cd)pyrene	1.744	1.444	1.630	0.132
Benzo(ghi)perylene	2.535	2.204	2.352	0.156

PDMS_Shaking_PCBs_LR

Laboratory ID:	38	38	38	38	38	9	9
Porewater PCBs low res (ng/L)	Rep_1	Rep_2	Rep_3	Average	Std Dev	Rep_1	Rep_2
PCB-008	7.300	7.043	6.943	7.095	0.184	8.297	11.185
PCB-018	12.976	14.299	12.035	13.104	1.137	10.759	14.144
PCB-028	3.445	3.919	4.017	3.794	0.306	5.712	8.335
PCB-044	1.026	1.058	0.992	1.025	0.033	2.572	3.275
PCB-052	1.384	1.365	1.304	1.351	0.042	3.141	3.186
PCB-066	0.750	0.607	0.601	0.653	0.084	0.662	0.777
PCB-101	0.210	0.183	0.193	0.196	0.014	0.170	0.177
PCB-105	0.023	0.021	0.025	0.023	0.002	0.048	0.053
PCB-118	0.033	0.030	0.033	0.032	0.002	0.062	0.063
PCB-138	0.019	0.016	0.022	0.019	0.003	0.015	0.014
PCB-153	0.012	0.010	0.014	0.012	0.002	0.013	0.012
PCB-170	0.002	0.002	0.002	0.002	0.000	ND	ND
PCB-180	0.002	0.002	0.002	0.002	0.000	0.004	0.005
PCB-187	0.003	0.003	0.004	0.004	0.001	0.004	0.004

PDMS_Shaking_PCBs_LR

Laboratory ID:	9	9	9	9	9	83	83
Porewater PCBs low res (ng/L)	Rep_3	Rep_4	Rep_5	Average	Std Dev	Rep_1	Rep_2
PCB-008	10.878	9.775	11.692	10.365	1.353	16.960	16.298
PCB-018	12.819	11.584	14.739	12.809	1.674	31.001	29.305
PCB-028	7.968	6.443	8.595	7.411	1.264	6.398	6.279
PCB-044	3.077	2.397	3.228	2.910	0.400	5.662	5.111
PCB-052	3.132	2.310	3.090	2.972	0.372	4.339	3.917
PCB-066	0.718	0.569	0.765	0.698	0.085	1.091	1.073
PCB-101	0.171	0.121	0.169	0.162	0.023	0.303	0.281
PCB-105	0.043	0.036	0.044	0.045	0.006	ND	0.079
PCB-118	0.068	0.058	0.066	0.063	0.004	0.099	0.100
PCB-138	0.016	0.011	0.015	0.014	0.002	0.051	0.045
PCB-153	0.013	0.008	0.012	0.012	0.002	ND	0.067
PCB-170	ND	ND	ND	ND	ND	0.012	0.010
PCB-180	0.005	0.003	0.004	0.004	0.001	0.023	0.019
PCB-187	0.004	0.002	0.003	0.003	0.001	0.016	0.014

PDMS_Shaking_PCBs_LR

Laboratory ID:	83	83	83	83	83	83	19
Porewater PCBs low res (ng/L)	Rep_3	Rep_4	Rep_5	Rep_6	Average	Std Dev	Rep_1
PCB-008	11.448	16.457	17.782	17.172	16.019	2.301	14.674
PCB-018	20.514	28.568	30.983	30.559	28.488	4.027	36.070
PCB-028	4.801	6.272	6.958	6.600	6.218	0.741	6.662
PCB-044	3.717	4.686	5.301	5.212	4.948	0.680	4.775
PCB-052	3.011	4.018	4.471	4.170	3.988	0.520	4.353
PCB-066	0.817	1.031	1.127	1.125	1.044	0.117	1.033
PCB-101	0.227	0.251	0.301	0.303	0.278	0.032	0.451
PCB-105	ND	ND	0.074	ND	0.076	0.003	ND
PCB-118	0.067	0.086	0.102	0.100	0.093	0.014	0.088
PCB-138	0.034	0.039	0.046	ND	0.043	0.007	0.061
PCB-153	ND	0.055	0.069	ND	0.064	0.007	ND
PCB-170	0.011	0.010	0.012	0.012	0.011	0.001	ND
PCB-180	0.017	0.018	0.021	0.021	0.020	0.002	ND
PCB-187	0.012	0.011	0.014	0.014	0.014	0.002	ND

PDMS_Shaking_PCBs_LR

Laboratory ID:	19	19	19	19	19	19	19
Porewater PCBs low res (ng/L)	Rep_2	Rep_3	Rep_4	Rep_5	Rep_6	Average	Std Dev
PCB-008	20.870	15.644	18.569	18.240	15.545	17.257	2.364
PCB-018	44.804	33.688	39.133	38.565	31.760	37.337	4.616
PCB-028	9.193	6.307	6.928	7.728	5.818	7.106	1.206
PCB-044	5.969	4.476	4.887	4.961	3.917	4.831	0.675
PCB-052	5.579	4.292	4.384	4.997	3.434	4.506	0.725
PCB-066	1.362	1.042	1.131	1.172	0.887	1.104	0.160
PCB-101	0.569	0.416	0.453	0.461	0.333	0.447	0.076
PCB-105	0.077	ND	ND	0.073	ND	0.075	0.003
PCB-118	0.115	0.089	0.091	0.098	0.072	0.092	0.014
PCB-138	0.078	0.058	0.057	0.068	ND	0.064	0.009
PCB-153	0.074	ND	0.062	0.062	ND	0.066	0.007
PCB-170	ND	ND	ND	ND	ND	ND	ND
PCB-180	ND	ND	ND	ND	ND	ND	ND
PCB-187	ND	ND	ND	ND	ND	ND	ND

PDMS_Shaking_PCBs_HR

Laboratory ID:	38	38	38	38	38	48
Porewater High Res PCBs (ng/L)	Rep_1	Rep_2	Rep_3	Average	Std Dev	Rep_1
PCB-008	1.700	5.927	3.833	3.820	2.114	13.179
PCB-018	3.130	9.708	6.701	6.513	3.293	20.163
PCB-028	0.766	2.476	1.956	1.733	0.876	6.128
PCB-044	0.230	0.626	0.445	0.434	0.198	3.352
PCB-052	0.302	0.858	0.609	0.590	0.279	2.812
PCB-066	0.137	0.368	0.257	0.254	0.115	0.882
PCB-101	0.037	0.112	0.070	0.073	0.037	0.161
PCB-105	0.003	0.015	0.009	0.009	0.006	0.048
PCB-118	0.008	0.022	0.015	0.015	0.007	0.063
PCB-138	0.008	0.015	0.012	0.012	0.003	0.027
PCB-153	0.002	0.008	0.005	0.005	0.003	0.020
PCB-170	0.001	0.002	0.001	0.001	0.000	0.003
PCB-180	0.001	0.002	0.001	0.001	0.001	0.007
PCB-187	0.002	0.003	0.002	0.002	0.001	0.005

PDMS_Shaking_PCBs_HR

Laboratory ID:	48	48	48	48	48	48
Porewater High Res PCBs (ng/L)	Rep_2	Rep_3	Rep_4	Rep_5	Rep_6	Average
PCB-008	13.285	13.355	13.548	12.653	13.758	13.296
PCB-018	19.421	22.637	22.143	20.411	23.009	21.297
PCB-028	6.181	6.181	6.128	6.128	6.603	6.225
PCB-044	3.339	3.425	3.439	3.280	3.734	3.428
PCB-052	2.777	2.835	2.865	2.689	3.108	2.847
PCB-066	0.919	0.795	0.816	0.808	0.917	0.856
PCB-101	0.168	0.179	0.181	0.172	0.215	0.179
PCB-105	0.050	0.052	0.056	0.053	0.063	0.054
PCB-118	0.068	0.073	0.077	0.073	0.088	0.074
PCB-138	0.031	0.029	0.033	0.031	0.038	0.032
PCB-153	0.023	0.022	0.024	0.023	0.030	0.024
PCB-170	0.003	0.003	0.004	0.003	0.005	0.004
PCB-180	0.008	0.008	0.009	0.008	0.012	0.009
PCB-187	0.005	0.008	0.007	0.007	0.011	0.007

