EXECUTIVE SUMMARY

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

ESTCP Project ER-201735

JANUARY 2020

Mandy Michalsen, Alan Kennedy, Gui Lotufo
U.S. Army Engineer Research Developmental Center

Kristen Kerns, Alison Suess
Seattle District, U.S. Army Corps of Engineers

Mingta Lin
Pyron Environmental Inc.

Marc Mills, Matthew Lambert
U.S. Environmental Protection Agency

Danny Reible, Magdalena Rakowska, Adesewa Odetayo
Texas Tech University

Upal Ghosh, Mandar Bokare, Songjing Yan
University of Maryland

Philip Gschwend
Massachusetts Institute of Technology

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ACRONYMS AND ABBREVIATIONS

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<tr>
<td>CERCLA</td>
<td>Comprehensive Environmental Response, Compensation, and Liability Act</td>
</tr>
<tr>
<td>C_free</td>
<td>freely-dissolved organic contaminant concentrations in sediment porewater</td>
</tr>
<tr>
<td>LDPE</td>
<td>low-density polyethylene</td>
</tr>
<tr>
<td>PAH</td>
<td>polycyclic aromatic hydrocarbon</td>
</tr>
<tr>
<td>PCB</td>
<td>polychlorinated biphenyl</td>
</tr>
<tr>
<td>PDMS</td>
<td>polydimethylsiloxane</td>
</tr>
<tr>
<td>PRC</td>
<td>performance reference compound</td>
</tr>
<tr>
<td>µm</td>
<td>micrometers</td>
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ACKNOWLEDGMENTS

This report represents the results and conclusions of a collaborative effort between scientists and engineers at U.S. Army Engineer Research Development Center, Seattle District U.S. Army Corps of Engineers, Massachusetts Institute of Technology, Texas Tech University, University of Maryland Baltimore County, and Pyron Environmental, Inc. All performers contributed to data analysis and interpretation of results presented in this report. In addition to expert technical support during the project, TTU produced excellent instruction videos for using polymeric samplers, which have been posted on YouTube. Commercial laboratory participants in this study included Battelle Memorial Institute, Analytical Resources, Inc., SGS-Axys Enviro Lab, and Test America Lab. This demonstration project was funded by the Environmental Security Technology Certification Program (ESTCP) with the goals of: (1) standardizing polymeric sampling methods for quantifying freely-dissolved concentrations of polycyclic aromatic hydrocarbon and polychlorinated biphenyl in sediment porewater; (2) increasing commercial availability; and (3) promoting technology transfer.

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

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

2.0 TECHNOLOGY DESCRIPTION

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

Isotopically-labeled performance reference compounds (PRCs) are pre-loaded into the organic polymer prior to deployment; the ratio of PRC compound lost to the environment during deployment provides a measure of the polymeric sampler’s progress toward reaching equilibrium with target contaminants in the sediment porewater.
3.0 PERFORMANCE ASSESSMENT

Demonstration Task 1 involved developing a standardized methodology for LDPE and PDMS polymeric sampler preparation and analysis, including how to: 1) prepare polymeric samplers, including cleaning polymers and loading PRCs; 2) expose polymeric samplers to sediment in the laboratory (ex situ); 3) retrieve polymeric samplers from sediment and extract the organic contaminants and PRCs; 4) perform chemical analysis of polymeric sampler extracts; and 5) interpret results and use them to determine the freely-dissolved organic contaminant concentrations present in the sediment’s porewater. Participating laboratories then used the standard method to extract replicate LDPE and PDMS samplers that had been “preloaded” with PRCs by expert academic laboratories. Results showed most labs met accuracy and precision success criteria established for Task 1; exceedances were occasional, not systematic, and thus supported a “Go” decision to proceed to Task 2. Important lessons learned during Task 1 were: (1) LDPE strip area/weight ratios should be measured prior to placing LDPE strips into the PRC loading solution, to ensure target PRC loading is uniformly achieved; and (2) solvent type and quantity variations when preparing the PRC loading solution can impact polymer loadings. The standard method was updated to reflect both lessons learned prior to proceeding to Task 2.
In Demonstration Task 2, participating labs using the standardized polymeric sampling method independently loaded PRCs into the polymeric samplers, then extracted and quantified PRC concentrations in sampler extracts. All labs achieved good precision with PRC loading, however, varied PRC loading solution solvents and solvent/working solution ratios caused differences in the loaded PRC concentrations achieved between labs. The standard method was updated once more to tighten solvent types and ratios used to prepare PRC loading solutions.

In Demonstration Task 3, participating labs using the standardized polymeric sampling method measured PAHs and PCBs in a sediment sample. Each lab used PRC-loaded polymeric samplers in “active” (continuously mixed) and “static” (no mixing) exposures in the laboratory for approximately 30 days. Polymeric sampler results were corrected for progress toward equilibrium as needed using PRC losses. Results between labs were generally in good agreement for target PAH and PCB compounds. Moreover, the polymeric sampler results were in good agreement with the manual porewater extraction method for compounds that could be measured using both methods. Full participation by four commercial laboratories and three academic laboratories met the minimum interlaboratory method validation study requirement for SW846 method application, thus laying the foundation for a future SW846 application. Section 6 (please visit the ER-201735 project page on the SERDP & ESTCP web site to view the full Final Report) of the final demonstration report describes results in detail; Appendix B includes the Standard Operating Methods for polymeric sampler use; and instruction videos for LDPE and PDMS developed under this demonstration are posted online.

4.0 COST ASSESSMENT

The original intent of this project was to provide unit costs from each participating laboratory for polymeric sampler preparation and analysis. However, due to the unique nature of estimating costs for individual project needs, development of a cost per polymeric sampler was not possible. Rather, cost estimates for polymeric sampler preparation and analysis to measure PAHs and PCBs in sediment porewater can be obtained from any of the points of contact listed for the commercial laboratories identified in Table 2-1 of the report. Cost considerations should account for sampler preparation and loading with PRCs, as well as analytical costs for the appropriate analytes. Field blanks and any samplers needed to meet quality assurance/quality control requirements should also be accounted for. Calculations to support conversion of extract concentrations to porewater concentrations may be performed by the commercial laboratory or by a separate contractor familiar with passive sampling. Cost savings can be realized through potential compositing of samplers and use of low-resolution methods. While costs can vary by lab, low resolution analysis for PCBs and PAHs can range from $100 to $300 per sample, and high-resolution methods can cost $600 to $1,000 per sample. A cost estimate for sediment characterization using polymeric samplers at a hypothetical site is provided in Section 7 (please visit the ER-201735 project page on the SERDP & ESTCP web site to view the full Final Report) of the main report; an example scope of work (Appendix H) for acquiring polymeric sampler sediment characterization services is provided as well.
5.0 IMPLEMENTATION ISSUES

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

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

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

Standardized polymeric sampler methods
PDMS TASK 3 INSTRUCTIONS

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

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

Part A: PRC loading on PDMS

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

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

- For PCBs, the total amount of PDMS needed for the loading and sampling exercise is 30 pieces of 5 cm segments resulting in a total fiber length of 150 cm. Choose a vessel to accommodate the PDMS and water-methanol (80:20) inside without much headspace (here 120 mL amber glass bottle is used). For the PDMS length (10 cm) and extract volume (100 µL for high sensitivity and 50 µL for low resolution), calculate the concentration in PDMS. Here, the calculated concentration for each PRC in PDMS is 474 ng/mL for High sensitivity and is 790 ng/mL for Low resolution. Use the PDMS-water partition coefficients (Ghosh et al., 2014) to calculate the concentration in water (only) at equilibrium ($C_{w,eq}$).

- For PAHs, 15 pieces of 5 cm segment (resulting in 75 cm length of fiber) is provided. 120 mL volume of amber vessel is likewise used to accommodate the fiber and water-methanol (80:20) solution. Although 5 cm length PDMS fiber will be required for loading, only 2 cm length will be used for extraction. Here, the 2 cm length fiber per extract volume (500 µL for high sensitivity and 200 µL for low resolution) is required. Therefore, the concentration for each PRC in PDMS is 11844 ng/mL for High sensitivity and is 15792 ng/mL for Low resolution. The additional 3 cm can be used as contingency samplers or as additional replication, if needed.

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

$$C_{\text{initial solution}} = \frac{C_{\text{PDMS}} \times L_{\text{fiber}} \times V_{\text{PDMS}} + C_{w,eq} \times V_{w}}{V_{w}}$$

(1)

where, $C_{\text{PDMS}}$ is the concentration of PRC in PDMS (e.g 474 ng/mL for high sensitivity instruments), $L_{\text{fiber}}$ is the fiber length, $V_{\text{PDMS}}$ is the volume of PDMS coating (0.633 µL/cm for the
fibers provided). $C_{w, eq}$ is the concentration of PRCs in water at equilibrium and $V_W$ is the volume of water:MeOH (100 mL).

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

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

**PCBs – High Sensitivity Instruments**

<table>
<thead>
<tr>
<th>fiber</th>
<th>Water:MeOH (80:20) volume:</th>
<th>100 ml</th>
<th>5 cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>extract solvent (µl):</td>
<td>100 µl</td>
<td>30 No of 5 cm segments</td>
<td></td>
</tr>
<tr>
<td>Total fiber spiked:</td>
<td>150 cm</td>
<td>150 total fiber spiked cm</td>
<td></td>
</tr>
<tr>
<td>PDMS volume (µL/cm):</td>
<td>0.633 µL/cm</td>
<td>Based upon geometry of fibers used</td>
<td></td>
</tr>
<tr>
<td>Fiber length per sample extract:</td>
<td>10 cm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Working standard needed</td>
<td>18 µL</td>
<td>(Calculated in worksheet)</td>
<td></td>
</tr>
</tbody>
</table>

**PCBs – Low Sensitivity Instruments**

<table>
<thead>
<tr>
<th>fiber</th>
<th>Water:MeOH (80:20) volume:</th>
<th>100 ml</th>
<th>5 cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>extract solvent (µl):</td>
<td>50 µl</td>
<td>30 No of 5 cm segments</td>
<td></td>
</tr>
<tr>
<td>Total fiber spiked:</td>
<td>150 cm</td>
<td>150 total fiber spiked cm</td>
<td></td>
</tr>
<tr>
<td>PDMS volume (µL/cm):</td>
<td>0.633 µL/cm</td>
<td>Based upon geometry of fibers used</td>
<td></td>
</tr>
<tr>
<td>Fiber length per sample extract:</td>
<td>10 cm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Working standard needed</td>
<td>30 µL</td>
<td>(Calculated in worksheet)</td>
<td></td>
</tr>
</tbody>
</table>

**PAHs – High Sensitivity Instruments**

<table>
<thead>
<tr>
<th>fiber</th>
<th>Water:MeOH (80:20) volume:</th>
<th>100 ml</th>
<th>5 cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>extract solvent (µl):</td>
<td>500 µl</td>
<td>15 No of 5 cm segments</td>
<td></td>
</tr>
<tr>
<td>Total fiber spiked:</td>
<td>75 cm</td>
<td>75 total fiber spiked cm</td>
<td></td>
</tr>
<tr>
<td>PDMS volume (µL/cm):</td>
<td>0.633 µL/cm</td>
<td>Based upon geometry of fibers used</td>
<td></td>
</tr>
</tbody>
</table>
PAHs – Low Sensitivity Instruments

<table>
<thead>
<tr>
<th>Fiber length per sample extract:</th>
<th>2 cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Working standard needed</td>
<td>247 µL (Calculated in worksheet)</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>fiber</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water:MeOH (80:20) volume: 100 ml</td>
</tr>
<tr>
<td>extract solvent (µL): 200 µL</td>
</tr>
<tr>
<td>Total fiber spiked: 75 cm</td>
</tr>
<tr>
<td>PDMS volume (µL/cm): 0.633 µL/cm</td>
</tr>
<tr>
<td>Fiber length per sample extract: 2 cm</td>
</tr>
<tr>
<td>Working standard needed 330 µL (Calculated in worksheet)</td>
</tr>
</tbody>
</table>

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

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

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

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

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

1. After confirmation of Co (s), porewater concentration is assessed using the pre-loaded PDMS fibers. The PDMS fiber must be enclosed in a mesh bag before insertion into the sediment. A prototype of the mesh bag is provided and each lab is expected to fabricate their mesh bags from the stainless mesh sheet provided. The mesh bag with PDMS is exposed for 28 days. After exposure to the sediment for 28 days is completed, retrieve the fiber from the sediment and mesh bag. Then, wipe the PDMS fiber with deionized water (DI) wetted kimwipes till it is clean. Dry away the moisture using kimwipes. **Note: DI**
wetted wipes are recommended for cleaning the fiber. The use of solvent such as dichloromethane introduces the risk of analyte loss from PDMS fiber. It is also advised to work as quickly as possible to prevent loss of volatile analytes during PDMS fiber processing.

