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

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

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14. ABSTRACT
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 (Cfree) 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. Cfree measured by polymeric samplers represents the fraction of contaminants not sorbed to settling solids or associated with suspended colloidal matter.

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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 ±30% of known concentrations for non-isotopically-labeled analytes; ±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 ≥ ±50% of known concentrations for the isotopically-labeled PRCs • Percent Relative Standard Deviation (% RSD) ≤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 ±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 ≤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 method [10] • 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 ≤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}C6-phenanthrene, ^{13}C6-fluoranthene, ^{13}C6-chrysene, ^{13}C6-indeno(1,2,3-cd)pyrene
- PCBs PRCs (Regular Sens): ^{13}C-labled PCB congeners 37, 47, 54, 111, 138, 178
- PCBs PRCs (High-Sen): ^{13}C-labled 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 ±30% of known concentrations for PCB and PAH natives 83% of the time, and were within ±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 (≤±38%, Table 3). Lab 62 reported 2 out of range results for native PCB congeners (≤±36%); Lab 11 reported 1 out of range (≤±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-c,d)pyrene-^{13}C6 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.

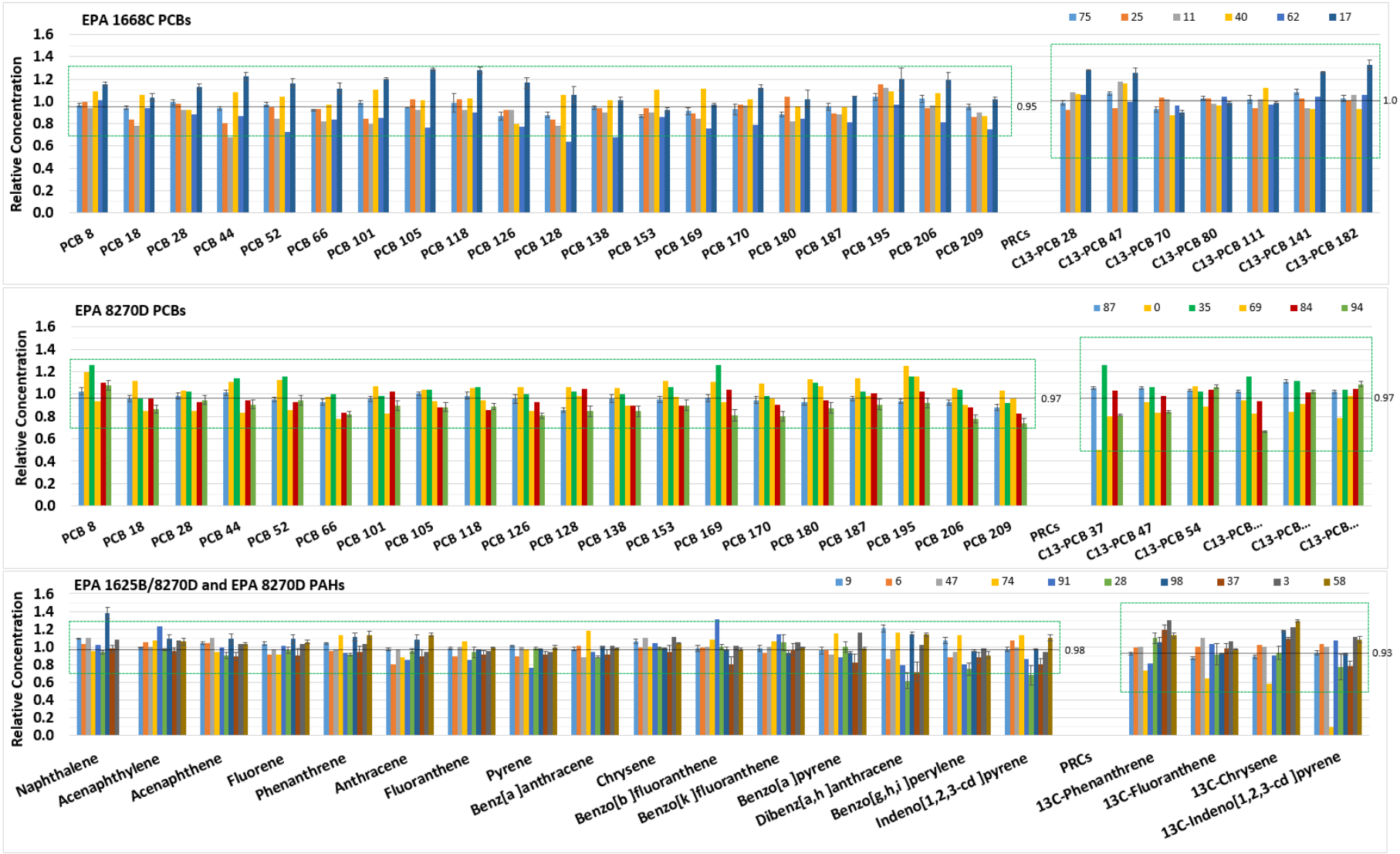

Figure 1. Calibration check standards results in relative units (Creported/Cknown). PAHs analyzed by regular- and high-sensitivity methods are shown at the bottom, PCB congeners analyzed by high-sensitivity and regular-sensitivity method are respectively shown at the top and middle of the figure. The acceptable range for native and PRC results (respectively ±30% and ±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 ±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 ±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 ±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 ±30% for all of the native target analytes and ±50% for all of the PRCs. A few labs reported results for a few analytes that were slightly out-of-range (e.g. ±38% for one or two natives; ±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}C6 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}C6 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 ±50% acceptance criteria for all the individual PCBs and PAHs. A single lab reported an exceedance (-58%) for a single PAH PRC ($^{13}C_6$-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 shipped "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, then quantified 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-^{13}C6 does not provide sufficient m/z distinction for low resolution GC/MS analysis; corrective measures associated with use of 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 ^{13}C 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 uL 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.

^{13}C 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 µl	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 ^{13}C 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 ^{13}C 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 µL of the working standard (20000 ng/mL) containing PAH16 and 12.5 µL of 13C-phenanthrene, 13C-fluoranthene, 13C-chrysene and 13C-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

High Res PAHs	check standard MIX ng/mL in ISO-OCTANE
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

^{13}C 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 2

Task 1.1 Calibration Check Standard:
Data Validation Report

Data Validation Report

Standardizing Polymeric Sampling for Measuring Freely Dissolved Organic Contaminants in Sediment Porewater
ER 201735

Task 1 - Calibration Standard Analyses

Prepared by:

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March 15, 2018

ACRONYMS

%D	percent difference
%D_f	percent drift
%R	percent recovery
%RSD	percent relative standard deviation
CCV	continuing calibration verification
CLP	U.S. EPA Contract Laboratory Program
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
IPR	initial precision and recovery
LCL	lower control limit
LCS	laboratory control sample
LCSD	laboratory control sample duplicate
m/z	mass-to-charge ratio
MB	method blank
MDL	method detection limit
MS	matrix spike
MSD	matrix spike duplicate
NFGs	CLP National Functional Guidelines for Data Review (EPA 2014, 2016 & EPA2017)
ng/kg	nanogram per kilogram
ng/L	nanogram per liter
OPR	ongoing precision and recovery
PCB	polychlorinated biphenyl
PFK	perfluorokarosene
QA/QC	quality assurance/quality control
QAPP	quality assurance project plan
RF	response factor

RPD	relative percent difference
RRT	relative retention time
S/N	signal-to-noise ratio
SDG	sample delivery group
SICP	selected ion current profile