PDMS_Shaking_PCBs_HR

Laboratory ID:	48	98	98	98	98	98
Porewater High Res PCBs (ng/L)	Std Dev	Rep_1	Rep_2	Rep_3	Rep_4	Rep_5
PCB-008	0.376	8.642	12.963	12.387	11.522	13.251
PCB-018	1.485	15.548	22.503	20.457	20.048	22.503
PCB-028	0.187	4.003	6.138	5.782	5.604	6.227
PCB-044	0.161	2.300	3.451	3.220	3.144	3.527
PCB-052	0.141	2.017	2.993	2.732	2.732	3.058
PCB-066	0.057	0.557	0.870	0.766	0.731	0.835
PCB-101	0.019	0.135	0.213	0.177	0.179	0.200
PCB-105	0.006	0.033	0.053	0.043	0.043	0.046
PCB-118	0.008	0.047	0.072	0.062	0.062	0.068
PCB-138	0.004	0.025	0.041	0.032	0.033	0.040
PCB-153	0.003	0.019	0.030	0.023	0.025	0.027
PCB-170	0.001	0.003	0.006	0.004	0.002	0.005
PCB-180	0.002	0.007	0.011	0.009	0.009	0.009
PCB-187	0.002	0.004	0.008	0.006	0.006	0.007

PDMS_Shaking_PCBs_HR

Laboratory ID:	98	98	98
Porewater High Res PCBs (ng/L)	Rep_6	Average	Std Dev
PCB-008	12.963	11.955	1.736
PCB-018	22.503	20.594	2.710
PCB-028	6.138	5.649	0.842
PCB-044	3.451	3.182	0.457
PCB-052	2.993	2.754	0.387
PCB-066	0.835	0.766	0.114
PCB-101	0.195	0.183	0.027
PCB-105	0.048	0.044	0.007
PCB-118	0.069	0.063	0.009
PCB-138	0.039	0.035	0.006
PCB-153	0.027	0.025	0.004
PCB-170	0.005	0.004	0.001
PCB-180	0.011	0.009	0.002
PCB-187	0.009	0.007	0.002

PDMS_Static_PAHs

Porewater PAH Low-Res. (ng/L)	64	64	64	64	64	48	48	48	48	48	48	48	48	84	84
PRCs for Ct=0	Rep_1	Rep_2	Rep_3	Average	Std Dev	Rep_1	Rep_2	Rep_3	Rep_4	Rep_5	Rep_6	Average	Std Dev	Rep_1	Rep_2
Naphthalene	158298.401	172234.103	113151.359	147894.621	30884.812	43237.376	473818.912	560069.635	607115.485	649680.777	546627.964	480091.691	222081.107	60071.615	45937.117
Acenaphthylene	536.293	508.835	564.107	536.412	27.636	237.788	325.327	338.795	342.583	400.662	297.971	323.854	53.950	444.869	498.792
Acenaphthene	29380.004	31870.538	31731.997	30994.180	1399.633	29738.737	37059.041	37478.434	37669.067	40414.181	37059.041	36569.750	3576.462	18317.370	19538.528
Fluorene	16437.017	16679.470	19282.714	17466.400	1577.638	15302.709	16060.268	16757.223	16908.735	15817.849	17908.714	16459.250	927.356	12607.078	12607.078
Phenanthrene	14089.228	14178.749	15513.849	14593.942	797.919	15847.623	16354.747	16481.528	16354.747	16735.090	16227.966	16333.617	293.702	11605.210	12005.389
Anthracene	3688.743	3788.957	3776.429	3751.376	54.603	3775.563	3912.856	4105.066	3679.457	3857.938	3597.081	3821.327	180.407	3300.131	3430.400
Fluoranthene	3102.766	2744.003	3299.367	3048.712	281.600	3138.452	3207.721	3159.766	3122.466	3282.320	3069.182	3163.318	73.884	2294.200	2458.072
Pyrene	2194.126	2018.213	2196.243	2136.194	102.180	2575.596	2603.962	2581.269	2552.903	2638.000	2524.538	2579.378	39.414	1922.780	1922.780
Benz[a]anthracene	192.010	233.939	261.566	229.172	35.023	290.217	290.217	292.433	290.217	303.510	288.002	292.433	5.605	234.282	261.057
Chrysene	237.344	251.249	277.154	255.249	20.204	243.716	251.908	253.956	268.292	282.629	247.812	258.052	14.655	197.921	210.291
Benzo(b)fluoranthene	14.942	22.592	28.627	22.054	6.858	31.380	31.940	32.500	31.590	33.201	35.092	32.617	1.380	30.142	34.448
Benzo(k)fluoranthene	34.915	38.652	42.597	38.722	3.841	36.013	33.389	36.013	34.900	36.013	36.092	35.403	1.086	12.648	16.539
Benzo(a)pyrene	26.965	31.718	46.057	34.914	9.939	34.625	34.102	34.849	33.655	31.267	34.849	33.891	1.368	21.280	22.882
Dibenzo(a,h)anthracene	2.298	3.102	3.363	2.921	0.555	1.014	0.861	1.020	0.904	0.950	1.154	0.984	0.104	ND	ND
Indeno(1,2,3-cd)pyrene	6.648	9.921	8.741	8.437	1.658	5.428	5.122	5.530	5.089	5.597	5.530	5.383	0.222	2.736	3.065
Benzo(ghi)perylene	5.685	9.536	9.042	8.088	2.095	4.426	4.155	4.459	4.324	4.763	4.831	4.493	0.259	3.033	3.250

PDMS_Static_PAHs

Porewater PAH Low-Res. (ng/L)	84	84	84	84	84	84	83	83	83	83	83	83	83	83
PRCs for Ct=0	Rep_3	Rep_4	Rep_5	Rep_6	Average	Std Dev	Rep_1	Rep_2	Rep_3	Rep_4	Rep_5	Rep_6	Average	Std Dev
Naphthalene	42403.493	53004.366	45937.117	88340.610	55949.053	17081.215	476648.691	242191.167	226909.489	320199.313	470338.038	306482.041	340461.456	109115.667
Acenaphthylene	444.869	512.273	579.677	566.197	507.779	57.617	972.715	873.459	939.630	1065.355	1134.834	1118.292	1017.381	104.913
Acenaphthene	18317.370	19538.528	21980.844	23202.002	20149.107	2006.567	36571.753	32741.482	35221.126	39449.698	36191.422	35466.695	35940.363	2179.524
Fluorene	12607.078	13576.853	14546.628	15516.403	13576.853	1226.679	21576.418	21217.919	24074.040	26695.119	23850.869	21730.739	23190.851	2103.631
Phenanthrene	11605.210	12405.569	13606.108	13606.108	12472.265	927.059	18310.955	18431.813	19314.856	22430.847	19126.747	18592.633	19367.975	1551.583
Anthracene	3256.709	3560.668	3994.896	3908.050	3575.142	311.516	5710.050	5910.013	5715.340	6724.676	6001.001	5579.916	5940.166	413.122
Fluoranthene	2294.200	2458.072	2621.943	2621.943	2458.072	146.571	3456.962	3446.646	3664.070	4251.274	3517.269	3340.712	3612.822	330.251
Pyrene	1922.780	1922.780	2097.578	2097.578	1981.046	90.265	2609.577	2655.738	2789.562	3351.117	2672.254	2569.768	2774.669	292.023
Benz[a]anthracene	240.976	261.057	281.138	287.832	261.057	21.168	302.868	345.703	327.709	432.646	308.441	285.193	333.760	52.748
Chrysene	210.291	228.846	247.401	235.031	221.630	18.521	282.807	286.916	284.128	359.856	272.827	260.500	291.173	35.022
Benzo(b)fluoranthene	27.989	30.142	36.601	32.295	31.937	3.169	64.897	64.801	67.263	91.069	60.600	62.048	68.446	11.327
Benzo(k)fluoranthene	18.972	21.404	17.999	21.161	18.120	3.262	24.659	28.622	34.842	38.585	26.916	31.264	30.815	5.190
Benzo(a)pyrene	21.509	22.882	25.170	25.170	23.149	1.703	29.025	31.294	31.861	48.719	25.365	25.055	31.886	8.730
Dibenzo(a,h)anthracene	ND	ND	ND	1.178	1.178	NA	ND	ND	ND	ND	ND	ND	ND	ND
Indeno(1,2,3-cd)pyrene	2.846	3.284	3.502	3.393	3.138	0.307	2.845	2.595	3.870	5.144	2.709	2.231	3.232	1.086
Benzo(ghi)perylene	3.033	3.466	3.791	3.683	3.376	0.324	1.932	3.773	3.182	5.023	3.000	2.409	3.220	1.088