- For PCBs, 10 cm length of PDMS fiber is required per sediment jar and prepared per extract volume to assess target PCB congeners.

- For PAHs, 5 cm length of PDMS is inserted in sediment jar. However, only 2 cm length of this PDMS is sectioned and prepared per extract volume for PAHs analysis.

2. Section the PDMS fiber into smaller lengths (e.g. 1 cm) and transfer into inserts.

3. Add the extract solvent (inclusive of the internal standard, IS). For instance; for HR C13-PCB, 100 µL of final extract solvent (Hexane + IS) is advised for extraction and 50 µL of final extract solvent (Hexane + IS) for LR C13-PCBs. For HR C13-PAHs, 500 µL is required for extraction of 2 cm length PDMS and for LR C13-PAHs, 200 µL is required for the 2 cm length PDMS fiber processed. Note that the sediments to be analyzed are expected to have relatively high levels of PAHs and different volumes may be needed to ensure detection in the calibration range of your instruments. The extra length of PAHs may be useful if your analysis must be repeated.

4. After adding the solvent, vortex for 2 minutes and store at -17°C until analysis. Analyze after a minimum of 24 hours.

5. After analysis of ex-situ samples, convert equipment concentration to concentration on PDMS and then to porewater concentration. The porewater concentration of PAHs or PCBs can be calculated using:

\[ C_{\text{pw,target}} = \frac{C_{\text{PDMS}}}{K_{\text{PDMS-W}}} \]

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

**Part D: Fraction steady state (fss).**

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

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

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

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

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

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

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

To apply the model for estimating FSS and freely dissolved concentration, only the “PRC model”, “cyl_fitted_plot”, “rec_fitted_plot” and “kinetic_fitted_plot” worksheets. The highlighted cells in green in “PRC model” worksheet are variables that can be changed and peculiar to the PDMS fiber parameter and PRC compounds used. For this exercise, the fiber
parameters remain same for all the PRC compounds used. There are three (3) parts that require inputs;

**Steps**

- **Input PDMS fiber parameter.**
  The dimensions of the PDMS fiber being used are input as well as the sampling time or period. The PDMS is assumed to be a cylindrical annulus with an outside and inside dimension along with the time period of the passive sampler deployment. In the section, the dimensions of PDMS fiber are supplied already as 0.025 cm for inner radius and 0.029 cm for outer radius.

- **Input PRCs and its properties.**
  Here, the number of PRCs employed, the corresponding Log Kow, Log KPDMS-W (Ghosh et.al, 2014) and measured fss (PRC) are to be entered in the worksheet “PRC model”.

- **The log value of Kow and KPDMS-W of targets compounds should be entered in worksheets titled “cyl_fitted_plot”, “rec_fitted_plot” and “kinetic_fitted_plot”.** The partition coefficients correlations for PAHs and PCBs from Ghosh et.al, 2014 as shown below are to be supplied as well as the measured fss for the PRC compounds on PRC.

  For PCBs, \[ \log K_f = 0.947 \times \log K_{ow} - 0.017 \]

  For PAHs, \[ \log K_f = 0.725 \times \log K_{ow} + 0.479 \]

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

- **Finally, the FSS for the target compounds are copied from worksheet “cyl_fitted_plot”**. The fss are used to correct for equilibrium of the obtained porewater concentration using the relationship:

  \[ C_{pw, corrected} = \frac{C_{pw, target}}{fss} \]

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

Illustration of the use of the model is available in Appendix A.
Appendix A. Example fitting of FSS for Target PCB/PAHs.

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

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

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

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

4. Copy the fss data from either “cyl_fitted_plot” or “rec_fitted_plot”. But for this exercise the fss for the cylindrical model will be used.
LDPE TASK 3 INSTRUCTIONS

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

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

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

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

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

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

With such preliminary calculations, one can choose “reasonable” PRC loading levels to enhance the chances that both target contaminants and PRCs will be present in extracts at similar levels, thereby facilitating the likelihood that extracts can be analyzed once without needing to rerun for widely disparate injection masses. In the case of Indiana Harbor PAHs, one might choose to load
the PRCs at about 10 ug/0.025 gPE = 400 ug/gPE, while the individual PCB PRCs might be loaded at about 100 ng/0.025 gPE = 4 ug/gPE.

**Part A: PE film Preparations – PRC loading into LDPE fils**

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

2. These \( f_{eq} \) results will then be used:
   a. in the “active” sampling cases to ascertain whether individual PAHs and PCBs were equilibrated between the sediment and the PE films.
   b. in the “passive” sampling cases to adjust the measured concentration of PAHs and PCBs upward to obtain estimates of their concentrations in the PE samplers had deployment times been sufficient to achieve sediment-PE equilibration.

3. Finally, the \( K_{PEw} \) values of each target PAH and PCB will we used to calculated the porewater concentrations of each target contaminant:

\[
    C_{porewater} \ (\text{ng/L}) = \frac{C_{PE \ at \ equilibrium} \ (\text{ng/kg PE})}{K_{PEw}}
\]
ATTACHMENT 1 – POLYMERIC SAMPLER
STANDARD OPERATING PROCEDURES
Standard Operating Procedure for the Preparation, Extraction, and Analysis of Solid Phase Micro-extraction Polydimethylsiloxane Fibers used as a Passive Sampling Technique in Sediment and Surface Waters

1. SCOPE AND APPLICATION
1.1. This method is an operating procedure for handling and loading solid phase micro-extraction polydimethylsiloxane (SPME-PDMS) fibers with performance reference compounds (PRCs) for measuring environmental contaminant concentrations in sediment pore water and overlying water.
1.2. The method is applicable to hydrophobic organic contaminants (HOCs) and the focus herein is on polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs).
1.3. This procedure generates extracts suitable for High Performance Liquid Chromatography (HPLC) and gas chromatography with mass spectroscopy detection GC-MS analysis for priority and alkyl PAHs (PAH-38); and GC-MS/MS and gas chromatography with electron capture detection (GC-ECD) for PCBs.
1.4. The method can be applied in situ (field) or ex-situ (laboratory) but both approaches entail exposing PDMS fibers to the sediments by direct insertion into the sediment for a period of time followed by extraction and chemical analysis.

2. SUMMARY OF METHOD
2.1. A specific length of PDMS-coated fiber is cleaned by consecutive extraction with dichloromethane, hexane, methanol and ultrapure water.
2.2. Performance reference compounds are loaded onto cleaned PDMS fiber in water-methanol (80:20%) solution.
2.3. A shaker table is required to facilitate well-mixing of the PRC spiking solution and contact with the PDMS fibers.
2.4. The PDMS fibers are kept in the PRC solution until preparation for deployment.
2.5. Upon retrieval from a field location or from laboratory sediment, any adhering material is removed from the PDMS fiber with a lint-free damp tissue before segmentation into appropriate lengths along the PDMS fiber to acquire a concentration depth profile into the sediment or into the water column.
2.6. The PDMS fibers are extracted with an appropriate solvent (i.e., acetonitrile or hexane) overnight. The PDMS fibers are removed from the extract before analysis via HPLC or GC methods.

3. INTERFERENCES
3.1. In general, the use of PDMS as an extracting phase limits the amount of extraneous compounds from the sample and provides a phase that is easily extracted. This limits the
amount of sample cleanup necessary as well as the need for surrogates to test extraction efficiency. However, both may be necessary under some conditions.

3.2. PDMS fibers can become contaminated from atmospheric and surficial sources, and therefore techniques to limit the amount of undesired exposure must be followed.

3.3. Biofilms, adhering sediment, or chemical residues like NAPL residues can be removed by wiping the PDMS fiber with a MilliQ water-wetted Kimwipe®

3.4. Method detection limits are related to compound hydrophobicity and, therefore, the method must be used with caution when analyzing relatively volatile constituents which exhibit greater losses and relatively poor detection limits.

3.5. Sediments that are contaminated with oil or other non-aqueous phase liquid (NAPL) will greatly complicate the interpretation of the results. The NAPL can absorb directly onto the PDMS and will also affect the partitioning into water. Use of the technique in NAPL-contaminated sediments should not be expected to provide quantitation on mobile phase contaminants.

4. APPARATUS AND MATERIALS

4.1. Washing, PRC loading, and storage vessel (250 mL, amber/clear glass depending on the analytes of interest) with foil-lined cap.

4.2. Solid phase micro-extraction polydimethylsiloxane fibers – commercially available through suppliers like Polymicro Technologies™ (Molex, Phoenix, AZ, USA) and Fiberguide (Stirling, NJ, USA).

4.3. Extraction vessels – 2 mL amber (for PAHs) or clear glass (for PCBs) autosampler vials.

4.4. 300 μL glass inserts with springs for ultra-low solvent volumes.

4.5. PTFE/Silicone/PTFE screw caps and PTFE lined solid tops for long-term storage.

4.6. Kimwipes®

4.7. Food-grade aluminum foil

4.8. Tweezers

4.9. Ceramic Cutter or nippers

4.10. Shaker table or overhead tumbler

5. REAGENTS

5.1. Dichloromethane (i.e., methylene chloride, CH₂Cl₂)

5.2. Hexane

5.3. Acetonitrile

5.4. Methanol

5.5. MilliQ Water (Barnstead, GenPure Pro) or equivalent

5.6. Research grade deuterated or ¹³C labeled compounds as performance reference compounds (PRCs) from Ultra Scientific and Cambridge Isotope Laboratories (Appendix 1).

5.7. Research grade deuterated or ¹³C labeled compounds as surrogates (Appendix 1) or internal standards for GC-MS or GC-MS/MS analysis: d-acenaphthene, d-phenanthrene and d-perylene for PAHs (working standard concentration of 1000 ng/mL in hexane),
and $^{13}$C mix containing PCBs 9/118/188 (working standard concentration of 1000 ng/mL in hexane).

6. **HANDLING AND PRESERVATION**

6.1. All personnel should wear nitrile or powder-free gloves when handling the sampling devices and the PDMS fiber.

6.2. Clean PDMS should be stored in clean, sealed, glass vessels.

6.3. Solvent rinsed tweezers/column cutter or nippers should be used when handling the PDMS.

6.4. The loaded PDMS fibers should be stored in the PRC solution until further use.

7. **PROCEDURE**

7.1. PDMS fiber is purchased from Polymicro Technologies™ on a spool with a nominal PDMS coating of 35 μm. Other thicknesses can be used depending on application. The fiber is cut into desired lengths, for example 5 cm, which can be easily inserted in small vials with sediment. The 5 cm lengths can be easily cut into smaller segments (i.e., 2+2+1 cm) for extraction and processing and may also provide replication and/or contingency in situations when 2 cm lengths are used for analysis and data interpretation. Details on the quantity of fiber per sampling exercise are provided in Appendix 2.