INTRODUCTION

This report presents and discusses findings of the data validation performed on analytical data for calibration standards submitted to participating commercial laboratories in August and September 2017, as part of the effort for Task 1 identified in the project demonstration plan (USACE *et. al.*, 2017). Participating commercial laboratories and respective analytical methodologies applied to this study are summarized as follows:

Participating Commercial Laboratory	Analytical Method	
	PCB Congeners	PAHs
ALS 1317 S. 13th Ave Kelso, WA 98626	SW846 Method 8270D Modified	SW846 Method 8270D Modified
Analytical Resources, Inc. (ARI) 4611 S. 134th Place, Suite 100 Tukwila, WA 98168	SW846 Method 8270D Modified	SW846 Method 8270D Modified
TestAmerica Laboratories 5815 Middlebrook Pike Knoxville, TN 37921	EPA Method 1668C	SW846 Method 8270D Modified EPA Method 1625
SGS AXYS Analytical Laboratory 2045 Mills Road West Sidney, BC V8L5X2	EPA Method 1668C	SW846 Method 8270D Modified EPA Method 1625
Vista Analytical Laboratory 1104 Windfield Way El Dorado Hills, CA 95762	EPA Method 1668C	SW846 Method 8270D Modified EPA Method 1625
Battelle Norwell Operations 141 Longwater Drive Suite 202 Norwell, MA 02061	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.

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 may choose the submit the EDDs in Excel or csv. Format. Each laboratory report and EDD are assigned a unique sample delivery group (SDG) number. Laboratory deliverables, after fully validated, are archive in 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
ALS	K1708791.02	K1710426.01
ARI	17K0231	17K0231
TestAmerica Laboratories	140-9494-1	140-9513-1
SGS AXYS Analytical Laboratory	DPWG61670	DPWG61670
Vista Analytical Laboratory	1701157	1701146
Battelle Norwell Operations	DP-18-0022	DP-18-0023

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 1A and 2B***.

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)

Four participation commercial laboratories – AXYs-SGS, TestAmerica, and Vista chose to use this methodology for the study.

1.1 HRGC/HRMS Instrument Performance Check

The EPA Method 1668C and laboratory 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 ≥8,000 throughout the mass range and ≥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 ≤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.

1.2 Initial Calibration (ICAL)

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 ≤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 standard (second source standard) was analyzed to verify the calibration curve. The percent difference for each target compound is less than or equal to 30% and the initial calibration is assumed to be valid.

In addition to the method requirements, laboratories imposed more criteria based on their specific instrumentation and internal practices (e.g., adding ICAL standards lower than CS1 or higher than CS5). All laboratories met the method requirements and their SOP criteria for initial calibrations.

1.3 Calibration Verification

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 ratios should meet the same criteria as for initial calibrations.

All laboratories met calibration verification criteria.

1.4 Method Blanks

Method blanks are not applicable for this calibration standard analysis since the standards were pre-made and submitted to the laboratories. Sample did not require extraction or substantial preparation in the laboratories and therefore no method blanks were prepared along with sample preparation. Given the concentrations of calibration standard (5 µg/L in solvent), which is two orders of magnitude than conceivable laboratory contamination. The lack of method blank results had no significant effects on data quality.

1.5 Initial Precision and Recovery Study (IPR) and Ongoing Precision and Recovery (OPR)

IPR study results are normally maintained in the laboratory, and were not included in data packages. Tis information will be required in data packages reported for the following phases of this study.

1.6 Laboratory Control Sample (LCS) and LCS Duplicate (LCSD)

LCS and LCSD are not applicable for this calibration standard analysis since the standards were pre-made and submitted to the laboratories. Sample did not require extraction or substantial preparation in the laboratories and therefore no need to prepare LCS and/or LCSD along with sample preparation. This information will be required for regular sample analyses in the following phases of this study.

1.7 Matrix Spike and Matrix Spike Duplicate (MS/MSD)

MS and MSD are not applicable for this calibration standard analysis

1.8 Labeled Compound Recovery

Labeled internal standards and three cleanup recovery 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.

1.9 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 ±2 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 method control limits or laboratory control limits.

Co-elution of selected target PCB congeners with non-target PCBs were noted by all laboratories as a method default. Since the calibration standards analyzed in this phase contained only target congeners. This co-elution effect, which likely cause high-bias of a congeners' result, will be further evaluated in Phase 2 and Phase 3 analyses now that samples may contain PCB congeners more than target compounds.

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. Sample-specific EDLs were adjusted with sample weights, internal standard peak height, and noise levels as required by the method. In general, sample-specific MRLs were significantly elevated (from the project goal for quantitation limits) due to the high PCB congener concentrations in samples. Samples required dilutions for proper instrument analyses and the MRLs were therefore elevated proportionally. 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.

1.11 Overall Assessment of PCB Congener Data Usability

PCB congener data were of known quality and acceptable for use.

2. PCB Congeners by GC/MS - SIM (EPA Method SW8270D-SIM)

Two laboratories – ALS, ARI, and Battelle chose to use this methodology for PCB congeners analysis.

2.1 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.

2.2 Initial Calibration (ICAL)

The 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 ≤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. All ICALs met the requirements.

An ICV standard (second source standard) was analyzed to verify the calibration curve. %D values were either within ±20%, or the exceedance had no adverse effects on data usability (*e.g.,* biased high ICV recovery for a compound not detected in samples).

2.3 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 ±20%.

2.4 Method Blanks

Method blanks are not applicable for this calibration standard analysis as explained in Section 1.4.

2.5 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.

2.6 Matrix Spike (MS) and MS Duplicate (MSD)

MS and MSD analyses were not applicable for the calibration standard analysis.

2.7 Laboratory Control Sample (LCS) and LCS Duplicate (LCSD)

LCS and LCSD are not applicable for this calibration standard analysis as explained in Section 1.6.

2.8 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.

Both laboratories followed method requirements and met all the criteria for internal standards.

2.9 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.

2.10 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. RLs were supported with adequate initial calibration concentrations. In cases where target compound concentrations exceeded ICAL calibration ranges, proper dilution analyses were performed for definitive quantitation of the compounds. Only affected compounds were to be reported from dilution analyses.

2.11 Overall Assessment of PCB Congeners Data Usability

PCB Congeners data are of known quality and acceptable for use.

3. PAHs by Isotope Dilution GC/MS (EPA Method SW8270D Modified and EPA Method 1625 Modified)

Three laboratories chose to use this methodology for this study – AXYs-SGS, TestAmerica, and Vista.

3.1 GC/MS Instrument Performance Check

The method requires that DFTPP tuning was 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.

3.2 Initial Calibration (ICAL)

The 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 ≤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. All ICALs met the requirements.

An ICV standard (second source standard) was analyzed to verify the calibration curve. %D values were either within ±20%, or the exceedance had no adverse effects on data usability (*e.g.*, biased high ICV recovery for a compound not detected in samples).

3.3 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 ±20%.

3.4 Method Blanks

Method blank is not applicable for this calibration standard analysis, as explained in Section 1.4.

3.5 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.

3.6 Matrix Spike (MS) and MS Duplicate (MSD)

MS and MSD analyses were not applicable for the calibration standard analysis.

3.7 Laboratory Control Sample (LCS) and LCS Duplicate (LCSD)

LCS and LCSD analyses were not applicable for the calibration standard analysis, as explained in Section 1.6.

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 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. RLs were supported with adequate initial calibration concentrations. In cases where target compound concentrations exceeded ICAL calibration ranges, proper dilution analyses were performed for definitive quantitation of the compounds. Only affected compounds were to be reported from dilution analyses.