PDMS_Static_PAHs

Porewater PAH Low-Res. (ng/L)	19	19	19	19	19	19	19	19	9	9	9	9	9	9
PRCs for Ct=0	Rep_1	Rep_2	Rep_3	Rep_4	Rep_5	Rep_6	Average	Std Dev	Rep_1	Rep_2	Rep_3	Rep_4	Rep_5	Rep_6
Naphthalene	193551.305	253966.163	95768.738	258441.337	29648.032	110872.453	157041.338	92870.136	ND	ND	ND	ND	ND	ND
Acenaphthylene	ND	ND	ND	ND	ND	ND	ND	ND	661.739	622.235	1189.025	959.341	985.798	911.172
Acenaphthene	22113.418	24872.870	20374.585	24872.870	17010.321	21962.215	21867.713	2964.959	14098.856	11205.801	22752.606	17891.066	16399.824	17354.600
Fluorene	12477.744	14063.644	12028.904	13973.876	10293.390	12896.661	12622.370	1398.309	11406.482	8827.846	18015.123	13918.366	14982.269	13934.888
Phenanthrene	10337.834	11601.212	10349.982	11540.473	8916.534	10993.819	10623.309	1000.405	7995.442	6601.101	13014.504	11010.404	10860.423	9587.012
Anthracene	2971.204	3076.847	2971.204	3301.338	2522.222	3142.874	2997.615	263.446	2428.358	1916.280	4373.040	3615.822	3609.059	2869.076
Fluoranthene	2279.543	2497.798	2269.843	2395.946	1872.136	2313.494	2271.460	213.551	2010.245	1185.754	2417.480	2080.958	2128.779	1988.549
Pyrene	1783.645	1949.566	1804.385	1913.270	1519.209	1840.680	1801.793	152.293	1690.804	1078.397	2059.659	1779.768	1814.585	1695.551
Benz[a]anthracene	159.395	175.963	156.920	158.253	117.880	157.300	154.285	19.252	169.110	84.549	221.272	179.538	186.664	169.084
Chrysene	175.186	189.201	148.733	168.880	133.142	175.186	165.055	20.434	204.683	108.701	282.262	229.904	237.165	218.805
Benzo(b)fluoranthene	ND	15.370	ND	ND	ND	ND	15.370	NA	10.541	4.569	12.639	9.868	10.230	9.097
Benzo(k)fluoranthene	ND	ND	ND	ND	ND	ND	ND	ND	11.162	5.162	13.081	10.560	10.794	9.802
Benzo(a)pyrene	ND	ND	ND	ND	ND	ND	ND	ND	12.965	6.343	16.173	12.930	13.387	12.175
Dibenzo(a,h)anthracene	ND	ND	ND	ND	ND	ND	ND	ND	0.684	0.312	0.947	0.817	0.804	0.713
Indeno(1,2,3-cd)pyrene	ND	ND	ND	ND	ND	ND	ND	ND	1.408	0.623	1.843	1.462	1.560	1.412
Benzo(ghi)perylene	ND	ND	ND	ND	ND	ND	ND	ND	2.095	1.183	2.616	2.119	2.211	2.040

Porewater PAH Low-Res. (ng/L)	9	9	9
PRCs for Ct=0	Rep_7	Average	Std Dev
Naphthalene	ND	ND	ND
Acenaphthylene	791.265	874.368	198.196
Acenaphthene	14505.179	16315.419	3635.596
Fluorene	12738.839	13403.402	2877.311
Phenanthrene	9222.227	9755.873	2112.564
Anthracene	2746.955	3079.799	833.991
Fluoranthene	1789.526	1943.042	383.460
Pyrene	1543.850	1666.088	303.226
Benz[a]anthracene	140.233	164.350	42.747
Chrysene	182.082	209.086	54.001
Benzo(b)fluoranthene	7.129	9.153	2.610
Benzo(k)fluoranthene	7.770	9.762	2.576
Benzo(a)pyrene	9.155	11.875	3.193
Dibenzo(a,h)anthracene	0.499	0.682	0.214
Indeno(1,2,3-cd)pyrene	0.947	1.322	0.407
Benzo(ghi)perylene	1.469	1.962	0.481

PDMS_Static_PCBs_LR																			
Laboratory ID:	38	38	38	38	38	9	9	9	9	9	9	9	9	9	83	83	83	83	83
Porewater PCBs Low-Res. (ng/L)	Rep_1	Rep_2	Rep_3	Average	Std Dev	Rep_1	Rep_2	Rep_3	Rep_4	Rep_5	Rep_6	Rep_7	Average	Std Dev	Rep_1	Rep_2	Rep_3	Rep_4	Rep_5
PCB-008	5.935	6.955	6.525	6.472	0.512	12.350	11.443	10.915	14.267	13.320	12.935	11.948	12.454	1.149	9.377	12.247	12.645	11.104	11.742
PCB-018	11.029	13.404	13.190	12.541	1.314	13.027	12.938	12.461	14.260	14.246	14.565	12.116	13.373	0.974	16.480	21.473	22.271	19.283	20.582
PCB-028	3.422	4.144	4.482	4.016	0.542	8.604	8.381	7.727	9.369	9.241	8.792	7.505	8.517	0.707	3.978	4.879	5.058	4.553	4.763
PCB-044	0.954	0.917	0.891	0.921	0.032	2.720	2.594	2.556	2.980	3.117	3.147	2.615	2.818	0.256	2.990	3.704	3.824	3.517	3.591
PCB-052	1.291	1.225	1.321	1.279	0.049	2.485	2.713	2.521	2.616	2.938	3.051	2.572	2.699	0.216	2.410	3.106	3.191	2.857	2.936
PCB-066	0.551	0.547	0.485	0.528	0.037	0.598	0.552	0.599	0.690	0.727	0.748	0.628	0.649	0.073	0.715	0.888	0.945	0.859	0.891
PCB-101	0.170	0.185	0.147	0.167	0.019	0.134	0.123	0.134	0.150	0.163	0.176	0.138	0.145	0.019	0.191	0.242	ND	0.229	ND
PCB-105	0.016	0.023	0.020	0.020	0.004	0.032	0.029	0.033	0.040	0.041	0.050	0.034	0.037	0.007	0.068	0.081	0.083	0.070	0.072
PCB-118	0.022	0.030	0.026	0.026	0.004	0.037	0.040	0.046	0.047	0.057	0.068	0.053	0.050	0.010	0.085	0.096	0.100	0.093	0.095
PCB-138	0.015	0.017	0.020	0.017	0.002	0.012	0.015	0.013	0.011	0.015	0.015	0.013	0.013	0.001	0.040	0.046	0.049	0.044	0.040
PCB-153	0.008	0.013	0.009	0.010	0.003	0.008	0.011	0.010	0.009	0.011	0.013	0.010	0.010	0.002	0.063	0.074	0.077	0.074	0.070
PCB-170	0.002	0.003	0.002	0.002	0.000	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.012	0.014	0.016	0.014	0.016
PCB-180	0.002	0.002	0.004	0.003	0.001	0.003	0.004	0.003	0.003	0.004	0.004	0.004	0.003	0.000	0.027	0.028	0.030	0.028	0.028
PCB-187	0.003	0.003	0.003	0.003	0.000	0.002	0.003	0.003	0.002	0.002	0.003	0.002	0.003	0.000	0.016	0.014	0.019	0.016	0.016