7.2. PDMS washing procedure

7.2.1. The cut PDMS fibers are placed in the 120 ml glass vessel and cleaned by washing consecutively by soaking in three solvents (i.e., dichloromethane (2x), hexane (2x) and methanol (2x)) for 30 minutes each on a shaker table. Larger vessels and volumes are recommended for large sampling efforts. Care should be taken to avoid PDMS breakage during washing with solvents especially if the vessel is filled with solvent half way. Therefore, gentle shaking is recommended or unobstructed movement of the PDMS in the washing vessel. After the methanol solvent wash, the fibers are rinsed with MilliQ water at least three times. The rinsed PDMS fibers are then blotted dry with lint-free tissues.

7.2.2. A portion of the cleaned fibers should be checked for residual contamination by pipetting 1 mL of clean hexane or equivalent solvent down the fiber length, collecting the solvent at the bottom of the PDMS fiber, and analytically checking for contamination. The cleaning process is repeated until any analytes of concern are not detected in the test solvent.

7.2.3. The cleaned PDMS fibers should be stored closed in the glass vessel until further use.

7.3. Loading of PDMS with performance reference compounds

7.3.1. PRCs should be chosen to assess kinetic dissipation/uptake rates during field deployments. PRCs are loaded onto the PDMS before deployment.

7.3.2. 100 mL of spiking solution (water and 20% methanol) is placed in the glass vessel with cleaned PDMS. Deuterated/C$^{13}$ labeled versions of the analytes of interest
Appendix 1 at working concentration of 2500 ng/ml in acetone or methanol are
added to the water-20% methanol solution.

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

7.3.3. The spiking solution with PDMS is agitated (approximately 120-130 strokes per
minute) using a shaker table for a minimum of 7 days with deuterated PAHs and a
minimum of three weeks with C\textsubscript{13} labeled PCBs before using the PRC loaded
PDMS. Longer equilibration times may be required for thicker samplers. Note, with
minimal headspace the movement of PDMS during 1D agitation at 130 strokes per
minute is not vigorous even at high mixing rates. If fewer than 130 strokes is used,
longer PDMS exposure to PRC solution is required. For example, 130 strokes
agitation achieves acceptable loading of PCBs in 3 weeks but 60 strokes agitation
may require 5 weeks. Alternatively, effective loading of PRCs onto PDMS within 3
weeks can be achieved using a roller mixer with ca. 45-50 rpm. A horizontal
placement of the loading vessel in a tumbler and mixing at 45 rpm may also be used
but in this case the vessel should allow unobstructed movement of the PDMS to
avoid breakage. Overhead tumbling of the vessel is not recommended as PDMS at
both ends may break.

7.3.4. The loaded PDMS fibers should be stored in the PRC solution until further use.

7.3.5. PRC loaded PDMS fibers should be used for exposure into sediments and a subset
of the simultaneously prepared fibers should be analyzed for initial PRC
concentrations in the fibers via the methods in Section 7.7. At least 6 PRC loaded
PDMS fibers should be analyzed for initial PRC concentrations.

7.4. Deployment of PDMS in sediment samples

7.4.1. The loaded PDMS fiber (5 cm) is withdrawn from the PRC solution using clean
tweezers, rinsed with MilliQ water and liquids blotted on Kimwipes® and allowed
to evaporate
7.4.2. The 5 cm loaded PDMS fiber is deployed in sediment and the sediment placed on a shaker table if desired. A shaker tool can speed equilibration if the sediment contains sufficient moisture (e.g. above the liquid limit).

7.5. Retrieval

7.5.1. All surfaces that the PDMS fiber will come into contact with must be covered with clean food grade aluminum foil.

7.5.2. Hexane or equivalent (other solvents can be selected based upon analytes of interest) rinsed tweezers and ceramic column cutters are used for segmentation of the PDMS fiber.

7.5.3. All laboratory and field personnel must wear nitrile or powder-free gloves when handling the PDMS fiber.

7.5.4. After 21-28 d the vials are removed from the shaker table and the 5 cm PDMS fiber is carefully withdrawn from the sediment. Any adhering sediment, particles, biofilm, or residue is removed from the PDMS fiber using a MilliQ water wetted Kimwipe®. After cleaning, the fiber should be blotted dry prior to segmentation and extraction.

7.5.5. Segmentation of the 5 cm PDMS fiber should be performed as quickly as possible to minimize volatilization of more volatile analytes of concern.

7.5.6. The 5 cm PDMS fibers are segmented using a ceramic column cutter into 2+2+1 cm lengths.

7.6. Extraction: the 2+2+1 cm fiber segments are then transferred to 2 mL amber vials with glass inserts prefilled with 250 μL of the appropriate solvent depending upon the subsequent analysis. The solvent volume in the insert should be sufficient for the complete immersion of the PDMS fiber segments. Extraction can also be into a greater volume (e.g., amber vial without insert) if needed, for subsequent processing. The sample can also be reduced in volume by solvent evaporation to concentrate the sample for improvement of detection.

7.6.1. Examples of solvent extract volumes: 250 μL for 5-cm segments of PDMS fiber with a PDMS thickness of greater than or equal to 30 μm and 100 μL for 1-cm segments of PDMS fiber with a PDMS thickness of 10 μm.

7.6.2. The PDMS fiber segments are left in the solvent overnight and stored at -17°C to avoid any losses if employing a volatile solvent (e.g. hexane).

7.6.3. Following overnight extraction, vials with inserts containing SPME segments and solvent are sonicated for 1 min to ensure homogenization.

7.6.4. A portion of the extract should be transferred to a new vial with insert and internal standard (IS) should be added at target concentration before analysis. Extracts in GC vials without inserts can be vortexed before transfer and IS addition.

7.6.5. Priority pollutant PAHs can be analyzed without cleanup steps by EPA Method 8310 or 8270 and PCB congeners by EPA Method 8082/8270 or modified Method 1668. Cleanup steps can be optional when complex matrices are analyzed.
8. QUALITY CONTROL & METHOD PERFORMANCE

8.1. PRC loading before deployment: at t=0 i.e. after withdrawing PDMS from PRC solution: 6 samples of loaded PDMS (5 cm segments) must be collected from different parts of the PDMS fiber, extracted, and analyzed prior to deployment (see section 7.3.5).

8.2. Blanks

8.2.1. Solvent Blanks: Solvent blanks will be analyzed at the time of filling the inserts with designated solvent. If these contain significant levels of contamination, new vials with inserts will be filled with a separate source and the process will be repeated.

10. REFERENCES


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

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

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

<table>
<thead>
<tr>
<th>Method 8270</th>
<th>Method 1668</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PRCs</strong></td>
<td><strong>PRCs</strong></td>
</tr>
<tr>
<td>PCBs #</td>
<td>PAHs</td>
</tr>
<tr>
<td>Low Sensitivity</td>
<td>Low Sensitivity</td>
</tr>
<tr>
<td>C13-37</td>
<td>C13-PHENANTHRENE</td>
</tr>
<tr>
<td>C13-47</td>
<td>C13-FLUORANTHRENE</td>
</tr>
<tr>
<td>C13-54</td>
<td>C13-CHRYSENE</td>
</tr>
<tr>
<td>C13-111</td>
<td>C13-INDENO(123-cd)PYRENE</td>
</tr>
<tr>
<td>C13-138</td>
<td></td>
</tr>
<tr>
<td>C13-178</td>
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<table>
<thead>
<tr>
<th>Example surrogates</th>
<th>Example surrogates</th>
</tr>
</thead>
<tbody>
<tr>
<td>d10-anthracene</td>
<td>C13-52</td>
</tr>
<tr>
<td>d10-fluoranthene</td>
<td>C13-101</td>
</tr>
<tr>
<td>d12-benz(a)anthracene</td>
<td>C13-138</td>
</tr>
<tr>
<td></td>
<td>C13-153</td>
</tr>
<tr>
<td></td>
<td>C13-180</td>
</tr>
<tr>
<td></td>
<td>C13-209</td>
</tr>
</tbody>
</table>

Appendix 2. Example spreadsheet for calculating spiking of Performance Reference Compounds onto PDMS.

**Step 1:** Indicate the desired concentration of PRCs in extract after analysis to meet the requirements of detection. Here, an example with 30 ng per mL of extract (high resolution) and 150 ng/mL (low resolution) is provided. Note, after exposure of the loaded PDMS with sediment or overlying water, part of the PRCs will leave the fiber resulting in lower concentrations for analysis. Therefore, one may design the loading calculation in such way that the initial concentration of PRCs in the extract and thus fiber is a factor of 2-3 higher to meet the requirements for detection after PRCs exposure. For example, if the initial concentration of PCB-28 in the PDMS extract is 30 ng/mL and approximately 80% of the compound is lost from the PDMS within the exposure timeframe (28 days), the expected concentration in the extract will be 6 ng/mL after 28 d.
Step 2: Indicate the length of PDMS per sample (extract). Here, we have chosen 10 cm per sample extract and six replications. Therefore, the total amount of PDMS needed for the loading and sampling exercise is 12 pieces of 5 cm segments resulting in a total fiber length of 60 cm. Choose a vessel to accommodate the PDMS and water-methanol (80:20) inside without much headspace (here 120 mL amber glass bottle is used). For the PDMS length (10 cm) and extract volume (250 µL), calculate the concentration in PDMS. Here, the calculated concentration in PDMS is 1184 ng/mL. Use the PDMS-water partition coefficients (Ghosh et al., 2014) to calculate the concentration in water (only) at equilibrium (C_{w,eq}).

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

$$C_{initial \ solution} = \frac{C_{PDMS} \times L_{fiber} \times V_{PDMS} + C_{W,eq} \times V_{W}}{V_{W}}$$

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

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

$$V_{working \ stand} = \frac{C_{initial \ solution} \times V_{W:M}}{C_{working \ stand}}$$

The calculated volume of working standard is 18 µL. The $C_{initial \ solution}$ concentration of PRCs is 0.455 ng/mL and $C_{working \ stand}$ is the concentration of PRCs in working standard (2500 ng/ml) in acetone. The working standard (2500 ng/ml) is prepared by diluting the stock solution (40000 ng/ml). Here we used 125 uL of stock solution and diluted with acetone to a final volume of 2000 µL. Nonane is miscible in acetone. The fraction of nonane in the prepared working standard is 0.06. Caution should be taken in preparing working standards because of the potential for solvent incompatibility. The solvent ratios employed here lead to homogeneous solutions. Use of different solvents or different solvent amounts may lead to phase separation in the preparation of the working standard or the loading solution which can lead to an inability to achieve targeted PRC concentrations.
<table>
<thead>
<tr>
<th>Fiber Parameters</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>S75</td>
<td>core diameter with PDMS coating (µm)</td>
<td>Water:MeOH (80:20) volume: 100 ml</td>
</tr>
<tr>
<td>S50</td>
<td>core diameter without PDMS coating (µm)</td>
<td>5 cm</td>
</tr>
<tr>
<td>0.001806416</td>
<td>area (m²)</td>
<td>extract solvent (µL): 250 µL</td>
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<tr>
<td>6.33227E-08</td>
<td>volume (m³)</td>
<td>12 No of 5 cm segments</td>
</tr>
<tr>
<td>3.50543E-05</td>
<td>length (m) i.e. coating thickness</td>
<td>Fiber length per sample extract: 10 cm</td>
</tr>
<tr>
<td>35.05</td>
<td>length (µm) i.e. coating thickness</td>
<td></td>
</tr>
</tbody>
</table>