3.11 Overall Assessment of PAHs Data Usability

PAHs data are of known quality and acceptable for use.

4. PAHs by GC/MS - SIM (EPA Method SW8270D-SIM)

Two laboratories – ALS, ARI, and Battelle chose to use this methodology for PAHs analysis.

4.1 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.

4.2 Initial Calibration (ICAL)

The 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 ≤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. All ICALs met the requirements.

An ICV standard (second source standard) was analyzed to verify the calibration curve. %D values were either within ±20%, or the exceedance had no adverse effects on data usability (*e.g.,* biased high ICV recovery for a compound not detected in samples).

4.3 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 ±20%. The laboratories met the CCV criteria, except that tow compounds in one of ALS' CCV did not meet the criteria. The %D values for benzo(a)pyrene of 22% (a high bias) and fluoranthene-C^{13} of -22% (a low bias) were slightly outside the ±20% range. This deviation has no significant effects on data quality.

4.4 Method Blanks

Method blank was not applicable for this calibration standard analysis, as explained in Section 1.4.

4.5 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..

4.6 Matrix Spike (MS) and MS Duplicate (MSD)

MS and MSD analyses were not applicable for this calibration standard analysis

4.7 Laboratory Control Sample (LCS) and LCS Duplicate (LCSD)

LCS and LCSD analyses were not applicable for this calibration standard analysis, as explained in Section 1.6.

4.8 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. Internal standards in samples and associated QC analyses met the criteria.

4.9 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.

4.10 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. RLs were supported with adequate initial calibration concentrations. In cases where target compound

concentrations exceeded ICAL calibration ranges, proper dilution analyses were performed for definitive quantitation of the compounds. Only affected compounds were to be reported from dilution analyses.

4.11 Overall Assessment of PAHs Data Usability

PAHs data are of known quality and acceptable for use.

REFERENCES

USEPA. 2017. Contract Laboratory Program National Functional Guidelines for Organic Superfund Data Review. Office of Superfund Remediation and Technical Innovation. January 2017. OLEM 9355.0-136. EPA-540-R-2017-002.

USEPA. 2016. *Contract Laboratory Program National Functional Guidelines for High Resolution Methods Data Review,* Office of Superfund Remediation and Technical Innovation, U.S. Environmental Protection Agency. April 2016. USEPA 542-B-16-001.

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.

USEPA. 2009. *Guidance for Labeling Externally Validated Laboratory Analytical Data for Superfund Use.* January 13, 2009. EPA 540-R-08-005.

USEPA. 1996. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Third Edition, December 1996.

USEPA. 1989. *Method 1625C: Semi-volatile Organic Compounds by Isotope Dilution GCMS.* USEPA Office of Science and Technology Engineering and Analysis Division. June 1989.

USACE. 2017. *Demonstration Plan for Standardizing Polymeric Sampling for Measuring Freely Dissolved Organic Contaminants in Sediment Porewater.* U.S. Army Engineer Research Developmental Center, *et. al*. October 31, 2017. ER201735.

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					
	ALS (EPA 8270D)	**ARI (EPA 8270D)**	**AXYs-SGS (EPA 1668C)**	**Battelle (EPA 8270D Modified)**	**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	Prior to initial calibration. Prior to CCV if system idle for >24 hrs. Criteria same as 8270D.	Same as Method	• Same as Method. • An appropriate lock mass will be monitored for each descriptor and shall not vary by more than □ 20% throughout the respective retention time window.
GC Column Performance Check Prior to ICAL or calibration verification.	N/A	N/A	Same as Method	N/A	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 8270D.	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.	At the beginning and end of 10 injections or each 24 hour period (whichever is more frequent)	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 Modified)**	**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 ≥ ½ limit of quantitation or ≥ 5% of the associated regulatory limit for the analyte or ≥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 *p*g/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.	Analyte concentration in PB should be < MDL and must be < 5 MDL No analytes detected > ½ RL. For common laboratory contaminants, no analytes detected > RL.	Target analytes must be less than estimated maximum levels (EMLs) in SOP Table 4	≤ 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.	Same as Method Blank.	Target analytes must be less than EMLs in SOP Table 4	≤ 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.	70 to 130% recovery vs. SIS 40 to 120% recovery vs. IS	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 ≤ 30%	%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	Within control limits for OPR
Sample Duplicate or MS Duplicate (MSD) (OPTIONAL)	RPD ≤ 30%	RPD ≤ 30%	RPD ≤ 20% (applicable to concentrations ≥10 times the DL)	RPD ≤ 30%	N/A	RPD ≤ 25%

QC Parameters and Performance Frequency	Laboratory and Referenced Analytical Method					
	ALS (EPA 8270D)	**ARI (EPA 8270D)**	**AXYs-SGS (EPA 1668C)**	**Battelle (EPA 8270D Modified)**	**TestAmerica (EPA 1668C)**	**Vista (EPA 1668C)**
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 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	• Same as Method • The absolute retention times of the internal standards shall be within □15 seconds of the retention times obtained during calibration.
Compound Identification	Same as Method	Same as Method)	Same as Method	• Same as 8270D	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 A2 – 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 8720C-SIM** **EPA 1625 (HRGC/MS)**	**Battelle** **(EPA 8270D Modified)**	**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 *p*g 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.	Prior to initial calibration. Prior to CCV if system idle for >24 hrs. Criteria same as 8270D.	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 peak width 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	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 Modified)**	**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.	RT window for an analyte is ± 15s from the determined RT of the analyte in the ICAL.	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 ± 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 ± 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 ≤20% for targets with a labelled analog present and all labelled compounds, ≤ 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 ± 25% of expected value.	• SOP Table 3 lists ICAL concentrations. %RSD must be ≤30% for analytes and internal standards. • Verify ICAL with one second-source standard at mid-point (CS4) concentration. Value for all analytes within ±30% of expected value.	• Calibration standard solutions are presented in SOP Table 2. • The signal to noise ratio (s/n) must be ≥10:1 for all ions monitored. • The percent relative standard deviation for the mean relative response factors must be no greater that 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 Modified)**	**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 ≤ 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 ≤ 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 ±25% of expected values for all targets. • Closing Cal Ver: Concentrations of native compounds must be within ±25% of expected values. • Concentrations of labelled surrogates must be within ±25% of expected values, with any two (2) values allowed to be within ±40%. • Ion ratios for authentic and labelled dibenz[ah]anthracene, indeno[1,2,3-cd]pyrene and benzo[ghi]perylene must be within ±35% of the mid-point of the I-CAL. • All other native analytes and labelled surrogates must be within ±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 ≤ 25% • Grand mean of % difference ≤ 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 ≤ 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 (sin} must be ≥10:1 for all ions monitored. • The percent relative standard deviation for the mean relative response factors must be no greater that 30% for the un-labeled analytes and 35% for the internal standards. • If the criteria cannot be met, recalibrate.