PDMS_Static_PCBs_LR											
Laboratory ID:	83	83	83	48	48	48	48	48	48	48	48
Porewater PCBs Low-Res. (ng/L)	Rep_6	Average	Std Dev	Rep_1	Rep_2	Rep_3	Rep_4	Rep_5	Rep_6	Average	Std Dev
PCB-008	11.264	11.396	1.147	12.045	12.719	15.414	14.379	13.261	12.916	13.456	1.229
PCB-018	19.803	19.982	2.030	23.820	27.223	28.244	26.769	26.882	25.294	26.372	1.570
PCB-028	4.670	4.650	0.372	4.344	4.575	5.063	5.330	4.575	4.797	4.780	0.363
PCB-044	3.377	3.500	0.293	2.593	2.876	3.197	3.055	2.958	2.816	2.916	0.208
PCB-052	2.795	2.883	0.275	2.170	2.581	2.606	2.523	2.462	2.498	2.473	0.158
PCB-066	0.818	0.853	0.079	0.654	0.738	0.806	0.767	0.719	0.705	0.731	0.052
PCB-101	0.222	0.221	0.022	0.369	0.406	ND	0.421	ND	0.380	0.394	0.024
PCB-105	0.060	0.072	0.008	ND	ND	ND	ND	ND	ND	ND	ND
PCB-118	0.085	0.092	0.006	ND	ND	ND	ND	ND	ND	ND	ND
PCB-138	0.040	0.043	0.004	ND	ND	ND	ND	ND	ND	ND	ND
PCB-153	0.065	0.070	0.006	ND	ND	ND	ND	ND	ND	ND	ND
PCB-170	0.011	0.014	0.002	ND	ND	ND	ND	ND	ND	ND	ND
PCB-180	0.025	0.028	0.002	ND	ND	ND	ND	ND	ND	ND	ND
PCB-187	0.014	0.016	0.002	ND	ND	ND	ND	ND	ND	ND	ND

PDMS_Static_PCBs_HR																			
Laboratory ID:	64	64	64	64	64	48	48	48	48	48	48	48	48	98	98	98	98	98	
Porewater High Res PCBs (ng/L)	Rep_1	Rep_2	Rep_3	Average	Std Dev	Rep_1	Rep_2	Rep_3	Rep_4	Rep_5	Rep_6	Average	Std Dev	Rep_1	Rep_2	Rep_3	Rep_4	Rep_5	
PCB-008	7.628	6.375	7.143	7.049	0.632	12.739	15.623	12.792	13.217	12.757	13.677	13.468	1.118	12.767	12.767	12.477	13.057	11.316	
PCB-018	14.651	12.169	13.439	13.419	1.241	17.923	20.054	19.177	18.801	18.675	20.555	19.197	0.962	22.741	19.846	20.673	20.467	18.192	
PCB-028	4.059	3.703	3.258	3.673	0.401	5.302	7.354	5.543	5.872	5.598	5.982	5.942	0.733	6.104	5.921	6.012	6.195	5.375	
PCB-044	1.093	0.933	0.894	0.973	0.105	3.247	4.155	3.100	3.204	3.105	3.461	3.379	0.403	3.309	3.230	3.388	3.388	2.994	
PCB-052	1.441	1.318	1.132	1.297	0.155	2.605	3.142	2.597	2.679	2.601	2.862	2.748	0.218	2.887	2.887	2.954	2.887	2.618	
PCB-066	0.612	0.566	0.603	0.594	0.024	0.714	1.001	0.792	0.810	0.776	0.854	0.825	0.098	0.807	0.733	0.770	0.770	0.697	
PCB-101	0.207	0.173	0.191	0.190	0.017	0.040	0.056	0.052	0.051	0.049	0.053	0.050	0.005	0.183	0.166	0.164	0.172	0.152	
PCB-105	0.024	0.017	0.019	0.020	0.003	0.049	0.066	0.058	0.058	0.054	0.059	0.057	0.006	0.045	0.039	0.041	0.043	0.034	
PCB-118	0.030	0.026	0.028	0.028	0.002	0.066	0.092	0.079	0.082	0.073	0.083	0.079	0.009	0.066	0.058	0.056	0.061	0.055	
PCB-138	0.018	0.016	0.019	0.018	0.002	0.031	0.044	0.033	0.034	0.030	0.036	0.035	0.005	0.032	0.025	0.028	0.029	0.028	
PCB-153	0.012	0.009	0.011	0.010	0.002	0.023	0.032	0.024	0.025	0.021	0.026	0.025	0.004	0.026	0.020	0.020	0.020	0.018	
PCB-170	0.002	0.002	0.002	0.002	0.000	0.004	0.005	0.004	0.004	0.004	0.005	0.004	0.001	0.004	0.003	0.003	0.003	0.004	
PCB-180	0.002	0.002	0.002	0.002	0.000	0.009	0.013	0.010	0.010	0.010	0.011	0.011	0.001	0.008	0.007	0.007	0.007	0.008	
PCB-187	0.003	0.003	0.004	0.003	0.000	0.006	0.008	0.008	0.008	0.007	0.008	0.008	0.001	0.007	0.005	0.006	0.005	0.005	

Laboratory ID:	98	98	98
Porewater High Res PCBs (ng/L)	Rep_6	Average	Std Dev
PCB-008	11.897	12.380	0.653
PCB-018	20.053	20.329	1.472
PCB-028	5.921	5.921	0.288
PCB-044	3.309	3.270	0.147
PCB-052	2.887	2.853	0.118
PCB-066	0.770	0.758	0.038
PCB-101	0.177	0.169	0.011
PCB-105	0.043	0.041	0.004
PCB-118	0.063	0.060	0.004
PCB-138	0.032	0.029	0.003
PCB-153	0.022	0.021	0.003
PCB-170	0.004	0.003	0.001
PCB-180	0.008	0.007	0.001
PCB-187	0.006	0.006	0.001

APPENDIX H

Template Scope of Work (SOW) for polymeric sampler-based sediment porewater assessment

Appendix X: Example Performance Work Statement

[This Appendix provides an example that may be used in creating a Performance Work Statement for polymeric passive sampling. Edit as necessary. Any italicized text in within brackets is instructional and should be replaced or deleted as appropriate.]

PERFORMANCE WORK STATEMENT

[DATE]

[CONTRACT NUMBER]

1. Introduction

Passive samplers are an alternative to actively sampling sediment porewater using Henry samplers and pumping or centrifugation. Passive samplers consist of hydrophobic polymers (e.g. polyethylene, polydimethylsiloxane), which sorb freely-dissolved organic compounds present in sediment porewater. Polymeric passive samplers can be directly inserted into saturated sediment in the laboratory or in the field to yield depth-discrete measures of freely dissolved (C_{free}) organic contaminant concentrations present in sediment porewater. C_{free} measured by polymeric samplers represents the fraction of contaminants not sorbed to settling solids or associated with suspended colloidal matter and has been linked directly to exposure and risk to sediment-dwelling organisms.