**CALCULATIONS FOR PRC LOADING --> individual compound spiking**

\[
\log K_{PDMS-W} = 0.947 \log K_{ow} - 0.017 \text{ (PCB)}
\]

\[
\log K_{PDMS-W} = 0.725 \log K_{ow} + 0.479 \text{ (PAH)}
\]

<table>
<thead>
<tr>
<th>High Res PCBs</th>
<th>logKow (Hawker and Connell, 1988)</th>
<th>logKPDMS-W (Ghosh et al., 2014)</th>
<th>Final Concentration in solvent extract ng/mL</th>
<th>mass in solvent µg</th>
<th>Conc on PDMS ng/ml</th>
<th>Conc in water (eq) ng/mL</th>
<th>fraction in PDMS in water only</th>
<th>Initial concentration ng/mL</th>
<th>volume of working standard needed based on log KPDMS-W ml</th>
<th>volume of working standard needed based on log KPDMS-W µl</th>
<th>volume of working standard in acetone ng/mL</th>
<th>working standard in nonane ng/mL</th>
<th>stock solution in nonane ng/mL</th>
<th>volume of stock solution ml</th>
<th>volume of stock solution µl</th>
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<tbody>
<tr>
<td>C13-28</td>
<td>5.67</td>
<td>5.35</td>
<td>30</td>
<td>0.0075</td>
<td>1184</td>
<td>0.00526</td>
<td>0.9884</td>
<td>0.455</td>
<td>0.02</td>
<td>18.2</td>
<td>2500</td>
<td>40000</td>
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<tr>
<td>C13-47</td>
<td>5.85</td>
<td>5.52</td>
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<td>0.0075</td>
<td>1184</td>
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</tr>
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<td>30</td>
<td>0.0075</td>
<td>1184</td>
<td>0.00166</td>
<td>0.9963</td>
<td>0.452</td>
<td>0.02</td>
<td>18.1</td>
<td>2500</td>
<td>40000</td>
<td>0.125</td>
<td>125</td>
<td></td>
</tr>
<tr>
<td>C13-80</td>
<td>6.48</td>
<td>6.12</td>
<td>30</td>
<td>0.0075</td>
<td>1184</td>
<td>0.00090</td>
<td>0.9980</td>
<td>0.451</td>
<td>0.02</td>
<td>18.0</td>
<td>2500</td>
<td>40000</td>
<td>0.125</td>
<td>125</td>
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<tr>
<td>C13-111</td>
<td>6.76</td>
<td>6.38</td>
<td>30</td>
<td>0.0075</td>
<td>1184</td>
<td>0.00049</td>
<td>0.9989</td>
<td>0.450</td>
<td>0.02</td>
<td>18.0</td>
<td>2500</td>
<td>40000</td>
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<tr>
<td>C13-141</td>
<td>6.82</td>
<td>6.44</td>
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<td>0.00043</td>
<td>0.9990</td>
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<td>0.02</td>
<td>18.0</td>
<td>2500</td>
<td>40000</td>
<td>0.125</td>
<td>125</td>
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<tr>
<td>C13-182</td>
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<td>1184</td>
<td>0.00019</td>
<td>0.9996</td>
<td>0.450</td>
<td>0.02</td>
<td>18.0</td>
<td>2500</td>
<td>40000</td>
<td>0.125</td>
<td>125</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Color Legends</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume of solvent for extract</td>
<td>Fiber length per sample extract</td>
</tr>
</tbody>
</table>

**Target extract concentration**

**Target concentration on PDMS**

**Volume of working standard**

**Concentration of working standard**

\[
\text{fraction of nonane in working std} = 0.06 (-)
\]

\[
\text{fraction of nonane in water:MeOH spiking solution} = 0.00125 (-)
\]
Standard Operating Procedure for the Preparation of Polyethylene (PE) Used for Passive Sampling

Philip M. Gschwend and John K. MacFarlane
Dept. of Civil and Environmental Engineering
Massachusetts Institute of Technology
Cambridge, MA 02139

ESTCP Project Number: ER-201735

October 2017
Standard Operating Procedure for the Preparation of Polyethylene (PE) 
Used for Passive and Active Sampling of HOCs

SCOPE AND APPLICATION

1.1 This method describes a procedure for preparing and handling polyethylene (PE) films that will be cut into strips and deployed to sample hydrophobic organic compounds (HOCs) in environmental media.

1.2 This method generates PE that can be deployed for passive or active (i.e., using mixing) sampling of HOCs in atmospheric, aqueous, or sediment-porewater systems.

1.3 PE that is prepared by this method is suitable for \textit{ex situ} laboratory or \textit{in situ} field deployment.

SUMMARY OF METHOD

2.1 A known mass of low density polyethylene (LDPE) sheet, usually gram quantities, is cleaned by sequentially extracting with methylene chloride, methanol, and ultrapure water in a closed glass vessel.

2.2 Clean PE is equilibrated with performance reference compounds (PRCs) dissolved in water or methanol-water (see Appendix 1 for possible PRCs).

2.3 PRC-impregnated PE is stored in water or aqueous PRC loading solution in glass vessels until use.

2.4 Shortly before deployment, the PE is cut into suitably sized strips and prepared for deployment.

2.5 During deployment, the PE is exposed to the environmental medium of concern. HOCs in the medium diffuse into the PE, while PRCs diffuse out.

INTERFERENCES

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

APPARATUS AND MATERIALS

4.1 Extraction vessels: 1-L glass bottles or screw capped jars (foil-lined lids).

4.2 Storage vessels: bottles with glass stoppers or amber jars (foil-lined lids).

4.3 Bottle/jar tumbler, shaker table, bottle roller, or equivalent.

4.4 Low density polyethylene (LDPE): commercial grade, large sheet at 25\textmu m (1 mil) or 51\textmu m (2 mil) thickness. The thickness is chosen to be strong enough to withstand stresses during deployment (e.g., insertion into sediment), but thin enough to exchange a significant fraction (e.g., >20\%) of its PRCs during the deployment time to be used.

4.5 Food grade aluminum foil (solvent cleaned and/or combusted to remove any organic residue from foil production)
4.6 Stainless steel forceps
4.7 Teflon (or similar non-contaminating material) cutting board

REAGENTS
5.1 Methylene chloride, CH₂Cl₂, pesticide grade or equivalent
5.2 Methanol, CH₃OH, pesticide grade or equivalent
5.3 Organic-free reagent water (as defined in SW-846 Chapter 1)
5.4 Research grade PRCs certified >98+% pure.

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

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

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

7.1.1 Methylene chloride is placed into the extraction vessel, and the PE strips are immersed in the container for 24 hours to enable time for diffusive transfers
out of the PE. The initial methylene chloride extract is discarded and a second methylene chloride extraction is performed for 24 hours. The second methylene chloride extract is discarded and replaced by methanol to remove methylene chloride from the PE. Methanol immersion is also done for 24 hours. The initial methanol extract is discarded and followed by a second methanol soak for 24 hours. Finally, the second methanol extract is discarded and the PE undergoes three 24-hour soaks with organic-free reagent water (within the same extraction vessel) to remove residual methanol from the PE.

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

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

$$f_{PE} = \frac{(r_{PEw})(K_{PEw})}{(1 + r_{PEw}K_{PEw})}$$

$$= \frac{(1 \text{ gPE}/1000 \text{ mLw})(10^5\text{mLw/gPE})}{[1 + (1 \text{ gPE}/1000 \text{ mLw})(10^5\text{mLw/gPE})]}$$

$$= 0.99$$

or 9.9 ug of the PRC is in the PE at equilibrium (i.e., 9.9 ugPRC/gPE)

and the water concentration has dropped to 0.1 ugPRC/Lw.

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

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

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

\[
\text{Concentration in PE (ng/kg)} \sim K_{PE-water} \ast \text{concentration in (pore)water (ng/L)}
\]

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

7.3.3 Aqueous PRC Loading: A solvent-cleaned and dried glass container is filled with ultrapure water that has been spiked with known concentrations of PRCs (e.g., based on calculations like those shown in Appendix 2). A known mass of pre-cleaned PE is then added and weighted to insure complete PE submersion.
and full exposure of PE surfaces to the solution. The vessel is agitated to remove any air pockets/bubbles adhering to the submerged PE. Equilibration times vary for different PRC/PE thickness combinations and the PE-water phase ratio. For PAHs and PCBs, one should use at least 30 days to insure homogeneous distributions of the PRCs throughout the entire thickness of the PE film unless faster equilibration has been confirmed with PRC/PE specific time-course testing of PRC concentrations in the PE or by showing that concentrations of PRCs are the same for films of different thicknesses, but the same masses. Generally, PE is stored in the aqueous PRC solution until that PE is to be deployed.

7.3.4 Methanol-Aided PRC Loading: A solvent-cleaned and dried glass container is filled with an 80:20 mixture of pesticide grade methanol and ultrapure water (e.g., Booij et al. 2002). This solvent mixture is then spiked with known concentrations of PRCs (e.g., see calculations in Appendix 2). Commonly, 13C-labelled PRCs are obtained dissolved in solvents like nonane. If one adds too much of a solvent like nonane to 80:20 methanol:water (e.g., >10 mL/L), then one will see nonane floating on the PRC loading solution or a cloudy solution if shaking is employed. When PE strips are added to such a multiphase loading solution, the immiscible solvent is likely to (a) accumulate in the PE and change the polymer’s affinity for the PRCs and/or (b) remain as a separate phase competing for the PRCs (note that even 1 mL of separate phase nonane is virtually the same volume as 1 g of PE strips, perhaps causing comparable partitioning of the PRCs into this solvent and the LDPE strips.) Consequently, one should be sure to look for the occurrence of a separate solvent phase when spiking the PRC loading solution. For the particular case of nonane, adding less than about 2 mL nonane per liter of the methanol:water loading solution appears to be acceptable. Spiking volumes of other solvents (e.g., hexane) should be tested for their miscibility with the PRC loading solution before use.

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

QUALITY CONTROL

8.1 PRC Loading Validation: At least six representative samples of prepared PE should be collected from different parts of the PRC-loaded PE (e.g., 1 cm x 10 cm x 25 um
pieces weighing about 25 mg each), extracted, and analyzed prior to field deployment to validate that the PRC concentrations are consistent with their intended loadings and these PRCs have uniform concentrations in a batch of PE.

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

METHOD PERFORMANCE

9.1 PRC data, obtained from PE samples collected from >six pieces of the prepared PE, should be consistent within about ±10% (i.e., 100 x standard deviation / mean).