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 Modified)**	**TestAmerica** **EPA 8270C-SIM** **EPA 1625 (GC/MS)**	**Vista** **EPA 8270C-SIM** **EPA 1625 (HRGC/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	• 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.	• Recovery of the internal standards must be within 50-150% recovery. • If outside of this criterion, the SIN must be ≥ 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.
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.	Analyte concentration in PB should be < MDL and must be < 5 MDL No analytes detected > ½ RL. For common laboratory contaminants, no analytes detected > RL.	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	See Laboratory QA Plan (LQAP). Reported along with LCS results.	See Laboratory QA Plan (LQAP). Reported along with	SOP Table 8.	70 to 130% recovery vs. SIS	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 Modified)**	**TestAmerica EPA 8270C-SIM EPA 1625 (GC/MS)**	**Vista EPA 8270C-SIM EPA 1625 (HRGC/MS)**
(LCS) One per preparation batch of 20 or less samples		LCS results.		40 to 120% recovery vs. IS		
Matrix Spike (MS) and MS Duplicate (MSD)	• For matrix evaluation, see LQAP. MS recovery is advisory. • RPD ≤ 30% (MS/ MSD or sample duplicate). Limits are advisory.	• For matrix evaluation, see LQAP. MS recovery is advisory. • RPD ≤ 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 ≤ 30%	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.	40 - 120% recovery	SOP Table 7	N/A
Laboratory Duplicates (Optional)	N/A	N/A	Duplicates must fall within ±20% of the mean (applicable to concentrations ≥10 times the DL). (Note that ±20% of the mean is equivalent to 40 relative percent difference)	≤ 30% RPD	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 Modified)**	**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.	• 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 quantitation ion must be present. • The internal standard quantitation ions must be present. • The relative intensities of confirmation ions should agree to within ±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	• 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 RRTs 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

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 Modified)**	**TestAmerica EPA 8270C-SIM EPA 1625 (GC/MS)**	**Vista EPA 8270C-SIM EPA 1625 (HRGC/MS)**
					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.	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

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 ^{13}C-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 ^{13}C-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 $^{13}C_6$-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 $^{13}C_6$-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 ±30% for regular PCB congener (*i.e.*, non-^{13}C-labelled PCBs) and ±50% for performance reference compounds (PRCs, *i.e.*, ^{13}C-labelled PCBs) were applied for accuracy evaluation. A regular PCB value outside ±30% (i.e. 70-130%) or a PRC value outside ±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 ≤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 ≤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 ±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 ≤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) $^{13}C6$ 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-^{13}C6 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-^{13}C6) 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-^{13}C-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-^{13}C6 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%

1. Each laboratory was randomly assigned a number to obscure laboratory identity.
2. Shaded number indicates that the result is outside the accuracy control limit for regular PCBs (70-130%, or 3.5-6.5 ng) or ^{13}C-labelled PCBs (50-150%, or 2.5-7.5 ng).
3. 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%

1. Each laboratory was randomly assigned a number to obscure laboratory identity.
2. Shaded number indicates that the result is outside the accuracy control limit for regular PCBs (70-130%, or 35.0-65.0 ng) or ^{13}C-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.
3. 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)

1. Each laboratory was randomly assigned a number to obscure laboratory identity.
2. Shaded number indicates that the result is outside the 70-130% (regular PAHs) or 50-150% (^{13}C-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.
3. Laboratories 91 used isotope dilution (EPA Method 1625A) technique for this study.
4. 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%
Benz(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:

1. Each laboratory was randomly assigned a number to obscure laboratory identity.
2. Shaded number indicates that the result is outside the 70-130% (regular PAHs) or 50-150% (^{13}C-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.
3. 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.
4. 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.

USEPA. 1996. *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Third Edition,* December 1996.

USEPA. 1989. *Method 1625C: Semi-volatile Organic Compounds by Isotope Dilution GCMS*. USEPA Office of Science and Technology Engineering and Analysis Division. June 1989.

USACE. 2018. *Demonstration Plan for Standardizing Polymeric Sampling for Measuring Freely Dissolved Organic Contaminants in Sediment Porewater.* U.S. Army Engineer Research Developmental Center, *et. al*. February, 2018. ER201735.

ATTACHMENT 4

Task 1.3 Pre-Loaded PDMS Polymeric Samplers: Data Validation Report

Data Validation Report

Standardizing Polymeric Sampling for Measuring Freely Dissolved Organic Contaminants in Sediment Porewater
ER 201735

Task 1.3 – Pre-Loaded Solid Phase Microextraction (SPME) Fiber Analyses

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ACRONYMS

%D	percent difference
%D_f	percent drift
%R	percent recovery
%RSD	percent relative standard deviation
CCV	continuing calibration verification
CLP	U.S. EPA Contract Laboratory Program
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
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
NFGs	CLP National Functional Guidelines for Data Review (EPA 2014, 2016 & EPA2017)
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	perfluorokarosene

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
SPME	solid phase microextraction
TTU	Texas Technology University

INTRODUCTION

This report presents and discusses findings of the data validation performed on analytical data for calibration standards submitted to participating commercial laboratories in January 2018, as part of the effort for Task 1.3 identified in the Project Demonstration Plan (USACE *et. al.*, 2018).

Each of the participating laboratories received two solid phase microextraction (SPME) fiber strips (submerged into a loading solution) from the Texas Tech University (TTU). The SPME fiber was coated with polydimethylsiloxane (PDMS) and each pre-loaded with PCB and PAH performance reference compounds (PRCs) respectively. 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 Concentration (ng/mL-PDMS)**	**PRCs**	**Target Concentration (ng/g-PDMS)**
^{13}C-PCB 28	1630	^{13}C-PCB 37	8670		
^{13}C-PCB 47	1680	^{13}C-PCB 47	9030	$^{13}C_6$-Phenanthrene	7010
^{13}C-PCB 70	1570	^{13}C-PCB 54	9170	$^{13}C_6$-Fluoranthene	7670
^{13}C-PCB 80	1450	^{13}C-PCB 111	8900	$^{13}C_6$-Chrysene	7620
^{13}C-PCB 111	1540	^{13}C-PCB 138	9310	$^{13}C_6$-Indeno[1,2,3-cd]pyrene	8540
^{13}C-PCB 141	1430	^{13}C-PCB 178	8750		
^{13}C-PCB 182	1460				

Notes:
ng/mL-PDMS: nanogram per milliliter of PDMS

Upon extraction, the fiber was rinsed with DI water, blot or air dried, and segment into 3 pieces into a 2 mL amber vial prefilled with hexane, and the vials were 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**
Analytical Resources, Inc. (ARI) 4611 S. 134th Place, Suite 100 Tukwila, WA 98168	SW846 Method 8270D Modified - SIM	SW846 Method 8270D Modified _SIM
TestAmerica Laboratories (TestAmerica) 5815 Middlebrook Pike Knoxville, TN 37921	EPA Method 1668C (Full Scan)	SW846 Method 8270D Modified EPA Method 1625 (Full Scan)

Participating Commercial Laboratory	Analytical Method	
	PCB Congeners	**PAHs**
SGS AXYS Analytical Laboratory (SGS) 2045 Mills Road West Sidney, BC V8L5X2	EPA Method 1668C - SIM	SW846 Method 8270D Modified EPA Method 1625 -SIM
Battelle Norwell Operations (Battelle) 141 Longwater Drive Suite 202 Norwell, MA 02061	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

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 may choose the submit the EDDs in Excel or csv. Format. Each laboratory report and EDD are assigned a unique sample delivery group (SDG) number. Laboratory deliverables, after fully validated, are archive in 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**
Analytical Resources, Inc.	18A0460	18A0460
TestAmerica Laboratories	140-10591-1	140-10591-1
SGS AXYS Analytical Laboratory	DPWG63181	DPWG63191
Battelle Norwell Operations	DP-18-0044	DP-18-0044

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 1A and 2B***.

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 participation commercial laboratories – SGS and TestAmerica chose to use this methodology 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 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.