Polymeric passive samplers shall be pre-loaded with performance reference compounds (PRCs) appropriate to the analyte class and analytical methods employed. PRCs are labeled versions of the analytes of interest, and are used to demonstrate that the polymeric passive sample reached equilibration or fractional approach to equilibrium (Fernandez, 2009 and Tcaciuc, 2014).

ESTCP #201735 developed Standard Methods for polymeric passive sampler analysis (Michalsen et.al., 2020), and these methods shall be employed.

1.1. Description of Services

This PWS describes services to be performed by the contractor in the following tasks:

1. Preparation *[or support of preparation]* of the Work Plan (WP) and Quality Assurance Project Plan (QAPP).
2. Preparation and supply of the polymeric passive samplers loaded with the appropriate performance reference compounds (PRCs) for the project.
3. Field support for polymeric passive sampler and retrieval at the site.
4. Extraction and laboratory analysis of recovered polymeric passive samplers and calculation of equilibrium porewater concentrations using PRCs. Laboratory analysis will include *[analyte class]* following EPA Method *[method number]* using *[technology, i.e. GC/MS]*.
5. Report equilibrium concentrations of the target analytes based on analysis of the polymeric passive samplers and PRC performance corrections.

The contractor shall provide all personnel, equipment, supplies, facilities, transportation, tools, materials, supervision, and other items and non-personal services necessary to perform the polymeric passive sampler deployment and analytical support as defined in this Performance Work Statement except for those items specified as government furnished property and services.

The Contractor shall conduct all necessary program management actions to ensure this delivery order remains on schedule and within budget. The Contractor's Project Manager is responsible for notifying *[the Agency's]* Project Manager and Contracting Officer's Representative (COR) of any problems that arise and to identify corrective solutions.

The Contractor shall perform all necessary project management tasks. Project management tasks shall include activities associated with communication, billing, staff assignments, materials approvals and overall management of the project. The project manager shall mobilize the project team and provide on-going team coordination, plan and schedule project activities.

The contractor shall perform to the standards as outlined in Attachment/Technical Exhibit 1, "Performance Requirements Summary".

1.2. Background

The *[Agency]* is evaluating potential chemical contamination of sediment porewater at an aquatic site. The site will use in-situ polymeric passive samplers to measure porewater concentrations of *[analyte class]*. The following section provides background for the program.

[Insert summary description of site, including nature and extent of contamination.]

1.3. Objectives

The specific performance objectives, acceptance criteria, and monitoring methods for this PWS are outlined in Attachment/Exhibit 1, and specific information about each milestone is provided in the following subsections of this PWS. The objectives for field and laboratory analysis are to produce data of known and appropriate quality to support project objectives per the finalized Work Plan.

Specific Contractor objectives included in Section 5.1 of this PWS are:

- Project Coordination and technical contribution to the Work Plan and UFP-QAPP.
- Supplying polymeric passive samplers with any needed deployment components and assisting in sampler field deployment and retrieval.
- Processing polymeric passive samplers for shipment and analysis upon retrieval and analysis of the samplers per Work Plan and UFP-QAPP requirements. Conducting Data Usability Assessment in conjunction with *[the Agency]*.
- Report results including equilibrium porewater concentrations of target analytes and PRC compounds. Participate in meetings to discuss the results and provide an interpretation of the data.

1.4. Scope

This scope of work is for preparation and deployment/retrieval of polymeric passive samplers at an aquatic site, extraction of the polymeric passive samplers, chemical analysis for *[analyte class]*, and other necessary services to report equilibrium porewater concentrations of those analytes. Services include preparation of the Work Plan and UFP-QAPP, preparation of the polymeric passive samplers including

any necessary PRCs, field support for polymeric passive sampler deployment and retrieval, extraction and analysis of extracts for target analytes specific to the site, Data Usability Assessment in conjunction with *[the Agency]*, and the calculation and reporting of equilibrium concentrations of porewater concentrations.

The approximate locations and numbers of samples is included in the task description.

1.5. Period of Performance

The period of performance shall be for *[time period, i.e. 27 months]*.

[Include any relevant information to the period of performance, such as if there are certain times during the year when aquatic work may be performed at the site.]

1.6. General Information

1.6.1 Quality Control: The contractor shall develop and maintain an effective quality control program to ensure services are performed in accordance with this PWS as defined in Section 5.0 of this PWS. The contractor shall develop and implement procedures to identify, prevent, and ensure non-recurrence of defective services. The contractor's quality control program is the means by which he assures himself that his work complies with the requirement of the contract. The contractor shall provide their institutions Quality Control Program to *[the Agency]* within 30 days after the contract award. Three copies of a comprehensive written QCP shall be submitted to the KO and COR within 5 working days when changes are made thereafter. After acceptance of the quality control plan the contractor shall receive the contracting officer's acceptance in writing of any proposed change to his QC system.

1.6.2 Quality Assurance: The government shall evaluate the contractor's performance under this contract in accordance with the Quality Assurance Surveillance Plan. This plan is primarily focused on what the Government must do to ensure that the contractor has performed in accordance with the performance standards. It defines how the performance standards will be applied, the frequency of surveillance, and the minimum acceptable defect rate(s).

1.6.3 Recognized Holidays: The contractor is not expected to work on recognized holidays.

New Year's Day	Labor Day
Martin Luther King Jr.'s Birthday	Columbus Day
President's Day	Veteran's Day
Memorial Day	Thanksgiving Day
Independence Day	Christmas Day

1.6.4 Hours of Operation: The contractor is responsible for conducting business, between the hours of 0900 to 1700 Monday thru Friday except Federal holidays or when the Government facility is closed due to local or national emergencies, administrative closings, or similar Government directed facility closings. For other than firm fixed price contracts, the contractor will not be reimbursed when the government facility is closed for the above reasons. The Contractor must at all times maintain an adequate workforce for the uninterrupted performance of all tasks defined within this PWS when the Government facility is not closed for the above reasons. When hiring personnel, the Contractor shall keep in mind that the stability and continuity of the workforce are essential.

1.6.5 Place of Performance: The work to be performed under this contract will be performed at the Contractor's offices and laboratories, with the exception of field work that will be conducted at the [site].

1.6.6 Type of Contract: *[Specify type of contract; i.e. "The government will award a sole source service contract."]*

1.6.7 Security Requirements: Contractor personnel performing work under this contract must acquire appropriate security clearance for access to project sites.

[Use this section if needed and add appropriate details for access to project sites.]

1.6.8 Special Qualifications: *[Use if applicable.]*

1.6.9 Post Award Conference/Periodic Progress Meetings: The Contractor agrees to attend any post award conference convened by the contracting activity or contract administration office in accordance with Federal Acquisition Regulation Subpart 42.5. The contracting officer, Contracting Officers Representative (COR), and other Government personnel, as appropriate, may meet periodically with the contractor to review the contractor's performance. At these meetings the contracting officer will apprise the contractor of how the government views the contractor's performance and the contractor will apprise the Government of problems, if any, being experienced. Appropriate action shall be taken to resolve outstanding issues. These meetings shall be at no additional cost to the government.

1.6.10 Contracting Officer Representative (COR): The (COR) will be identified by separate letter. The COR monitors all technical aspects of the contract and assists in contract administration. The COR is authorized to perform the following functions: assure that the Contractor performs the technical requirements of the contract: perform inspections necessary in connection with contract performance: maintain written and oral communications with the Contractor concerning technical aspects of the contract: issue written interpretations of technical requirements, including Government drawings, designs, specifications: monitor Contractor's performance and notifies both the Contracting Officer and Contractor of any deficiencies: coordinate availability of government furnished property, and provide site entry of Contractor personnel. A letter of designation issued to the COR, a copy of which is sent to the Contractor, states the responsibilities and limitations of the COR, especially with regard to changes in cost or price, estimates or changes in delivery dates. The COR is not authorized to change any of the terms and conditions of the resulting order.