9.2 Target HOC concentrations should be undetectable in the prepared PE at the levels of interest. For example, assuming a target HOC with a level of interest at 10 pg/L = 10⁻⁵ ng/mL_water and having $K_{PE\_water} = 10^5$ mL_water/g PE , requires background below:

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

REFERENCES


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

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

<table>
<thead>
<tr>
<th>Targets: PAHs</th>
<th>Method: EPA 8270d with GCMS-SIM</th>
</tr>
</thead>
<tbody>
<tr>
<td>PRCs</td>
<td>13C6-phenanthrene</td>
</tr>
<tr>
<td>Surrogates</td>
<td>d10-anthracene</td>
</tr>
<tr>
<td>Injection Standards</td>
<td>d10-acenaphthene</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Targets: PCBs</th>
<th>Method: EPA 8270d with GCMS-SIM</th>
</tr>
</thead>
<tbody>
<tr>
<td>PRCs</td>
<td>(^{13})C PCB-37</td>
</tr>
<tr>
<td>log (K_{ow})</td>
<td>5.68</td>
</tr>
<tr>
<td>number Cl's</td>
<td>3</td>
</tr>
<tr>
<td>Surrogates</td>
<td>(^{13})C PCB-3</td>
</tr>
<tr>
<td>number Cl's</td>
<td>1</td>
</tr>
<tr>
<td>Surrogates</td>
<td>(^{13})C PCB-180</td>
</tr>
<tr>
<td>number Cl's</td>
<td>7</td>
</tr>
<tr>
<td>Injection Standards</td>
<td>(^{13})C PCB-19</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Targets: DDTs</th>
<th>Method: GCMS</th>
<th>Detection Limit ~ 200 pg / 100 mg PE</th>
</tr>
</thead>
<tbody>
<tr>
<td>PRCs</td>
<td>(^{13})C 2,4'-DDE</td>
<td>(^{13})C 2,4'-DDD</td>
</tr>
<tr>
<td>Surrogates</td>
<td>(^{13})C-PCB1111</td>
<td>(^{13})C-PCB153</td>
</tr>
<tr>
<td>Injection Standards</td>
<td>d6 PCB 77</td>
<td>(^{13})C PCB 105</td>
</tr>
</tbody>
</table>
Appendix 2. Example of spreadsheet used to design a PRC solution needed to impregnate PE for PCB sampling.

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

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

\[
\text{fraction in PE} = 1 - \left(\frac{1}{1 + \text{Mass}_{\text{PE}} \cdot K_{\text{PE-solution}} / \text{Volume}_{\text{solution}}} \right) \quad \text{Eq. 1}
\]

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

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

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

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

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

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

\[
\text{fraction of each PRC remaining in PE after a single leach step} = 1 - \left(\frac{1}{1 + K_{\text{PE-H₂O}} \cdot \text{Mass}_{\text{PE}} / \text{Volume}_{\text{H₂O}}} \right) \quad \text{Eq. 3}
\]
For example, in the case of congener #52, one finds 99.66% of the PRC remains in the PE after the first leach (see below). Two additional leaches lower this to 99.32% and 98.98%, respectively. More hydrophobic congeners are leached even less in this case.

Example spreadsheet calculation for spiking PCB PRCs into LDPE from a 80:20 methanol-water solution.

<table>
<thead>
<tr>
<th>PCB congener</th>
<th>log KPE MeOH:water (ref 1)</th>
<th>log Kow (ref 2)</th>
<th>log KPE (80:20)</th>
<th>log Kow (ref 2)</th>
<th>log KPE MeOH:water (80:20)</th>
<th>fraction of each PRC in PE at equilib' (Eq. 1)</th>
<th>log Kpew = 1.14*log Kow-1.14 (ref 3)</th>
<th>mass of PE (g)</th>
<th>PRC in PE after solution concentration (ng/mL) in order to get</th>
<th>PE mass (g)</th>
<th>1st leach (Eq. 3)</th>
<th>2nd leach (Eq. 3)</th>
<th>3rd leach (Eq. 3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0.20</td>
<td>4.65</td>
<td>52</td>
<td>5.84</td>
<td>0.97</td>
<td>5.8%</td>
<td>11.3</td>
<td>5.22</td>
<td>0.997</td>
<td>0.993</td>
<td>0.990</td>
<td>1000 mL water</td>
<td>1000 mL water</td>
</tr>
<tr>
<td>29</td>
<td>1.05</td>
<td>5.6</td>
<td>101</td>
<td>6.38</td>
<td>1.26</td>
<td>10.7%</td>
<td>6.1</td>
<td>6.13</td>
<td>minimal leaching back into water</td>
<td>1.00</td>
<td>1.000</td>
<td>1000 mL water</td>
<td>1000 mL water</td>
</tr>
<tr>
<td>155</td>
<td>1.29</td>
<td>6.41</td>
<td>153</td>
<td>6.92</td>
<td>1.55</td>
<td>18.8%</td>
<td>3.5</td>
<td>6.75</td>
<td>1.000</td>
<td>1.00</td>
<td>1000 mL water</td>
<td>1000 mL water</td>
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<tr>
<td>204</td>
<td>1.67</td>
<td>7.3</td>
<td>180</td>
<td>7.36</td>
<td>1.78</td>
<td>28.4%</td>
<td>2.3</td>
<td>7.25</td>
<td>1.000</td>
<td>1.00</td>
<td>1000 mL water</td>
<td>1000 mL water</td>
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<tr>
<td>28</td>
<td>5.67</td>
<td>0.88</td>
<td>4.8%</td>
<td>13.8</td>
<td></td>
<td></td>
<td></td>
<td>5.32</td>
<td>0.995</td>
<td>0.990</td>
<td>0.985</td>
<td>minimal leaching back into water</td>
<td>1.00</td>
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<tr>
<td>47</td>
<td>5.85</td>
<td>0.98</td>
<td>5.9%</td>
<td>11.2</td>
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<td></td>
<td></td>
<td>5.53</td>
<td>minimal leaching back into water</td>
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<td>1.000</td>
<td>1000 mL water</td>
<td>1000 mL water</td>
</tr>
<tr>
<td>111</td>
<td>6.76</td>
<td>1.46</td>
<td>16.0%</td>
<td>4.1</td>
<td></td>
<td></td>
<td></td>
<td>6.57</td>
<td>1.000</td>
<td>1.00</td>
<td>1000 mL water</td>
<td>1000 mL water</td>
<td>1000 mL water</td>
</tr>
<tr>
<td>153</td>
<td>6.92</td>
<td>1.55</td>
<td>18.8%</td>
<td>3.5</td>
<td></td>
<td></td>
<td></td>
<td>6.75</td>
<td>1.000</td>
<td>1.00</td>
<td>1000 mL water</td>
<td>1000 mL water</td>
<td>1000 mL water</td>
</tr>
<tr>
<td>178</td>
<td>7.14</td>
<td>1.66</td>
<td>23.3%</td>
<td>2.8</td>
<td></td>
<td></td>
<td></td>
<td>7.00</td>
<td>1.000</td>
<td>1.00</td>
<td>1000 mL water</td>
<td>1000 mL water</td>
<td>1000 mL water</td>
</tr>
</tbody>
</table>

use to find following correlation:

\[ \log K_{PE-(80:20)\text{MeOH:water}} = 0.532 \pm 0.094 \times \log K_{ow}(\text{Hawker}) - 2.133 \pm 0.577 \]

PE mass = 5.3 geom ave

N = 4, R² = 0.94, S.E. 0.18

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

Philip M. Gschwend and John K. MacFarlane
Dept. of Civil and Environmental Engineering
Massachusetts Institute of Technology
Cambridge, MA 02139

ESTCP Project Number: ER-201735

October 2017
Standard Operating Procedure
for the Extraction and Analysis of Polyethylene (PE) Used
in Polyethylene Devices (PEDs)

SCOPE AND APPLICATION

1.1 This method describes procedures for chemical analysis of contaminants contained in polyethylene (PE) that has been deployed in passive samplers used to assess hydrophobic organic compounds (HOCs) in environmental media.

1.2 This procedure generates extracts suitable for High Resolution Gas Chromatography/Mass Spectrometry (GCMS) analysis.

1.3 This extraction procedure is applicable to PE used in laboratory (ex situ) - or field (in situ)-exposed usage.

1.4 Procedures for loading PE with PRCs are discussed in a companion SOP, “Standard Operating Procedure for the Preparation of Polyethylene (PE) Used for Passive Sampling”

SUMMARY OF METHOD

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

2.2 A shaker table or other suitable system is recommended for the extractions to facilitate PE-solvent contact.

INTERFERENCES

3.1 PE is susceptible to contamination from atmospheric and surficial sources, and so it must be handled using clean techniques.

3.2 While the sediment solids, biofilms, and inorganic precipitates on PE surfaces does not prevent HOC accumulation in the PE during in situ deployment, these coatings can substantially complicate subsequent chemical analysis. Careful removal of adhering sediment or surface growths via wiping with a water-wetted Kimwipe® may be necessary. Surface coatings of organic films on PE (e.g., oil or tar residues) can be
removed without compromising the sample by using solvent-saturated wipes (<minute contact times) followed by immediate Surrogate standard addition and solvent extraction.

APPARATUS AND MATERIALS

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

REAGENTS

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

PREPARATION AND HANDLING

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

7.1 Solvent Extraction: Laboratory and/or field blank and field-exposed PE is spiked with known quantities of surrogate compounds to assess analytical recoveries and extracted using organic solvents prior to analysis by GC/MS.

7.2 The PE is inspected for surface biofilms, particles, mud, or oily coatings. Biofilm mass should be removed as much as possible by using a clean wipe followed by a rinse with organic-free reagent water. Particles and sedimentary debris are removed by rinsing with organic-free reagent water and careful surface scraping if necessary to remove adhered/imbedded material. Oily coatings (e.g., coal tar staining or hydrocarbon slicks) are removed by soaking clean wipes in hexane and using forceps to hold and wipe both PE surfaces. This is not an exhaustive extraction and should be done quickly (<minute) and immediately prior to immersion in solvent. PE surfaces are blotted dry if water wet.

7.3 The PE is transferred to a pre-cleaned amber vial (size determined by dimensions of PE, typically 15-40 mL). Vial must be large enough for complete immersion of PE without excessive PE folding.

7.4 Known masses of surrogate compounds (Appendix 1) in a methylene chloride-compatible solvent are added to the vial. Typical additions are: 2.5-20 ng for aqueous samples; 50-250 ng for sediment samples, depending on target HOCs and their expected concentrations in the PE.

7.5 Methylene chloride is added to the vial to completely submerge the PE for a period of at least 12 hours.

7.6 The extract is transferred to a pre-cleaned glass concentration vessel. A second aliquot of methylene chloride is added to the extraction vial and agitated for >10 minutes. This step is repeated two more times.

7.7 After the final extract transfer, the PE is dried in air dry in the extraction vial and then weighed on an analytical balance until a consistent PE mass is obtained. This result is used to calculate the final target HOC concentrations measured in the PE sampler in units of HOC mass per PE mass.

7.8 Extracts are concentrated using rotary evaporation (or equivalent) down to suitable volumes for GCMS analysis; the resultant concentrated extracts are transferred to smaller vials (e.g., for autosamplers) according to standard laboratory practices. Before analysis, appropriate injection standards are added to the final extracts to allow for evaluation of the total volume of extract analyzed (Appendix 1).
   a. Typical final extract volumes are:
   b. 50-250 µL for water column-exposed PE
   c. 1-4 mL for contaminated sediment bed-exposed PE

QUALITY CONTROL

8.1 Method blanks, field blanks, matrix spikes, and/or replicate samples should be subjected to exactly the same analytical procedures as those used on field/lab-exposed PE samples.
8.2 QA/QC metrics, that are specific to the type of target HOCs of interest and the analytical methods used to quantify them, should be applied. Typical values for targets, like PAHs and PCBs, that are analyzed by capillary gas chromatography-low resolution mass spectrometry, in which picogram/uL detection is common, are:

8.2.1 Freshly prepared polyethylene and trip blanks: <0.1 ng HOC / g PE
Freshly cleaned PE samples, and samples of PE that traveled to and from the field site ("trip blank"), should have no significant peaks where PRCs, surrogate standards, injection standards, and target analytes elute.

8.2.2 PRC-loaded polyethylene reproducibility (±1σ/mean, N=6): <10%
Individual batches of PE loaded with PRCs should exhibit reproducible PRC concentrations in the PE before deployment.