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 ≥8,000 throughout the mass range and ≥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 ≤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)

TestAmerica chose to fully follow the EPA Method 1668C initial calibration 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 ≤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.

SGS 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 20%, and RT within 3 seconds between the two analyses. The ICAL met the laboratory SOP requirements.

1.4 Calibration Verification (CCV) and Ongoing Precision and Recovery (OPR)

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 or OPRs met the laboratory control criteria.

1.5 Method Blanks

A solvent blank was reported by each laboratory. Detections of PCB PRCs were detected and reported in the blank by Test America, and data were qualified as follows:

Blank ID	Analyte	Blank	Affected Sample	Original Result	Data Qualifier	Unit
40-17846/4-B	^{13}C-PCB28	10.4	C13-PCB PDMS-1 C13-PCB PDMS-2 C13-PCB PDMS-3	15 15 15	**R**	ng/g
40-17846/4-B	^{13}C-PCB111	10.6	C13-PCB PDMS-1 C13-PCB PDMS-2 C13-PCB PDMS-3	15 15 14	**R**	ng/g

Target PCB PRCs were not detected at or above the estimated detection limits (EDLs) for SGS.

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) 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 ^{13}C-labelled PRCs, the LCS analyzed/reported by the laboratories did not contain the target PRCs. However, the %R values in LCS were all within the laboratory control criteria.

1.8 Matrix Spike and Matrix Spike Duplicate (MS/MSD)

MS and MSD are not applicable for this calibration standard analysis.

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 SGS), (2) the S/N ratio of each of the two exact m/z's must be greater than or equal to 2.5 (S/N ratio was specified at 3 for SGS), (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 and 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 as qualified.

2. PCB Congeners by GC/MS - SIM (EPA Method SW8270D-SIM)

Two laboratories – ARI and Battelle chose to use this methodology 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 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 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 ≤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. Battelle'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 ^{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 ±20%. Battelle's criteria vary slightly from the method requirements. 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)

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 ^{13}C-labelled PRCs, the LCS analyzed/reported by the laboratories did not contain the target PRCs. However, the %R values in LCS were all within the laboratory control criteria.

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. Battelle 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.

Battelle's internal standard recovery could not be compared to those of the mid-point ICAL standard due to a change in final prepared for injection volume (PIV) amounts relative to what was anticipated in the original laboratory workplan. The amounts of internal standard added to the sample extracts differed from those in the ICAL, CCV, and QC analyses. After a thorough examination of the laboratory procedures and instrument printouts, the inconsistent internal standard recovery in this case was deemed to have no significant adverse effects on sample results. Data qualifiers were not assigned in this case.

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.

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 and 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.

3. PAHs by Isotope Dilution GC/MS (EPA Method SW8270D Modified and EPA Method 1625 Modified)

SGS and TestAmerica chose to use this methodology 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)

TestAmerical chose to fully follow the method requirements to establish ICAL for $^{13}C_6$-Labeled PAH PRCs. 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 ≤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 ±20%. The ICALs were considered valid.

SGS followed their SOP to establish ICAL for the $^{13}C_6$-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) and Ongoing Precision and Recovery (OPR)

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 ±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 Matrix Spike (MS) and MS Duplicate (MSD)

MS and MSD analyses were not applicable for the calibration standard analysis.

3.8 Laboratory Control Sample (LCS)

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 $^{13}C_6$-labelled PRCs, the LCS

analyzed/reported by the laboratories did not contain the target PRCs. However, the %R values in LCS were all within 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 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 and 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.

4. PAHs by GC/MS - SIM (EPA Method SW8270D-SIM)

ARI and Battelle 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)

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 ≤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. Battelle'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 $^{13}C_6$-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 ±20% (25% for Battelle). 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) 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 $^{13}C_6$-labeled PRCs, the LCS analyzed/reported by the laboratories did not contain the target PRCs. However, the %R values in LCS were all within the laboratory control criteria.

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. Battelle 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.

Battelle's internal standard recovery could not be compared to those of the mid-point ICAL standard due to a change in final prepared injection volume (PIV) amounts relative to what was anticipated in the original laboratory workplan. The amounts of internal standard added to the SPME and QC sample final extracts was lower (2x) than the response of the internal standard in the ICAL and below their internal standard area criteria. Additionally, when the second aliquot of the SPME extracts were removed for re-analysis at a lower PIV, the amount of IS added at that point to compensate for the change in PIV was also below what would normally be added for that PIV (error when scaling down from 250 µL PIV to 100 µL PIV), resulting in responses lower (4x) than the response of the internal standard in the ICAL and below Battelle's internal standard area criteria. After a thorough examination of the laboratory remaining extracts and instrument printouts, the lower internal standard recovery in this case was deemed to have no significant adverse effects on sample results. Data qualifiers were not assigned in this case.

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 and 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.

SUMMARY

Table 1. Data Affected by QC Anomalies

Sample ID	Analyte	Data Qualifier	Reason	Report Section
C13-PCB PDMS-1 C13-PCB PDMS-2 C13-PCB PDMS-3	^{13}C-PCB28	**R**	The analyte result was affected by laboratory contamination.	**1.5**
C13-PCB PDMS-1 C13-PCB PDMS-2 C13-PCB PDMS-3	^{13}C-PCB111	**R**	The analyte result was affected by laboratory contamination.	**1.5**

Table 2. Definitions of Data Qualifiers

Data Qualifier	Definition
J	The analyte was detected above the reported quantitation limit, and the reported concentration was approximate.
R	The result was rejected.
U	The analyte was analyzed for, but was considered not detected at the reporting limit or reported value.
UJ	The analyte was analyzed for, and the associated quantitation limit was approximate.

REFERENCES

USEPA. 2017. Contract Laboratory Program National Functional Guidelines for Organic Superfund Data Review. Office of Superfund Remediation and Technical Innovation. January 2017. OLEM 9355.0-136. EPA-540-R-2017-002.

USEPA. 2016. *Contract Laboratory Program National Functional Guidelines for High Resolution Methods Data Review*, Office of Superfund Remediation and Technical Innovation, U.S. Environmental Protection Agency. April 2016. USEPA 542-B-16-001.

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.

USEPA. 2009. *Guidance for Labeling Externally Validated Laboratory Analytical Data for Superfund Use.* January 13, 2009. EPA 540-R-08-005.

USEPA. 1996. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Third Edition, December 1996.

USEPA. 1989. *Method 1625C: Semi-volatile Organic Compounds by Isotope Dilution GCMS*. USEPA Office of Science and Technology Engineering and Analysis Division. June 1989.

USACE. 2018. *Demonstration Plan for Standardizing Polymeric Sampling for Measuring Freely Dissolved Organic Contaminants in Sediment Porewater*. U.S. Army Engineer Research Developmental Center, *et. al*. January, 2018. ER201735.