1.6.11 Key Personnel: Promptly following award of this Purchase Request, the Contractor shall designate a Principle Investigator, who will be responsible for the scheduled execution of the work and coordination with the *[Agency]* POC. The PI shall be responsible for the overall supervision of work and serve as liaison between the Contractor and the *[Agency]* POC for all work under this Purchase Request.

The contractor shall provide a contract manager who shall be responsible for the performance of the work. The name of this person and an alternate who shall act for the contractor when the manager is absent shall be designated in writing to the contracting officer. The contract manager or alternate shall have full authority to act for the contractor on all contract matters relating to daily operation of this contract. The contract manager or alternate shall be available between *[time period; i.e. 9:00 a.m. to 5:00 p.m.]*, Monday thru Friday except Federal holidays or when the government facility is closed for administrative reasons.

1.6.12 Identification of Contractor Employees: All contract personnel attending meetings, answering Government telephones, and working in other situations where their contractor status is not obvious to third parties are required to identify themselves as such to avoid creating an impression in the minds of

members of the public that they are Government officials. They must also ensure that all documents or reports produced by contractors are suitably marked as contractor products or that contractor participation is appropriately disclosed. Contractor may need to wear visitor identification badges while visiting facilities at the *[site]*.

1.6.13 Contractor Travel: Contractor will be required to travel CONUS and within the NCR during the performance of this contract to participate in field deployment and retrieval events. Contractor will be authorized travel expenses consistent with the substantive provisions of the Joint Travel Regulation (JTR) and the limitation of funds specified in this contract. All travel requires Government approval/authorization and notification to the COR.

[Add summary description of expected travel for deployment and retrieval.]

1.6.14 Other Direct Costs: Any additional direct costs will be included in the Contractors proposal and must be pre-approved by the contracting officer.

1.6.15 Data Rights: The Government has unlimited rights to all documents/material produced under this contract. All documents and materials, to include the source codes of any software, produced under this contract shall be Government owned and are the property of the Government with all rights and privileges of ownership/copyright belonging exclusively to the Government. These documents and materials may not be used or sold by the contractor without written permission from the Contracting Officer. All materials supplied to the Government shall be the sole property of the Government and may not be used for any other purpose. This excludes the contractor's right to produce data/documents for research or educational publication. This right does not abrogate any other Government rights.

1.6.16 Organizational Conflict of Interest: Contractor and subcontractor personnel performing work under this contract may receive, have access to, or participate in the development of proprietary or source selection information (e.g., cost or pricing information, budget information or analyses, specifications or work statements, etc.) or perform evaluation services which may create a current or subsequent Organizational Conflict of Interests (OCI) as defined in FAR Subpart 9.5. The Contractor shall notify the Contracting Officer immediately whenever it becomes aware that such access or participation may result in any actual or potential OCI and shall promptly submit a plan to the Contracting Officer to avoid or mitigate any such OCI. The Contractor's mitigation plan will be determined to be acceptable solely at the discretion of the Contracting Officer and in the event the Contracting Officer unilaterally determines that any such OCI cannot be satisfactorily avoided or mitigated, the Contracting Officer may effect other remedies as he or she deems necessary, including prohibiting the Contractor from participation in subsequent contracted requirements which may be affected by the OCI.

1.6.17 Phase In/Phase Out Period: *[Use if applicable.]*

2.0 Acronyms and Definitions

2.1. DEFINITIONS:

2.1.1. CONTRACTOR. A supplier or vendor awarded a contract to provide specific supplies or service to the government. The term used in this contract refers to the prime.

2.1.2. **CONTRACTING OFFICER.** A person with authority to enter into, administer, and or terminate contracts, and make related determinations and findings on behalf of the government. Note: The only individual who can legally bind the government.

2.1.3. **CONTRACTING OFFICER'S REPRESENTATIVE (COR).** An employee of the U.S. Government appointed by the contracting officer to administer the contract. Such appointment shall be in writing and shall state the scope of authority and limitations. This individual has authority to provide technical direction to the Contractor as long as that direction is within the scope of the contract, does not constitute a change, and has no funding implications. This individual does NOT have authority to change the terms and conditions of the contract.

2.1.4. **DEFECTIVE SERVICE.** A service output that does not meet the standard of performance associated with the Performance Work Statement.

2.1.5. **DELIVERABLE.** Anything that can be physically delivered, but may include non-manufactured things such as meeting minutes or reports.

2.1.6. **KEY PERSONNEL.** Contractor personnel that are evaluated in a source selection process and that may be required to be used in the performance of a contract by the Key Personnel listed in the PWS. When key personnel are used as an evaluation factor in best value procurement, an offer can be rejected if it does not have a firm commitment from the persons that are listed in the proposal.

2.1.7. **PHYSICAL SECURITY.** Actions that prevent the loss or damage of Government property.

2.1.8. **QUALITY ASSURANCE.** The government procedures to verify that services being performed by the Contractor are performed according to acceptable standards.

2.1.9. **QUALITY ASSURANCE SURVEILLANCE PLAN (QASP).** An organized written document specifying the surveillance methodology to be used for surveillance of contractor performance.

2.1.10. **QUALITY CONTROL.** All necessary measures taken by the Contractor to assure that the quality of an end product or service shall meet contract requirements.

2.1.11. **SUBCONTRACTOR.** One that enters into a contract with a prime contractor. The Government does not have privity of contract with the subcontractor.

2.1.12. **WORK DAY.** The number of hours per day the Contractor provides services in accordance with the contract.

2.1.12. **WORK WEEK.** Monday through Friday, unless specified otherwise.

2.2. ACRONYMS

ACOR	Alternate Contracting Officer's Representative
AFARS	Army Federal Acquisition Regulation Supplement
AR	Army Regulation
ASTM	American Society for Testing and Materials
CCE	Contracting Center of Excellence
CERCLA	Comprehensive Environmental Response, Compensation and Liability Act
CFR	Code of Federal Regulations

CONUS	Continental United States (excludes Alaska and Hawaii)
COR	Contracting Officer Representative
COTR	Contracting Officer's Technical Representative
COTS	Commercial-Off-the-Shelf
DD250	Department of Defense Form 250 (Receiving Report)
DD254	Department of Defense Contract Security Requirement List
DFARS	Defense Federal Acquisition Regulation Supplement
DMDC	Defense Manpower Data Center
DOD	Department of Defense
DOT	Department of Transportation
DWR	Department of Water Resources
FAR	Federal Acquisition Regulation
HAZWOPER	Hazardous Waste Operations and Emergency Response
HIPAA	Health Insurance Portability and Accountability Act of 1996
IDW	Investigation-Derived Waste
JTR	Joint Travel Regulation
KO	Contracting Officer
NAD	North American Datum
NAVD	North American Vertical Datum
NTP	Notice To Proceed
OCI	Organizational Conflict of Interest
OCONUS	Outside Continental United States (includes Alaska and Hawaii)
ODC	Other Direct Costs
PIPO	Phase In/Phase Out
POC	Point of Contact
PRC	Performance Reference Compound
PRS	Performance Requirements Summary
QA	Quality Assurance
QAP	Quality Assurance Program
QAPP	Quality Assurance Project Plan
QASP	Quality Assurance Surveillance Plan
QC	Quality Control
QCP	Quality Control Program
SSHP	Site-Specific Safety and Health Plan

3. Government Furnished Items and Services

3.1. Services

[Services provided; i.e. "The Government will provide vessel and diver support for LDPE deployment and retrieval."]

3.2. Facilities

[Facilities provided; i.e. "The Government will provide a work platform on the sampling vessel for use during LDPE deployment and retrieval. Project staff and field scientists will also be present in the field to direct and assist with field deployment and retrieval. If necessary, space for processing and/or preparation for shipping samplers will also be made available."]

3.3. Utilities

Not applicable.

3.4. Equipment

Not applicable.