8.2.3 Recoveries of Surrogate Standards: >70% to < 120%
Surrogate standards should be recovered from PE samples at nearly 100%, plus or minus analytical precision. An exception may be relatively volatile compounds (e.g., mono-, di-chlorobiphenyls, naphthalene) that may be significantly lost when extracts are evaporated (e.g., recovery down to 60%).

8.2.4 Precision of replicate PE extract analyses (N≥3): <25%
The reproducibility of all analytes (injection standards, surrogate standards, PRCs, and target compounds) determined with multiple instrumental analyses of the same PE sample extract, even run on different dates, should fall within suitably narrow bounds.

8.2.5 Detection limits using PE samples: ≤1 ng / g PE
Assuming 100 mg PE samples and 100 uL final extract volumes, target analytes, such as PAHs and PCBs, analyzed by GCMS (or methods with like sensitivity) should have <ppb detection limits.

METHOD PERFORMANCE

9.1 The method performance is assessed by determining the recovery and reproducibility in analyzing surrogate compounds (Appendix 1). All other lab-specific QA/QC metrics should be adhered to.

9.2 Successful PE deployment is achieved when significant (>method precision) losses of PRCs occurred, allowing one to use their behavior to adjust target compound levels in the PE up to equilibrium concentrations (Fernandez et al. 2009; Tcaciuc et al. 2014).
REFERENCES


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

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

<table>
<thead>
<tr>
<th>Targets: PAHs</th>
<th>Method: GCMS</th>
<th>Detection Limit ~ 100 pg / 100 mg PE</th>
</tr>
</thead>
<tbody>
<tr>
<td>PRCs</td>
<td>(^{13})C6-phenanthrene, (^{13})C6-fluoranthene, (^{13})C6-chrysene, (^{13})C6-indeno(1,2,3-cd)pyrene</td>
<td></td>
</tr>
<tr>
<td>Surrogates</td>
<td>d10-anthracene</td>
<td>d10-fluoranthene</td>
</tr>
<tr>
<td>Injection Standards</td>
<td>d10-acenaphthene</td>
<td>d14-m-terphenyl</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Targets: PCBs</th>
<th>Method: GCMS</th>
<th>Detection Limit ~ 100 pg / 100 mg PE</th>
</tr>
</thead>
<tbody>
<tr>
<td>PRCs</td>
<td>(^{13})C labelled PCB congeners: 37, 47, 54, 111, 138, 178</td>
<td></td>
</tr>
<tr>
<td>Surrogates</td>
<td>(^{13})C labelled PCB congeners: 3, 15, 28, 52, 118, 153, 180, 194, 208, 209</td>
<td></td>
</tr>
<tr>
<td>Injection Standards</td>
<td>(^{13})C labelled PCB congeners: 19, 105, 170</td>
<td></td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Targets: DDTs</th>
<th>Method: GCMS</th>
<th>Detection Limit ~ 200 pg / 100 mg PE</th>
</tr>
</thead>
<tbody>
<tr>
<td>PRCs</td>
<td>(^{13})C 2,4'-DDE</td>
<td>(^{13})C 2,4'-DDD</td>
</tr>
<tr>
<td>Surrogates</td>
<td>(^{13})C-PCB111</td>
<td>(^{13})C-PCB153</td>
</tr>
<tr>
<td>Injection Standards</td>
<td>d6 PCB 77</td>
<td>(^{13})C PCB 105</td>
</tr>
</tbody>
</table>
SOP QUESTIONS FROM COMMERCIAL LABORATORIES AND ANSWERS FROM THE POLYMERIC SAMPLER EXPERTS

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

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

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

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

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

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

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

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

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

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

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


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

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

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

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

Response: Amber.

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

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

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

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

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

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

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

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

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

Response: Precision in the 5-10% range is desired.
**Question 12:** Regarding “SOP PE (extractanalyze) - 2.2 Summary of Method:” - when the PRCs are loaded, are they rolled or shaken? Should the same mechanism be used for the extraction?

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

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

*Response:* No. See response to question 8.

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

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

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

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

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

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

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

*Response:* Add surrogate then immediately add the solvent.

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

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

Template Scope of Work (SOW) for polymeric sampler-based sediment porewater assessment
Appendix X: Example Performance Work Statement

(This Appendix provides an example that may be used in creating a Performance Work Statement for polymeric passive sampling. Edit as necessary. Any italicized text in within brackets is instructional and should be replaced or deleted as appropriate.)

PERFORMANCE WORK STATEMENT

[DATE]

[CONTRACT NUMBER]

1. Introduction
Passive samplers are an alternative to actively sampling sediment porewater using henry samplers and pumping or centrifugation. Passive samplers consist of hydrophobic polymers (e.g. polyethylene, polydimethylsiloxane), which sorb freely-dissolved organic compounds present in sediment porewater. Polymeric passive samplers can be directly inserted into saturated sediment in the laboratory or in the field to yield depth-discreet measures of freely dissolved ($C_{free}$) organic contaminant concentrations present in sediment porewater. $C_{free}$ measured by polymeric samplers represents the fraction of contaminants not sorbed to settling solids or associated with suspended colloidal matter and has been linked directly to exposure and risk to sediment-dwelling organisms.

Polymeric passive samplers shall be pre-loaded with performance reference compounds (PRCs) appropriate to the analyte class and analytical methods employed. PRCs are labeled versions of the analytes of interest, and are used to demonstrate that the polymeric passive sample reached equilibration or fractional approach to equilibrium (Fernandez, 2009 and Tcaciuc, 2014).

ESTCP #201735 developed Standard Methods for polymeric passive sampler analysis (Michalsen et al., 2020), and these methods shall be employed.

1.1. Description of Services
This PWS describes services to be performed by the contractor in the following tasks:

1. Preparation [or support of preparation] of the Work Plan (WP) and Quality Assurance Project Plan (QAPP).
2. Preparation and supply of the polymeric passive samplers loaded with the appropriate performance reference compounds (PRCs) for the project.
3. Field support for polymeric passive sampler and retrieval at the site.
4. Extraction and laboratory analysis of recovered polymeric passive samplers and calculation of equilibrium porewater concentrations using PRCs. Laboratory analysis will include [analyte class] following EPA Method [method number] using [technology, i.e. GC/MS].
5. Report equilibrium concentrations of the target analytes based on analysis of the polymeric passive samplers and PRC performance corrections.
The contractor shall provide all personnel, equipment, supplies, facilities, transportation, tools, materials, supervision, and other items and non-personal services necessary to perform the polymeric passive sampler deployment and analytical support as defined in this Performance Work Statement except for those items specified as government furnished property and services.

The Contractor shall conduct all necessary program management actions to ensure this delivery order remains on schedule and within budget. The Contractor’s Project Manager is responsible for notifying [the Agency’s] Project Manager and Contracting Officer’s Representative (COR) of any problems that arise and to identify corrective solutions.

The Contractor shall perform all necessary project management tasks. Project management tasks shall include activities associated with communication, billing, staff assignments, materials approvals and overall management of the project. The project manager shall mobilize the project team and provide ongoing team coordination, plan and schedule project activities.

The contractor shall perform to the standards as outlined in Attachment/Technical Exhibit 1, “Performance Requirements Summary”.

1.2. Background

The [Agency] is evaluating potential chemical contamination of sediment porewater at an aquatic site. The site will use in-situ polymeric passive samplers to measure porewater concentrations of [analyte class]. The following section provides background for the program.

[Insert summary description of site, including nature and extent of contamination.]

1.3. Objectives

The specific performance objectives, acceptance criteria, and monitoring methods for this PWS are outlined in Attachment/Exhibit 1, and specific information about each milestone is provided in the following subsections of this PWS. The objectives for field and laboratory analysis are to produce data of known and appropriate quality to support project objectives per the finalized Work Plan.

Specific Contractor objectives included in Section 5.1 of this PWS are:

- Project Coordination and technical contribution to the Work Plan and UFP-QAPP.
- Supplying polymeric passive samplers with any needed deployment components and assisting in sampler field deployment and retrieval.
- Processing polymeric passive samplers for shipment and analysis upon retrieval and analysis of the samplers per Work Plan and UFP-QAPP requirements. Conducting Data Usability Assessment in conjunction with [the Agency].
- Reporting results including equilibrium porewater concentrations of target analytes and PRC compounds. Participate in meetings to discuss the results and provide an interpretation of the data.

1.4. Scope

This scope of work is for preparation and deployment/retrieval of polymeric passive samplers at an aquatic site, extraction of the polymeric passive samplers, chemical analysis for [analyte class], and other necessary services to report equilibrium porewater concentrations of those analytes. Services include preparation of the Work Plan and UFP-QAPP, preparation of the polymeric passive samplers including
any necessary PRCs, field support for polymeric passive sampler deployment and retrieval, extraction and analysis of extracts for target analytes specific to the site, Data Usability Assessment in conjunction with [the Agency], and the calculation and reporting of equilibrium concentrations of porewater concentrations.

The approximate locations and numbers of samples is included in the task description.

1.5. Period of Performance
The period of performance shall be for [time period, i.e. 27 months].
[Include any relevant information to the period of performance, such as if there are certain times during the year when aquatic work may be performed at the site.]

1.6. General Information

1.6.1 Quality Control: The contractor shall develop and maintain an effective quality control program to ensure services are performed in accordance with this PWS as defined in Section 5.0 of this PWS. The contractor shall develop and implement procedures to identify, prevent, and ensure non-recurrence of defective services. The contractor’s quality control program is the means by which he assures himself that his work complies with the requirement of the contract. The contractor shall provide their institutions Quality Control Program to [the Agency] within 30 days after the contract award. Three copies of a comprehensive written QCP shall be submitted to the KO and COR within 5 working days when changes are made thereafter. After acceptance of the quality control plan the contractor shall receive the contracting officer’s acceptance in writing of any proposed change to his QC system.

1.6.2 Quality Assurance: The government shall evaluate the contractor’s performance under this contract in accordance with the Quality Assurance Surveillance Plan. This plan is primarily focused on what the Government must do to ensure that the contractor has performed in accordance with the performance standards. It defines how the performance standards will be applied, the frequency of surveillance, and the minimum acceptable defect rate(s).

1.6.3 Recognized Holidays: The contractor is not expected to work on recognized holidays.

New Year’s Day Labor Day
Martin Luther King Jr.’s Birthday Columbus Day
President’s Day Veteran’s Day
Memorial Day Thanksgiving Day
Independence Day Christmas Day

1.6.4 Hours of Operation: The contractor is responsible for conducting business, between the hours of 0900 to 1700 Monday thru Friday except Federal holidays or when the Government facility is closed due to local or national emergencies, administrative closings, or similar Government directed facility closings. For other than firm fixed price contracts, the contractor will not be reimbursed when the government facility is closed for the above reasons. The Contractor must at all times maintain an adequate workforce for the uninterrupted performance of all tasks defined within this PWS when the Government facility is not closed for the above reasons. When hiring personnel, the Contractor shall keep in mind that the stability and continuity of the workforce are essential.
1.6.5 **Place of Performance:** The work to be performed under this contract will be performed at the Contractor’s offices and laboratories, with the exception of field work that will be conducted at the [site].

1.6.6 **Type of Contract:** [Specify type of contract; i.e. “The government will award a sole source service contract.”]

1.6.7 **Security Requirements:** Contractor personnel performing work under this contract must acquire appropriate security clearance for access to project sites.

[Use this section if needed and add appropriate details for access to project sites.]

1.6.8 **Special Qualifications:** [Use if applicable.]