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					
	ALS (EPA 8270D)	**ARI (EPA 8270D)**	**AXYs-SGS (EPA 1668C)**	**Battelle (EPA 8270D Modified)**	**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	Prior to initial calibration. Prior to CCV if system idle for >24 hrs. Criteria same as 8270D.	Same as Method	• Same as Method. • An appropriate lock mass will be monitored for each descriptor and shall not vary by more than □ 20% throughout the respective retention time window.
GC Column Performance Check Prior to ICAL or calibration verification.	N/A	N/A	Same as Method	N/A	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 8270D.	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.	At the beginning and end of 10 injections or each 24 hour period (whichever is more frequent)	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 Modified)**	**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 ≥ ½ limit of quantitation or ≥ 5% of the associated regulatory limit for the analyte or ≥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 *p*g/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.	Analyte concentration in PB should be < MDL and must be < 5xMDL No analytes detected > ½ RL. For common laboratory contaminants, no analytes detected > RL.	Target analytes must be less than estimated maximum levels (EMLs) in SOP Table 4	≤ 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.	Same as Method Blank.	Target analytes must be less than EMLs in SOP Table 4	≤ 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.	70 to 130% recovery vs. SIS 40 to 120% recovery vs. IS	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 ≤ 30%	%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	Within control limits for OPR
Sample Duplicate or MS Duplicate (MSD) (OPTIONAL)	RPD ≤ 30%	RPD ≤ 30%	RPD ≤ 20% (applicable to concentrations ≥10 times the DL)	RPD ≤ 30%	N/A	RPD ≤ 25%

QC Parameters and Performance Frequency	Laboratory and Referenced Analytical Method					
	ALS (EPA 8270D)	**ARI (EPA 8270D)**	**AXYs-SGS (EPA 1668C)**	**Battelle (EPA 8270D Modified)**	**TestAmerica (EPA 1668C)**	**Vista (EPA 1668C)**
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 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	• Same as Method • The absolute retention times of the internal standards shall be within □15 seconds of the retention times obtained during calibration.
Compound Identification	Same as Method	Same as Method)	Same as Method	• Same as 8270D	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 A2 – 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 8720C-SIM** **EPA 1625 (HRGC/MS)**	**Battelle (EPA 8270D Modified)**	**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.	RT window for an analyte is ± 15s from the determined RT of the analyte in the ICAL.	N/A	The RRT of the analyte compared to the RRT of the labeled standard must be within +0.008RRTunits of theRRTs 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 ± 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 ± 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 ≤20% for targets with a labelled analog present and all labelled compounds, ≤ 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 ± 25% of expected value.	• SOP Table 3 lists ICAL concentrations. %RSD must be ≤30% for analytes and internal standards. • Verify ICAL with one second-source standard at mid-point (CS4) concentration. Value for all analytes within ±30% of expected value.	• Calibration standard solutions are presented in SOP Table 2. • The signal to noise ratio (s/n) must be ≥10:1 for all ions monitored. • The percent relative standard deviation for the mean relative response factors must be no greater that 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 Modified)**	**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 ≤ 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 ≤ 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 ±25% of expected values for all targets. • Closing Cal Ver: Concentrations of native compounds must be within ±25% of expected values. • Concentrations of labelled surrogates must be within ±25% of expected values, with any two (2) values allowed to be within ±40%. • Ion ratios for authentic and labelled dibenz[ah]anthracene, indeno[1,2,3-cd]pyrene and benzo[ghi]perylene must be within ±35% of the mid-point of the I-CAL. • All other native analytes and labelled surrogates must be within ±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 ≤ 25% • Grand mean of % difference ≤ 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 ≤ 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 (sin} must be ≥10:1 for all ions monitored. • The percent relative standard deviation for the mean relative response factors must be no greater that 30% for the un-labeled 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.	• 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.	• Recovery of the internal standards must be within 50-150% recovery. • If outside of this criterion, the SIN must be ≥ 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.

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 Modified)**	**TestAmerica EPA 8270C-SIM EPA 1625 (GC/MS)**	**Vista EPA 8270C-SIM EPA 1625 (HRGC/MS)**
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.	Analyte concentration in PB should be < MDL and must be < 5 MDL No analytes detected > ½ RL. For common laboratory contaminants, no analytes detected > RL.	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) One per preparation batch of 20 or less samples	See Laboratory QA Plan (LQAP). Reported along with LCS results.	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	Ongoing Precision and Recovery Samples (OPR); SOP Table 3.
Matrix Spike (MS) and MS Duplicate (MSD)	• For matrix evaluation, see LQAP. MS recovery is advisory. • RPD ≤ 30% (MS/ MSD or sample duplicate). Limits are advisory.	• For matrix evaluation, see LQAP. MS recovery is advisory. • RPD ≤ 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 ≤ 30%	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 Modified)**	**TestAmerica EPA 8270C-SIM EPA 1625 (GC/MS)**	**Vista EPA 8270C-SIM EPA 1625 (HRGC/MS)**
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.	40 - 120% recovery	SOP Table 7	N/A
Laboratory Duplicates (Optional)	N/A	N/A	Duplicates must fall within ±20% of the mean (applicable to concentrations ≥10 times the DL). (Note that ±20% of the mean is equivalent to 40 relative percent difference)	≤ 30% RPD	N/A	N/A
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.	• 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 quantitation ion must be present. • The internal standard quantitation ions must be present. • The relative intensities of confirmation ions should agree to within ±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	• 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 RRTs 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,

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 Modified)**	**TestAmerica** **EPA 8270C-SIM** **EPA 1625 (GC/MS)**	**Vista** **EPA 8270C-SIM** **EPA 1625 (HRGC/MS)**
					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.	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

ATTACHMENT 5

Task 1.3 Pre-Loaded LDPE Polymeric Samplers: Data Validation Report

Data Validation Report

Standardizing Polymeric Sampling for Measuring Freely Dissolved Organic Contaminants in Sediment Porewater
ER 201735

Task 1.3 – Pre-Loaded Polyethylene Strip Analyses

Prepared by:

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July 10, 2018

ACRONYMS

%D	percent difference
%D_f	percent drift
%R	percent recovery
%RSD	percent relative standard deviation
CCV	continuing calibration verification
CLP	U.S. EPA Contract Laboratory Program
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
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
NFGs	CLP National Functional Guidelines for Data Review (EPA 2014, 2016 & EPA2017)
ng/g	nanogram per gram
OPR	ongoing precision and recovery
PCB	polychlorinated biphenyl
PE	polyethylene
PFK	perfluorokarosene
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

INTRODUCTION

This report presents and discusses findings of the data validation performed on analytical data for calibration standards submitted to participating commercial laboratories in March 2018, as part of the effort for Task 1.3 identified in the Project Demonstration Plan (USACE *et. al.*, 2018).

Each of the participating laboratories received six polyethylene (PE) strip (submerged into a loading solution) from the Massachusetts Institute of Technology. Three of the PE strips were pre-loaded with PCB performance reference compounds (PRCs) and the other three pre-loaded with PAH PPRCs as 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/g-LDPE)**	**PRCs**	**Target Concentration (ng/g-LDPE)**	**PRCs**	**Target Concentration (ng/g-LDPE)**
^{13}C-PCB 28	35.3	^{13}C-PCB 37	126		
^{13}C-PCB 47	31.2	^{13}C-PCB 47	112	$^{13}C_6$-Phenanthrene	137
^{13}C-PCB 70	36.4	^{13}C-PCB 54	89.2	$^{13}C_6$-Fluoranthene	176
^{13}C-PCB 80	36.0	^{13}C-PCB 111	154	$^{13}C_6$-Chrysene	198
^{13}C-PCB 111	31.5	^{13}C-PCB 138	148	$^{13}C_6$-Indeno[1,2,3-cd]pyrene	173
^{13}C-PCB 141	33.4	^{13}C-PCB 178	155		
^{13}C-PCB 182	35.7				

Notes: ng/g-LDPE – nanogram per gram of LDPE

Upon extraction, the trips were rinsed with DI water, blot or air dried, and eachplaced into a 2 mL amber vial prefilled with hexane, and the vials were 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 in the table on the following page.