3.5. Materials

Not applicable.

4. Contractor Furnished Items and Responsibilities

4.1. General

The Contractor shall furnish all supplies, equipment, facilities and services required to perform work under this contract that are not listed under Section 3 of this PWS.

4.2. Facility Access Clearance

[Use if applicable.]

4.3. Materials

The Contractor shall furnish materials, supplies, and equipment necessary to meet the requirements under this PWS as defined in Section 5.

4.4. Equipment

The Contractor shall furnish all laboratory and field materials to meet the requirements under this PWS Section 5.

5. Tasks

The Contractor shall provide all materials, equipment, labor and services for deploying and retrieving up to *[number of samplers]* passive polymeric *[specify type of polymer, if chosen by the government]* porewater samplers and performing an equivalent number of analyses for *[analyte class(es); i.e. PCBs or PAHs]*, extraction and analysis of passive polymeric samplers for the target analytes, the calculation and reporting of equilibrium porewater concentrations, investigative derived waste management and written documentation reporting. The use of passive polymeric samplers shall be performed according to the Standard Methods developed by ESTCP 201735 (Michalsen et.al., 2020). Work is described in additional detail and broken out by the following tasks.

5.1: *[Name of Site or Project Area]*

The purpose of the work described in Task 5.1 of this PWS is to *[describe purpose, i.e. “collect/analyze porewater samples from locations that are most likely to contribute to the tissue concentrations observed*

in invertebrates and fish.”] [Describe general placement of samplers at the Site or project area.] [Describe general deployment and retrieval of samplers.] Following retrieval, the passive polymeric samplers will be extracted and analyzed for [analyte class(es)].

The following Tasks shall be accomplished at the [site]:

Task 5.1.1: Project Kickoff and Work Plan/QAPP Finalization Support:

The contractor shall create a Project Management Plan to be presented 14 calendar days after task order award. The government team will provide written comments. The Project Management Plan shall be revised and submitted as final after comment resolution. The plan shall include the following:

List Key Personnel and Outline of Responsibilities

Contractor personnel that are considered key personnel by the Government are defined in Section 1.6.11 and are further defined here as: Contract Project Manager, Principal Investigator, and Field Scientist. The contractor shall provide a list of personnel and key personnel to be involved with the project and describe their roles. The Contractor shall provide a contract project manager who shall be responsible for the performance of the work and the primary point of contact for the [Agency] PM and shall be responsible for the performance of the work. The name of this person and an alternate who shall act for the Contractor when the manager is absent shall be designated in writing to the contracting officer. The contract project manager or alternate shall have full authority to act for the Contractor on all contract matters relating to daily operation of this contract. The contract project manager or alternate shall be available between the core hours of 0900-1500, Monday through Friday except Federal holidays.

Work Plan

[Describe work required to complete the Work Plan; for example the Contractor may solely produce the Work Plan with [Agency] review, or the Contractor may contribute to an Agency-led Work Plan.]

UFP-QAPP

[Describe work required to complete the UFP-QAPP; for example the Contractor may solely produce the QAPP with [Agency] review, or the Contractor may contribute to an Agency-led QAPP.]

In accordance with OSWER Directive 9272.0-17, the QAPP shall be generated following the Uniform Federal Policy QAPP (UFP-QAPP) guidelines. The QAPP is a formal document describing in comprehensive detail the necessary quality assurance (QA), quality control (QC), and other technical activities (including sample acquisition and archiving) that must be implemented to ensure that the results of the work performed will satisfy the stated performance criteria. The QAPP presents the steps that should be taken to ensure that environmental data collected are of the correct type and quality required for a specific decision or use. It presents an organized and systematic description of the ways in which QA and QC should be applied to the collection and use of environmental data. A QAPP integrates technical and quality control aspects of a project throughout its life cycle, including planning, implementation, assessment, and corrective actions.

Quality Control Plan

[Describe work required to complete the Quality Control Plan.]

Health and Safety Plan

[Describe the Health and Safety Plan that the Agency requires, which the Contractor is required to prepare.]

The Contractor is responsible understanding the safety and health criteria, practices, and procedures to be implemented to provide proper control of and protection against the unique safety, chemical, physical, and biological hazards related to this project. The Contractor is also responsible for providing their own site-specific health and safety plan (SSHP) for activities conducted at their facilities.

Task 5.1.2: Passive Polymeric Sampler Preparation and Field Deployment/Retrieval

[Describe required parts of the task; example text is given below.]

The Contractor shall provide all materials required for passive polymeric sampler field deployment, processing following retrieval, and preservation for shipment to the contractor's laboratory for analysis (except as noted below). This includes the following:

- Up to *[number]* of passive polymeric samplers with appropriate PRCs for *[analyte class(es)]* analysis;
- All sample labels;
- Any chemicals required for sample extraction;
- Sample containers (for transport and extraction);
- Personal protective equipment;
- Shipping containers,
- Shipping costs to the Contractor's laboratory; and,
- Any other materials required for polymeric passive sampler deployment and sample processing following retrieval.

The Contractor shall participate in one (1) field work kick-off/field readiness review meeting via teleconference.

[If possible, add a figure showing the location and number of polymeric passive sampler deployment; or the general area for deployment, if distribution will be determined as part of the contract.]

The Contractor shall mobilize field staff to provide technical support in the field during polymeric passive sampler deployment, retrieval and processing, and field documentation during deployment. The anticipated minimum time for deployment and equilibration will be defined in the QAPP, but the contractor should anticipate *[general proposed schedule]*. The Contractor shall maintain schedule flexibility to support both deployment and retrieval.

[Describe support for deployment, and if it is the Contractor or Agency responsibility; i.e. "The Government will provide all support pertaining to in-water LDPE placement, including field equipment and boats."]

The Contractor shall complete all required sample processing in the field following polymeric passive sampler retrieval per the finalized QAPP. The Contractor shall ship all samples to the contractor's laboratory under standard chain of custody procedures.

Retrieved polymeric passive samplers will be *[describe post-removal storage requirements that accord with the ESTCP Standard Methods]*. The contractor should anticipate up to *[number]* discrete polymeric passive samples for extraction.

Performance criteria include:

- The Contractor shall participate in the field work kick-off/field readiness review meeting via telecom.
- The Contractor shall provide sufficient number of polymeric passive samplers as defined above.
- The Contractor shall mobilize field staff to provide technical support in the field during polymeric passive sampler deployment, retrieval and processing, and field documentation during deployment. The anticipated minimum time for deployment and equilibration is approximately *[time estimate]*. The Contractor shall maintain schedule flexibility to support the entire deployment and retrieval effort.
- The Contractor shall complete all required sample processing in the field following polymeric passive sampler retrieval per the finalized Work Plan. The Contractor shall ship all samples to the contractor's laboratory under standard chain of custody procedures.

Task 5.1.3: Chemical Analysis of Polymeric Passive Samplers

The Contractor shall analyze all samples consistent with requirements specified in the finalized Work Plan. The total number of field samples requiring analysis will be up to *[number]* discrete samples. *[If planned, describe any compositing that may be performed.]* The analysis of these samplers will be performed in accordance with EPA Method *[method number]*. The specific analytical method, detection limits, and QA/QC criteria will be developed with the Contractor as part of the QAPP. The lab will be required to archive the extracts for 6 months.

The Contractor shall participate in one (1) Data Usability Assessment review meeting via telecom. Data Usability will be evaluated by the Contractor and *[the Agency]* according to the UFP-QAPP.

Task 5.1.4: Final Report

The Contractor shall submit all deliverables as electronic files in MS Word™, MS Excel™ and PDF. *[Add any Agency-specific requirements for electronic data deliverable format for laboratory data.]* The Contractor shall submit the following deliverable in similar electronic media formats:

Draft and Final Work Plan. The Contractor shall *[produce/provide technical input to]* the draft Work Plan, respond to *[Agency]* review electronically with “tracked changes” and comment responses, and finalize the document after *[Agency]* acceptance of changes.