1.6.9 **Post Award Conference/Periodic Progress Meetings:** The Contractor agrees to attend any post award conference convened by the contracting activity or contract administration office in accordance with Federal Acquisition Regulation Subpart 42.5. The contracting officer, Contracting Officers Representative (COR), and other Government personnel, as appropriate, may meet periodically with the contractor to review the contractor's performance. At these meetings the contracting officer will apprise the contractor of how the government views the contractor's performance and the contractor will apprise the Government of problems, if any, being experienced. Appropriate action shall be taken to resolve outstanding issues. These meetings shall be at no additional cost to the government.

1.6.10 **Contracting Officer Representative (COR):** The (COR) will be identified by separate letter. The COR monitors all technical aspects of the contract and assists in contract administration. The COR is authorized to perform the following functions: assure that the Contractor performs the technical requirements of the contract; perform inspections necessary in connection with contract performance; maintain written and oral communications with the Contractor concerning technical aspects of the contract; issue written interpretations of technical requirements, including Government drawings, designs, specifications; monitor Contractor's performance and notifies both the Contracting Officer and Contractor of any deficiencies; coordinate availability of government furnished property, and provide site entry of Contractor personnel. A letter of designation issued to the COR, a copy of which is sent to the Contractor, states the responsibilities and limitations of the COR, especially with regard to changes in cost or price, estimates or changes in delivery dates. The COR is not authorized to change any of the terms and conditions of the resulting order.

1.6.11 **Key Personnel:** Promptly following award of this Purchase Request, the Contractor shall designate a Principle Investigator, who will be responsible for the scheduled execution of the work and coordination with the [Agency] POC. The PI shall be responsible for the overall supervision of work and serve as liaison between the Contractor and the [Agency] POC for all work under this Purchase Request.

The contractor shall provide a contract manager who shall be responsible for the performance of the work. The name of this person and an alternate who shall act for the contractor when the manager is absent shall be designated in writing to the contracting officer. The contract manager or alternate shall have full authority to act for the contractor on all contract matters relating to daily operation of this contract. The contract manager or alternate shall be available between [time period; i.e. 9:00 a.m. to 5:00 p.m.], Monday thru Friday except Federal holidays or when the government facility is closed for administrative reasons.

1.6.12 **Identification of Contractor Employees:** All contract personnel attending meetings, answering Government telephones, and working in other situations where their contractor status is not obvious to third parties are required to identify themselves as such to avoid creating an impression in the minds of
members of the public that they are Government officials. They must also ensure that all documents or reports produced by contractors are suitably marked as contractor products or that contractor participation is appropriately disclosed. Contractor may need to wear visitor identification badges while visiting facilities at the [site].

**1.6.13 Contractor Travel:** Contractor will be required to travel CONUS and within the NCR during the performance of this contract to participate in field deployment and retrieval events. Contractor will be authorized travel expenses consistent with the substantive provisions of the Joint Travel Regulation (JTR) and the limitation of funds specified in this contract. All travel requires Government approval/authorization and notification to the COR.

[Add summary description of expected travel for deployment and retrieval.]

**1.6.14 Other Direct Costs:** Any additional direct costs will be included in the Contractors proposal and must be pre-approved by the contracting officer.

**1.6.15 Data Rights:** The Government has unlimited rights to all documents/material produced under this contract. All documents and materials, to include the source codes of any software, produced under this contract shall be Government owned and are the property of the Government with all rights and privileges of ownership/copyright belonging exclusively to the Government. These documents and materials may not be used or sold by the contractor without written permission from the Contracting Officer. All materials supplied to the Government shall be the sole property of the Government and may not be used for any other purpose. This excludes the contractor’s right to produce data/documents for research or educational publication. This right does not abrogate any other Government rights.

**1.6.16 Organizational Conflict of Interest:** Contractor and subcontractor personnel performing work under this contract may receive, have access to, or participate in the development of proprietary or source selection information (e.g., cost or pricing information, budget information or analyses, specifications or work statements, etc.) or perform evaluation services which may create a current or subsequent Organizational Conflict of Interests (OCI) as defined in FAR Subpart 9.5. The Contractor shall notify the Contracting Officer immediately whenever it becomes aware that such access or participation may result in any actual or potential OCI and shall promptly submit a plan to the Contracting Officer to avoid or mitigate any such OCI. The Contractor’s mitigation plan will be determined to be acceptable solely at the discretion of the Contracting Officer and in the event the Contracting Officer unilaterally determines that any such OCI cannot be satisfactorily avoided or mitigated, the Contracting Officer may effect other remedies as he or she deems necessary, including prohibiting the Contractor from participation in subsequent contracted requirements which may be affected by the OCI.

**1.6.17 Phase In/Phase Out Period:** [Use if applicable.]

### 2.0 Acronyms and Definitions

**2.1. DEFINITIONS:**

2.1.1. CONTRACTOR. A supplier or vendor awarded a contract to provide specific supplies or service to the government. The term used in this contract refers to the prime.
2.1.2. CONTRACTING OFFICER. A person with authority to enter into, administer, and or terminate contracts, and make related determinations and findings on behalf of the government. Note: The only individual who can legally bind the government.

2.1.3. CONTRACTING OFFICER'S REPRESENTATIVE (COR). An employee of the U.S. Government appointed by the contracting officer to administer the contract. Such appointment shall be in writing and shall state the scope of authority and limitations. This individual has authority to provide technical direction to the Contractor as long as that direction is within the scope of the contract, does not constitute a change, and has no funding implications. This individual does NOT have authority to change the terms and conditions of the contract.

2.1.4. DEFECTIVE SERVICE. A service output that does not meet the standard of performance associated with the Performance Work Statement.

2.1.5. DELIVERABLE. Anything that can be physically delivered, but may include non-manufactured things such as meeting minutes or reports.

2.1.6. KEY PERSONNEL. Contractor personnel that are evaluated in a source selection process and that may be required to be used in the performance of a contract by the Key Personnel listed in the PWS. When key personnel are used as an evaluation factor in best value procurement, an offer can be rejected if it does not have a firm commitment from the persons that are listed in the proposal.

2.1.7. PHYSICAL SECURITY. Actions that prevent the loss or damage of Government property.

2.1.8. QUALITY ASSURANCE. The government procedures to verify that services being performed by the Contractor are performed according to acceptable standards.

2.1.9. QUALITY ASSURANCE SURVEILLANCE PLAN (QASP). An organized written document specifying the surveillance methodology to be used for surveillance of contractor performance.

2.1.10. QUALITY CONTROL. All necessary measures taken by the Contractor to assure that the quality of an end product or service shall meet contract requirements.

2.1.11. SUBCONTRACTOR. One that enters into a contract with a prime contractor. The Government does not have privity of contract with the subcontractor.

2.1.12. WORK DAY. The number of hours per day the Contractor provides services in accordance with the contract.

2.1.12. WORK WEEK. Monday through Friday, unless specified otherwise.

### 2.2. ACRONYMS

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACOR</td>
<td>Alternate Contracting Officer's Representative</td>
</tr>
<tr>
<td>AFARS</td>
<td>Army Federal Acquisition Regulation Supplement</td>
</tr>
<tr>
<td>AR</td>
<td>Army Regulation</td>
</tr>
<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
</tr>
<tr>
<td>CCE</td>
<td>Contracting Center of Excellence</td>
</tr>
<tr>
<td>CERCLA</td>
<td>Comprehensive Environmental Response, Compensation and Liability Act</td>
</tr>
<tr>
<td>CFR</td>
<td>Code of Federal Regulations</td>
</tr>
</tbody>
</table>
3. Government Furnished Items and Services

3.1. Services

[Services provided; i.e. “The Government will provide vessel and diver support for LDPE deployment and retrieval.”]

3.2. Facilities

[Facilities provided; i.e. “The Government will provide a work platform on the sampling vessel for use during LDPE deployment and retrieval. Project staff and field scientists will also be present in the field to direct and assist with field deployment and retrieval. If necessary, space for processing and/or preparation for shipping samplers will also be made available.”]
3.3. Utilities
Not applicable.

3.4. Equipment
Not applicable.

3.5. Materials
Not applicable.

4. Contractor Furnished Items and Responsibilities

4.1. General
The Contractor shall furnish all supplies, equipment, facilities and services required to perform work under this contract that are not listed under Section 3 of this PWS.

4.2. Facility Access Clearance
[Use if applicable.]

4.3. Materials
The Contractor shall furnish materials, supplies, and equipment necessary to meet the requirements under this PWS as defined in Section 5.

4.4. Equipment
The Contractor shall furnish all laboratory and field materials to meet the requirements under this PWS Section 5.

5. Tasks
The Contractor shall provide all materials, equipment, labor and services for deploying and retrieving up to [number of samplers] passive polymeric [specify type of polymer, if chosen by the government] porewater samplers and performing an equivalent number of analyses for [analyte class(es); i.e. PCBs or PAHs], extraction and analysis of passive polymeric samplers for the target analytes, the calculation and reporting of equilibrium porewater concentrations, investigative derived waste management and written documentation reporting. The use of passive polymeric samplers shall be performed according to the Standard Methods developed by ESTCP 201735 (Michalsen et.al., 2020). Work is described in additional detail and broken out by the following tasks.

5.1: [Name of Site or Project Area]
The purpose of the work described in Task 5.1 of this PWS is to [describe purpose, i.e. “collect/analyze porewater samples from locations that are most likely to contribute to the tissue concentrations observed]
in invertebrates and fish.""] [Describe general placement of samplers at the Site or project area.] [Describe general deployment and retrieval of samplers.] Following retrieval, the passive polymeric samplers will be extracted and analyzed for [analyte class(es)].

The following Tasks shall be accomplished at the [site]:

**Task 5.1.1: Project Kickoff and Work Plan/QAPP Finalization Support:**

The contractor shall create a Project Management Plan to be presented 14 calendar days after task order award. The government team will provide written comments. The Project Management Plan shall be revised and submitted as final after comment resolution. The plan shall include the following:

**List Key Personnel and Outline of Responsibilities**

Contractor personnel that are considered key personnel by the Government are defined in Section 1.6.11 and are further defined here as: Contract Project Manager, Principal Investigator, and Field Scientist. The contractor shall provide a list of personnel and key personnel to be involved with the project and describe their roles. The Contractor shall provide a contract project manager who shall be responsible for the performance of the work and the primary point of contact for the [Agency] PM and shall be responsible for the performance of the work. The name of this person and an alternate who shall act for the Contractor when the manager is absent shall be designated in writing to the contracting officer. The contract project manager or alternate shall have full authority to act for the Contractor on all contract matters relating to daily operation of this contract. The contract project manager or alternate shall be available between the core hours of 0900-1500, Monday through Friday except Federal holidays.

**Work Plan**

[Describe work required to complete the Work Plan; for example the Contractor may solely produce the Work Plan with [Agency] review, or the Contractor may contribute to an Agency-led Work Plan.]

**UFP-QAPP**

[Describe work required to complete the UFP-QAPP; for example the Contractor may solely produce the QAPP with [Agency] review, or the Contractor may contribute to an Agency-led QAPP.]

In accordance with OSWER Directive 9272.0-17, the QAPP shall be generated following the Uniform Federal Policy QAPP (UFP-QAPP) guidelines. The QAPP is a formal document describing in comprehensive detail the necessary quality assurance (QA), quality control (QC), and other technical activities (including sample acquisition and archiving) that must be implemented to ensure that the results of the work performed will satisfy the stated performance criteria. The QAPP presents the steps that should be taken to ensure that environmental data collected are of the correct type and quality required for a specific decision or use. It presents an organized and systematic description of the ways in which QA and QC should be applied to the collection and use of environmental data. A QAPP integrates technical and quality control aspects of a project throughout its life cycle, including planning, implementation, assessment, and corrective actions.
Quality Control Plan

[Describe work required to complete the Quality Control Plan.]