Participating Commercial Laboratory	Analytical Method	
	PCB Congeners	PAHs
Analytical Resources, Inc. (ARI) 4611 S. 134th Place, Suite 100 Tukwila, WA 98168	SW846 Method 8270D Modified	SW846 Method 8270D Modified
TestAmerica Laboratories (TestAmerica) 5815 Middlebrook Pike Knoxville, TN 37921	EPA Method 1668C	SW846 Method 8270D Modified EPA Method 1625
SGS AXYS Analytical Laboratory (SGS) 2045 Mills Road West Sidney, BC V8L5X2	EPA Method 1668C	SW846 Method 8270D Modified EPA Method 1625
Battelle Norwell Operations (Battelle) 141 Longwater Drive Suite 202 Norwell, MA 02061	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.

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 may choose the submit the EDDs in Excel or csv. Format. Each laboratory report and EDD are assigned a unique sample delivery group (SDG) number. Laboratory deliverables, after fully validated, are archive in 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
Analytical Resources, Inc.	18C0372	18C0372
TestAmerica Laboratories	140-11025-1	140-11025-1
SGS AXYS Analytical Laboratory	DPWG63691	DPWG63692
Battelle Norwell Operations	DP-18-0065	DP-18-0064

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 1A and 2B***.

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 participation commercial laboratories – SGS and TestAmerica chose to use this methodology 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 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.

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 ≥8,000 throughout the mass range and ≥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 ≤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)

TestAmerica chose to fully follow the EPA Method 1668C initial calibration 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 ≤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.

SGS 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 20%, and RT within 3 seconds between the two analyses. The ICAL met the laboratory SOP requirements.

1.4 Calibration Verification (CCV) and Ongoing Precision and Recovery (OPR)

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 or OPRs met the laboratory control criteria.

1.5 Method Blanks

Method blanks were prepared and analyzed as required by the method. Target PCB PRCs were not detected at or above the estimated detection limits (EDLs).

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) and LCS Duplicate (LCSD)

Since no matrix-specific (*i.e.,* PE 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 carbon-labelled PRCs, the LCS analyzed/reported by the laboratories did not contain the target ^{13}C-labeled PRCs. However, the %R values in LCS were all within the laboratory control criteria.

1.8 Matrix Spike and Matrix Spike Duplicate (MS/MSD)

MS and MSD are not applicable for this calibration standard analysis.

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 SGS), (2) the S/N ratio of each of the two exact m/z's must be greater than or equal to 2.5 (S/N ratio was specified at 3 for SGS), (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 and 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.

2. PCB Congeners by GC/MS - SIM (EPA Method SW8270D-SIM)

Two laboratories – ARI and Battelle chose to use this methodology 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 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 ≤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. Battelle'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 ^{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 ±20%. Battelle's criteria vary slightly from the method requirements. 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)

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 ^{13}C-labelled PRCs, the LCS analyzed/reported by the laboratories did not contain the target PRCs. However, the %R values in LCS were all within the laboratory control criteria.

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. Battelle 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.

Battelle's internal standard recovery could not be compared to those of the mid-point ICAL standard due to a change in final prepared for injection volume (PIV) amounts relative to what was anticipated in the original laboratory workplan. The amounts of internal standard added to the sample extracts differed from those in the ICAL, CCV, and QC analyses. After a thorough examination of the laboratory procedures and instrument printouts, the inconsistent internal standard recovery in this case was deemed to have no significant adverse effects on sample results. Data qualifiers were not assigned in this case.

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.

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 and 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.

3. PAHs by Isotope Dilution GC/MS (EPA Method SW8270D Modified and EPA Method 1625 Modified)

SGS and TestAmerica chose to use this methodology 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)

TestAmerica chose to fully follow the method requirements to establish ICAL for $^{13}C_6$-Labeled PAH PRCs. 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 ±20%. The ICALs were considered valid.

SGS followed their SOP to establish ICAL for the $^{13}C_6$-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) and Ongoing Precision and Recovery (OPR)

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 ±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 TestAmerica. $^{13}C_6$-Phenanthrene was detected at 1.29 ng/g in SGS method blank WG-63480-101. This detection did not meet the ion abundance ratio for analyte identification, and all sample results were greater than 10 times this concentration in method blank. Data quality was not adversely affected.

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 Matrix Spike (MS) and MS Duplicate (MSD)

MS and MSD analyses were not applicable for the calibration standard analysis.

3.8 Laboratory Control Sample (LCS)

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 $^{13}C_6$-labelled PRCs, the LCS analyzed/reported by the laboratories did not contain the target PRCs. However, the %R values in LCS were all within 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 and 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.

4. PAHs by GC/MS - SIM (EPA Method SW8270D-SIM)

ARI and Battelle chose to use this methodology for PAHs analysis. Neither EPA Method 8270D nor laboratory SOPs specified evaluation criteria for $^{13}C_6$-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 ≤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. Battelle'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 ±20% (25% for Battelle). 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) and LCS Duplicate (LCSD)

Since no matrix-specific (*i.e.*, PE 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 $^{13}C_6$-labelled labelled PRCs, the LCS analyzed/reported by the laboratories did not contain the target PRCs. However, the %R values in LCS were all within the laboratory control criteria.

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. Battelle 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.

Battelle's internal standard recovery could not be compared to those of the mid-point ICAL standard due to a change in final prepared for injection volume (PIV) amounts relative to what was anticipated in the original laboratory workplan. The amounts of internal standard added to the sample extracts differed from those in the ICAL, CCV, and QC analyses. After a thorough examination of the laboratory procedures and instrument printouts, the inconsistent internal standard recovery in this case was deemed to have no significant adverse effects on sample results. Data qualifiers were not assigned in this case.

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 and 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.

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.				

Table 2. Definitions of Data Qualifiers

Data Qualifier	Definition
J	The analyte was detected above the reported quantitation limit, and the reported concentration was approximate.
R	The result was rejected.
U	The analyte was analyzed for, but was considered not detected at the reporting limit or reported value.
UJ	The analyte was analyzed for, and the associated quantitation limit was approximate.

REFERENCES

USEPA. 2017. Contract Laboratory Program National Functional Guidelines for Organic Superfund Data Review. Office of Superfund Remediation and Technical Innovation. January 2017. OLEM 9355.0-136. EPA-540-R-2017-002.

USEPA. 2016. *Contract Laboratory Program National Functional Guidelines for High Resolution Methods Data Review*, Office of Superfund Remediation and Technical Innovation, U.S. Environmental Protection Agency. April 2016. USEPA 542-B-16-001.

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.

USEPA. 2009. *Guidance for Labeling Externally Validated Laboratory Analytical Data for Superfund Use.* January 13, 2009. EPA 540-R-08-005.

USEPA. 1996. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Third Edition, December 1996.

USEPA. 1989. *Method 1625C: Semi-volatile Organic Compounds by Isotope Dilution GCMS*. USEPA Office of Science and Technology Engineering and Analysis Division. June 1989.

USACE. 2018. *Demonstration Plan for Standardizing Polymeric Sampling for Measuring Freely Dissolved Organic Contaminants in Sediment Porewater*. U.S. Army Engineer Research Developmental Center, *et. al*. January, 2018. ER201735.