Draft and Final QAPP. The Contractor shall *[produce/provide technical input to]* the draft QAPP, respond to *[Agency]* review electronically with “tracked changes” and comment responses, and finalize the document after *[Agency]* acceptance of changes.

Field Report. The Contractor shall provide a brief field report summarizing field deployment methods, method variances and field observations and photos 7 days following the last day of LDPE field sample retrieval.

Draft and Final Data Deliverables. The Contractor shall submit the draft electronic data to *[the Agency]* as soon as data become available, i.e. in a piecemeal fashion. The final Data Deliverable will include *[data deliverable requirements; i.e. “all chemical data in a single MS Excel file, as well as PDF copies of all chain of custody forms.”]* The data shall comply with QC requirements specified in the final QAPP.

Draft and Final Report. The draft and final reports will present methods, materials, results and discussion of the findings. The Contractor shall *[produce/provide technical input to]* the draft Final Report, respond to *[Agency]* review electronically with “tracked changes” and comment responses, and finalize the document after *[Agency]* acceptance of changes. *[Add detail and scheduling if the report requires review by Stakeholders/Regulators outside of the Agency.]*

5.2 Submittals

A list of submittals and associated delivery dates are presented in Attachment/Exhibit 2.

5.3. Schedule

The following schedules shall apply to this contract unless delays are incurred by the Government through no fault of the Contractor. Schedule of tasks are presented in Table 1.

Table 1: Schedule for Task Completion

Activity	Schedule
Purchase Order Notice to Proceed (NTP)	<i>[Purchase Order NTP Date]</i>
Task 5.1.1 – Project Kickoff and Work Plan/QAPP Finalization Support	<i>[Start and Finalization Dates]</i>
Task 5.1.2 – Passive Polymeric Sampler Field Deployment/Retrieval	<i>[Deployment and retrieval planned schedule]</i>
Task 5.1.3 – Chemical Analysis of Polymeric Passive Samplers	Within 30 working days of receipt of all samples.
Task 5.1.4 – Final Report	Draft to <i>[Agency]</i> within 60 working days of receipt of all samples by the laboratory. Final Report within 2 weeks following receipt of <i>[Agency or Stakeholder/Regulator]</i> review comments. <i>[Add detail and scheduling if the report requires review by Stakeholders/Regulators outside of the Agency.]</i>

6. References

Fernandez, L.A., Harvey, C.F., and Gschwend, P.M. Using performance reference compounds in polyethylene passive samplers to deduce sediment pore water concentrations for numerous target chemicals. *Environ. Sci. Technol.*, 43, 8888-8894, 2009.

Tcaciuc, AP, JN Apell, and PM Gschwend. " Passive Sampler PRC Calculation Software and User's Guide". Available at <https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Sediments/ER-200915>. July 2014.

Michalsen, et.al.. Standardizing Polymeric Sampling for Measuring Freely Dissolved Organic Contaminants in Sediment Porewater. ER 201735. September 2020.

7. ATTACHMENT/TECHNICAL EXHIBIT LIST:

Attachment 1/Technical Exhibit 1 – Performance Requirements Summary

Attachment 2/Technical Exhibit 2 – Deliverables Schedule

Attachment 3/Technical Exhibit 3 – Figures

TECHNICAL EXHIBIT 1

Performance Requirements Summary

The Contractor service requirements are summarized into performance objectives that relate directly to mission essential items. The performance threshold briefly describes the minimum acceptable levels of service required for each requirement. These thresholds are critical to mission success.

Table 2: Performance Objectives and Acceptance Criteria

Performance Objectives	Performance Standard	Acceptable Quality Levels	Monitoring Method
Task 5.1.1: Project Kickoff and Work Plan/QAPP Finalization Support. The Contractor shall coordinate closely with [Agency] to finalize field deployment details, schedule, and Work Plan and UFP-QAPP elements to ensure these requirements are met. The Contractor shall also provide a step-by-step protocol for field deployment, retrieval, and post processing of passive polymeric samplers based on the requirements of this PWS.	- Submittal of Work Plan in draft, draft final, and final version. - Submittal of UFP-QAPP in draft, draft final, and final version. - Contractor's input and teleconference as needed to resolve questions and finalize field deployment details, schedule, protocol and details of Work Plan and UFP-QAPP elements.	- Submission on schedule per Section 5.0 of this PWS.	- 100% Government inspection of milestones/deliverables associated with objective.
Task 5.1.2: Passive Polymeric Sampler Preparation and Field Deployment/Retrieval. <i>[Summarize deployment/retrieval; i.e the provided example here.]</i> Contractor shall provide all sampling equipment, materials and field support required to prepare polymeric passive samplers for field deployment and process samplers for shipping and analysis to the lab following retrieval. Note that the Government will provide vessel and field support for deployment and retrieval.	- Field deployment methods, field activities completed and observations documented in a brief field report memo. This memo will ultimately serve as the basis for the field methods section of the Final Report.	- Submission on schedule per Section 5.0 of this PWS.	- 100% Government inspection of milestones/deliverables associated with objective.
Task 5.1.3: Chemical Analysis of Polymeric Passive Samplers. Contractor shall complete analysis of all polymeric passive samplers collected during field deployment consistent with requirements specified in the finalized UFP-QAPP.	- Contractor shall provide electronic file containing chemical analysis results for all samples as soon as this data is available and prior to development of the final report. Data reporting and	- Analysis and data reporting shall meet requirements specified in the QAPP. - Submission on schedule per	- 100% Government inspection of milestones/deliverables associated with objective - Accepted data package

	analysis should be performed per requirements specified in the UFP-QAPP. - Data Usability will be evaluated by the Contractor and <i>[the Agency]</i> according to the UFP-QAPP.	Section 5.0 of this PWS.	- Submission on schedule Section 5.0 of this PWS.
Task 5.1.4: Final Report. Contractor shall submit the draft report to <i>[the Agency]</i> for review. <i>[The Agency]</i> will request clarification and revisions to the draft report and Contractor shall prepare the draft final report, which will subsequently be reviewed by USACE. Contractor shall revise as needed to finalize report.	-Concurrence from <i>[the Agency]</i> that the report meets project requirements.	- Submission on schedule per Section 5.0 of this PWS.	- 100% Government inspection of report associated with objective.

TECHNICAL EXHIBIT 2

Table 3: DELIVERABLES SCHEDULE*

DELIVERABLE	FREQUENCY	# OF COPIES	MEDIUM/FORMAT	SUBMIT TO
Work Plan finalization with Quality Control Plan and Health and Safety Plan.	See scope of work (Schedule).	1	1 electronic copy in .docx or .pdf format emailed or mailed on compact disc.	Attn: <i>[COR Name, Address, Email, Phone]</i>
UFP-QAPP finalization.	See scope of work (Schedule).	1	1 electronic copy in .docx or .pdf format emailed or mailed on compact disc.	Attn: <i>[COR Name, Address, Email, Phone]</i>
Draft Laboratory Data Report	As laboratory analyses are complete. Not to exceed 60 days after field activities.	1	1 electronic copy in .xls format emailed or mailed on compact disc.	Attn: <i>[COR Name, Address, Email, Phone]</i>
Draft Report	Draft Within 60 days of receipt of all passive polymeric samplers by the laboratory.	1	1 electronic copy in .docx or .pdf format emailed or mailed on compact disc.	Attn: <i>[COR Name, Address, Email, Phone]</i>
Final Report	2 weeks following receipt of <i>[Agency or Stakeholder]</i> review comments.	1	1 electronic copy in .docx or .pdf format emailed or mailed on compact disc.	Attn: <i>[COR Name, Address, Email, Phone]</i>

TECHNICAL EXHIBIT 3

Figures

[Add any Figures.]