Health and Safety Plan

[Describe the Health and Safety Plan that the Agency requires, which the Contractor is required to prepare.]

The Contractor is responsible for understanding the safety and health criteria, practices, and procedures to be implemented to provide proper control of and protection against the unique safety, chemical, physical, and biological hazards related to this project. The Contractor is also responsible for providing their own site-specific health and safety plan (SSHP) for activities conducted at their facilities.

Task 5.1.2: Passive Polymeric Sampler Preparation and Field Deployment/Retrieval

[Describe required parts of the task; example text is given below.]

The Contractor shall provide all materials required for passive polymeric sampler field deployment, processing following retrieval, and preservation for shipment to the contractor’s laboratory for analysis (except as noted below). This includes the following:

- Up to [number] of passive polymeric samplers with appropriate PRCs for [analyte class(es)] analysis;
- All sample labels;
- Any chemicals required for sample extraction;
- Sample containers (for transport and extraction);
- Personal protective equipment;
- Shipping containers,
- Shipping costs to the Contractor’s laboratory; and,
- Any other materials required for polymeric passive sampler deployment and sample processing following retrieval.

The Contractor shall participate in one (1) field work kick-off/field readiness review meeting via teleconference.

[If possible, add a figure showing the location and number of polymeric passive sampler deployment; or the general area for deployment, if distribution will be determined as part of the contract.]

The Contractor shall mobilize field staff to provide technical support in the field during polymeric passive sampler deployment, retrieval and processing, and field documentation during deployment. The anticipated minimum time for deployment and equilibration will be defined in the QAPP, but the contractor should anticipate [general proposed schedule]. The Contractor shall maintain schedule flexibility to support both deployment and retrieval.

[Describe support for deployment, and if it is the Contractor or Agency responsibility; i.e. “The Government will provide all support pertaining to in-water LDPE placement, including field equipment and boats.”]
The Contractor shall complete all required sample processing in the field following polymeric passive sampler retrieval per the finalized QAPP. The Contractor shall ship all samples to the contractor’s laboratory under standard chain of custody procedures.

Retrieved polymeric passive samplers will be [describe post-removal storage requirements that accord with the ESTCP Standard Methods]. The contractor should anticipate up to [number] discrete polymeric passive samples for extraction.

Performance criteria include:

- The Contractor shall participate in the field work kick-off/field readiness review meeting via telecom.
- The Contractor shall provide sufficient number of polymeric passive samplers as defined above.
- The Contractor shall mobilize field staff to provide technical support in the field during polymeric passive sampler deployment, retrieval and processing, and field documentation during deployment. The anticipated minimum time for deployment and equilibration is approximately [time estimate]. The Contractor shall maintain schedule flexibility to support the entire deployment and retrieval effort.
- The Contractor shall complete all required sample processing in the field following polymeric passive sampler retrieval per the finalized Work Plan. The Contractor shall ship all samples to the contractor’s laboratory under standard chain of custody procedures.

**Task 5.1.3: Chemical Analysis of Polymeric Passive Samplers**

The Contractor shall analyze all samples consistent with requirements specified in the finalized Work Plan. The total number of field samples requiring analysis will be up to [number] discrete samples. [If planned, describe any compositing that may be performed.] The analysis of these samplers will be performed in accordance with EPA Method [method number]. The specific analytical method, detection limits, and QA/QC criteria will be developed with the Contractor as part of the QAPP. The lab will be required to archive the extracts for 6 months.

The Contractor shall participate in one (1) Data Usability Assessment review meeting via telecom. Data Usability will be evaluated by the Contractor and [the Agency] according to the UFP-QAPP.

**Task 5.1.4: Final Report**

The Contractor shall submit all deliverables as electronic files in MS Word™, MS Excel™ and PDF. [Add any Agency-specific requirements for electronic data deliverable format for laboratory data.] The Contractor shall submit the following deliverable in similar electronic media formats:

**Draft and Final Work Plan.** The Contractor shall [produce/provide technical input to] the draft Work Plan, respond to [Agency] review electronically with “tracked changes” and comment responses, and finalize the document after [Agency] acceptance of changes.

**Draft and Final QAPP.** The Contractor shall [produce/provide technical input to] the draft QAPP, respond to [Agency] review electronically with “tracked changes” and comment responses, and finalize the document after [Agency] acceptance of changes.
Field Report. The Contractor shall provide a brief field report summarizing field deployment methods, method variances and field observations and photos 7 days following the last day of LDPE field sample retrieval.

Draft and Final Data Deliverables. The Contractor shall submit the draft electronic data to [the Agency] as soon as data become available, i.e. in a piecemeal fashion. The final Data Deliverable will include [data deliverable requirements; i.e. “all chemical data in a single MS Excel file, as well as PDF copies of all chain of custody forms.”] The data shall comply with QC requirements specified in the final QAPP.

Draft and Final Report. The draft and final reports will present methods, materials, results and discussion of the findings. The Contractor shall [produce/provide technical input to] the draft Final Report, respond to [Agency] review electronically with “tracked changes” and comment responses, and finalize the document after [Agency] acceptance of changes. [Add detail and scheduling if the report requires review by Stakeholders/Regulators outside of the Agency.]

5.2 Submittals
A list of submittals and associated delivery dates are presented in Attachment/Exhibit 2.

5.3. Schedule
The following schedules shall apply to this contract unless delays are incurred by the Government through no fault of the Contractor. Schedule of tasks are presented in Table 1.

Table 1: Schedule for Task Completion

<table>
<thead>
<tr>
<th>Activity</th>
<th>Schedule</th>
</tr>
</thead>
<tbody>
<tr>
<td>Purchase Order Notice to Proceed (NTP)</td>
<td>[Purchase Order NTP Date]</td>
</tr>
<tr>
<td>Task 5.1.1 – Project Kickoff and Work Plan/QAPP Finalization Support</td>
<td>[Start and Finalization Dates]</td>
</tr>
<tr>
<td>Task 5.1.2 – Passive Polymeric Sampler Field Deployment/Retrieval</td>
<td>[Deployment and retrieval planned schedule]</td>
</tr>
<tr>
<td>Task 5.1.3 – Chemical Analysis of Polymeric Passive Samplers</td>
<td>Within 30 working days of receipt of all samples.</td>
</tr>
<tr>
<td>Task 5.1.4 – Final Report</td>
<td>Draft to [Agency] within 60 working days of receipt of all samples by the laboratory. Final Report within 2 weeks following receipt of [Agency or Stakeholder/Regulator] review comments. [Add detail and scheduling if the report requires review by Stakeholders/Regulators outside of the Agency.]</td>
</tr>
</tbody>
</table>
6. References


7. ATTACHMENT/TECHNICAL EXHIBIT LIST:

Attachment 1/Technical Exhibit 1 – Performance Requirements Summary
Attachment 2/Technical Exhibit 2 – Deliverables Schedule
Attachment 3/Technical Exhibit 3 – Figures
Performance Requirements Summary

The Contractor service requirements are summarized into performance objectives that relate directly to mission essential items. The performance threshold briefly describes the minimum acceptable levels of service required for each requirement. These thresholds are critical to mission success.

Table 2: Performance Objectives and Acceptance Criteria

<table>
<thead>
<tr>
<th>Performance Objectives</th>
<th>Performance Standard</th>
<th>Acceptable Quality Levels</th>
<th>Monitoring Method</th>
</tr>
</thead>
</table>
| **Task 5.1.1: Project Kickoff and Work Plan/QAPP Finalization Support.** The Contractor shall coordinate closely with [Agency] to finalize field deployment details, schedule, and Work Plan and UFP-QAPP elements to ensure these requirements are met. The Contractor shall also provide a step-by-step protocol for field deployment, retrieval, and post processing of passive polymeric samplers based on the requirements of this PWS. | - Submittal of Work Plan in draft, draft final, and final version.  
- Submittal of UFP-QAPP in draft, draft final, and final version.  
- Contractor’s input and teleconference as needed to resolve questions and finalize field deployment details, schedule, protocol and details of Work Plan and UFP-QAPP elements. | - Submission on schedule per Section 5.0 of this PWS. | - 100% Government inspection of milestones/deliverables associated with objective. |
| **Task 5.1.2: Passive Polymeric Sampler Preparation and Field Deployment/Retrieval.** [Summarize deployment/retrieval; i.e the provided example here.] Contractor shall provide all sampling equipment, materials and field support required to prepare polymeric passive samplers for field deployment and process samplers for shipping and analysis to the lab following retrieval. Note that the Government will provide vessel and field support for deployment and retrieval. | - Field deployment methods, field activities completed and observations documented in a brief field report memo. This memo will ultimately serve as the basis for the field methods section of the Final Report. | - Submission on schedule per Section 5.0 of this PWS. | - 100% Government inspection of milestones/deliverables associated with objective. |
| **Task 5.1.3: Chemical Analysis of Polymeric Passive Samplers.** Contractor shall complete analysis of all polymeric passive samplers collected during field deployment consistent with requirements specified in the finalized UFP-QAPP. | - Contractor shall provide electronic file containing chemical analysis results for all samples as soon as this data is available and prior to development of the final report. Data reporting and analysis and data reporting shall meet requirements specified in the QAPP. | - Submission on schedule per  
- Accepted data package | - 100% Government inspection of milestones/deliverables associated with objective. |
## Task 5.1.4: Final Report

Contractor shall submit the draft report to [the Agency] for review. [The Agency] will request clarification and revisions to the draft report and Contractor shall prepare the draft final report, which will subsequently be reviewed by USACE. Contractor shall revise as needed to finalize report.

- Concurrence from [the Agency] that the report meets project requirements.
- Submission on schedule per Section 5.0 of this PWS.
- 100% Government inspection of report associated with objective.
<table>
<thead>
<tr>
<th>Deliverable</th>
<th>Frequency</th>
<th># of Copies</th>
<th>Medium/Format</th>
<th>Submit To</th>
</tr>
</thead>
<tbody>
<tr>
<td>Work Plan finalization with Quality Control Plan and Health and Safety Plan.</td>
<td>See scope of work (Schedule).</td>
<td>1</td>
<td>1 electronic copy in .docx or .pdf format emailed or mailed on compact disc.</td>
<td>Attn: [COR Name, Address, Email, Phone]</td>
</tr>
<tr>
<td>UFP-QAPP finalization.</td>
<td>See scope of work (Schedule).</td>
<td>1</td>
<td>1 electronic copy in .docx or .pdf format emailed or mailed on compact disc.</td>
<td>Attn: [COR Name, Address, Email, Phone]</td>
</tr>
<tr>
<td>Draft Laboratory Data Report</td>
<td>As laboratory analyses are complete. Not to exceed 60 days after field activities.</td>
<td>1</td>
<td>1 electronic copy in .xls format emailed or mailed on compact disc.</td>
<td>Attn: [COR Name, Address, Email, Phone]</td>
</tr>
<tr>
<td>Draft Report</td>
<td>Draft Within 60 days of receipt of all passive polymeric samplers by the laboratory.</td>
<td>1</td>
<td>1 electronic copy in .docx or .pdf format emailed or mailed on compact disc.</td>
<td>Attn: [COR Name, Address, Email, Phone]</td>
</tr>
<tr>
<td>Final Report</td>
<td>2 weeks following receipt of [Agency or Stakeholder] review comments.</td>
<td>1</td>
<td>1 electronic copy in .docx or .pdf format emailed or mailed on compact disc.</td>
<td>Attn: [COR Name, Address, Email, Phone]</td>
</tr>
</tbody>
</table>
FIGURES

[Add any Figures.]