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					
	ALS (EPA 8270D)	**ARI (EPA 8270D)**	**AXYs-SGS (EPA 1668C)**	**Battelle (EPA 8270D Modified)**	**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	Prior to initial calibration. Prior to CCV if system idle for >24 hrs. Criteria same as 8270D.	Same as Method	• Same as Method. • An appropriate lock mass will be monitored for each descriptor and shall not vary by more than □ 20% throughout the respective retention time window.
GC Column Performance Check Prior to ICAL or calibration verification.	N/A	N/A	Same as Method	N/A	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 8270D.	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.	At the beginning and end of 10 injections or each 24 hour period (whichever is more frequent)	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 Modified)**	**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 ≥ ½ limit of quantitation or ≥ 5% of the associated regulatory limit for the analyte or ≥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 *p*g/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.	Analyte concentration in PB should be < MDL and must be < 5xMDL No analytes detected > ½ RL. For common laboratory contaminants, no analytes detected > RL.	Target analytes must be less than estimated maximum levels (EMLs) in SOP Table 4	≤ 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.	Same as Method Blank.	Target analytes must be less than EMLs in SOP Table 4	≤ 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.	70 to 130% recovery vs. SIS 40 to 120% recovery vs. IS	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 ≤ 30%	%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	Within control limits for OPR
Sample Duplicate or MS Duplicate (MSD) (OPTIONAL)	RPD ≤ 30%	RPD ≤ 30%	RPD ≤ 20% (applicable to concentrations ≥10 times the DL)	RPD ≤ 30%	N/A	RPD ≤ 25%

QC Parameters and Performance Frequency	Laboratory and Referenced Analytical Method					
	ALS (EPA 8270D)	**ARI (EPA 8270D)**	**AXYs-SGS (EPA 1668C)**	**Battelle (EPA 8270D Modified)**	**TestAmerica (EPA 1668C)**	**Vista (EPA 1668C)**
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 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	• Same as Method • The absolute retention times of the internal standards shall be within □15 seconds of the retention times obtained during calibration.
Compound Identification	Same as Method	Same as Method)	Same as Method	• Same as 8270D	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 A2 – 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 8720C-SIM** **EPA 1625 (HRGC/MS)**	**Battelle (EPA 8270D Modified)**	**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.	RT window for an analyte is ± 15s from the determined RT of the analyte in the ICAL.	N/A	The RRT of the analyte compared to the RRT of the labeled standard must be within +0.008RRTunits of theRRTs 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 ± 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 ± 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 ≤20% for targets with a labelled analog present and all labelled compounds, ≤ 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 ± 25% of expected value.	• SOP Table 3 lists ICAL concentrations. %RSD must be ≤30% for analytes and internal standards. • Verify ICAL with one second-source standard at mid-point (CS4) concentration. Value for all analytes within ±30% of expected value.	• Calibration standard solutions are presented in SOP Table 2. • The signal to noise ratio (s/n) must be ≥10:1 for all ions monitored. • The percent relative standard deviation for the mean relative response factors must be no greater that 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 Modified)**	**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 ≤ 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 ≤ 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 ±25% of expected values for all targets. • Closing Cal Ver: Concentrations of native compounds must be within ±25% of expected values. • Concentrations of labelled surrogates must be within ±25% of expected values, with any two (2) values allowed to be within ±40%. • Ion ratios for authentic and labelled dibenz[ah]anthracene, indeno[1,2,3-cd]pyrene and benzo[ghi]perylene must be within ±35% of the mid-point of the I-CAL. • All other native analytes and labelled surrogates must be within ±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 ≤ 25% • Grand mean of % difference ≤ 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 ≤ 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 (sin} must be ≥10:1 for all ions monitored. • The percent relative standard deviation for the mean relative response factors must be no greater that 30% for the un-labeled 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.	• 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.	• Recovery of the internal standards must be within 50-150% recovery. • If outside of this criterion, the SIN must be ≥ 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.

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 Modified)**	**TestAmerica** **EPA 8270C-SIM** **EPA 1625 (GC/MS)**	**Vista** **EPA 8270C-SIM** **EPA 1625 (HRGC/MS)**
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.	Analyte concentration in PB should be < MDL and must be < 5 MDL No analytes detected > ½ RL. For common laboratory contaminants, no analytes detected > RL.	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) One per preparation batch of 20 or less samples	See Laboratory QA Plan (LQAP). Reported along with LCS results.	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	Ongoing Precision and Recovery Samples (OPR); SOP Table 3.
Matrix Spike (MS) and MS Duplicate (MSD)	• For matrix evaluation, see LQAP. MS recovery is advisory. • RPD ≤ 30% (MS/ MSD or sample duplicate). Limits are advisory.	• For matrix evaluation, see LQAP. MS recovery is advisory. • RPD ≤ 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 ≤ 30%	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 Modified)**	**TestAmerica EPA 8270C-SIM EPA 1625 (GC/MS)**	**Vista EPA 8270C-SIM EPA 1625 (HRGC/MS)**
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.	40 - 120% recovery	SOP Table 7	N/A
Laboratory Duplicates (Optional)	N/A	N/A	Duplicates must fall within ±20% of the mean (applicable to concentrations ≥10 times the DL). (Note that ±20% of the mean is equivalent to 40 relative percent difference)	≤ 30% RPD	N/A	N/A
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.	• 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 quantitation ion must be present. • The internal standard quantitation ions must be present. • The relative intensities of confirmation ions should agree to within ±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	• 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 RRTs 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,

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 Modified)**	**TestAmerica EPA 8270C-SIM EPA 1625 (GC/MS)**	**Vista EPA 8270C-SIM EPA 1625 (HRGC/MS)**
					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.	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

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: $^{13}C_6$-phenanthrene, $^{13}C_6$-fluoranthene, $^{13}C_6$-chrysene, $^{13}C_6$-indeno(1,2,3-cd)pyrene
- PCBs PRCs (Low-Sensitivity Methods): ^{13}C-labled PCB congeners 37, 47, 54, 111, 138, and 178
- PCBs PRCs (High-Sensitivity Methods): ^{13}C-labled 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 ±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: ±50% of known concentrations for isotopically-labeled laboratory control samples/verification samples (LCS/VS); ±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 ≤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 ≤20% applies only to *intralab* results; *interlab* average and %RSD values were provided for context only. *Interlab* variability could be ±50% of known concentrations for isotopically-labeled laboratory control samples/verification

samples (LCS/VS); ±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 $^{13}C_6$-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 ≤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 $^{13}C_6$-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 ≤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 ≤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 (Pyron 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 ≤20% criteria, except for $^{13}C_6$-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; $^{13}C_6$-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 $^{13}C_6$-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 $^{13}C_6$-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 ≤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 ≤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 ≤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
$^{13}C_6$-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 14 Average	University Laboratory 14 RSD	University Laboratory 72[A] Average	University Laboratory 72[A] RSD	University[B] Laboratory Average	University[B] Laboratory 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	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 ≤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	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	University Laboratory 52[(A)] 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% Low	50% 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	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 ≤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	Ave	RSD	Avg	RSD	Avg	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 ≤20% as guideline for intralab precision evaluation

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.

USEPA. 1996. *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Third Edition*, December 1996.

USEPA. 1989. *Method 1625C: Semi-volatile Organic Compounds by Isotope Dilution GCMS*. USEPA Office of Science and Technology Engineering and Analysis Division. June 1989.

USACE. 2018. *Demonstration Plan for Standardizing Polymeric Sampling for Measuring Freely Dissolved Organic Contaminants in Sediment Porewater.* U.S. Army Engineer Research Developmental Center, *et. al*. February, 2018. ESTCP Project ER201735.

USACE. 2018. *Standardizing Polymeric Sampling for Measuring Freely Dissolved Organic Contaminants in Sediment Porewater. Task 1 Go/No-Go Memorandum, Draft*. U.S. Army Engineer Research Developmental Center, *et. al*. June 13, 2018. ESTCP Project ER201735.