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OFFICE OF
RESEARCH AND DEVELOPMENT

MEMORANDUM

DATE: 28 July 2016

SUBJECT: Reconciliation Memorandum on Review of *Laboratory, Field, and Analytical Procedures for Using Passive Sampling in the Evaluation of Contaminated Sediments: User's Manual*

FROM: Robert M Burgess
Atlantic Ecology Division

TO: Virginia Houk
NHEERL Peer Review Coordinator / Designated Federal Officer

Please find below my responses to the comments by the six external reviewers on this draft User's Manual document. The six reviewers are thanked for their thoughtful and thorough reviews of the draft document. Every reviewer made substantial contributions to improving the clarity, scientific robustness, and usefulness of the document. Some of the comments were statements that did not require a specific action or revision and are noted in the reconciliation table below as *No response necessary*. Despite the quality of many of the comments, not all were incorporated into the revised document. Often this was because the comments addressed topics beyond the scope and intent of the current document or suggested changes to the structure and content of the document that were not intended to be altered at this point in the document's evolution (e.g., significant changes to the content of the document recommended by Reviewer #3). Finally, thank you very much for coordinating this review process, it is very much appreciated to have such an effective mechanism for having our research products reviewed by external experts.

As mentioned above, the responses are presented below in a reconciliation table listing the comments of the six reviewers, one reviewer at a time, by document section, and then the actual response. Corresponding to the responses below, revisions to the document (in the revised document) are identified by the Word track change feature.

This document is the result of a multi-author and multi-organization exercise. Consequently, version control of the document is more challenging than usual. The responses below were incorporated into a version of the document that differed to some extent from the version reviewed by the six reviewers last summer/fall (2015). However, the substance of the document did not change significantly between the version reviewed by the external reviewers and the version revised as part of this external review process. In addition, the final version of the document for publication will be further edited for clarity and continuity but the substance of the document will not change.

Please let me know if you have any questions or comments regarding my responses.

Reviewer	Document Section	Document Section Name	Reviewer's Comment	Author's Response
1	1	Introduction	In Section 1 and throughout, the manual is written in a clear and accessible style. The strengths and limitations of each sampler type and method of use are well presented. Sufficient references are provided to direct readers to where they may find more details on particular subtopics.	No response necessary.
			Technical details, such as polymer suppliers and deployment configurations, along with a list of passive sampling experts in this section will support commercial analytical laboratories in developing their own SOPs.	No response necessary.
			As this is the introduction, the equations provide the fundamental relationships exploited by the sampling methods. I have some concerns about Equation 1-4. If C_{free} is calculated using Eqn. 1-3, then Eqn 1-4 is calculating something else. $C_{free} \neq C_{PS}^{non-eq}/K_{PS}$. Perhaps $C_{free} > C_{PS}^{non-eq}/K_{PS}$.	Agreed; Equation 1-4 has been removed and the text revised to discourage calculation of " C_{free} " under non-equilibrium conditions.
			If the authors do not think it is too much for the introduction, a discussion of the expected time scales for different samplers and target compounds to fully equilibrate would be helpful in the area of pp. 28-29. For example only the smallest compounds being taken up by the thinnest PDMS layers may be expected to fully equilibrate with samplers exposed to in place sediments following exposures of a matter of weeks. Larger compounds in POM or LDPE could take years to reach equilibrium in many (most?) sediments.	A paragraph has been added to this section on the topic of this comment.
			No other resources that I can think of for this section.	No response necessary.

			Typo on the last line of the first column on page 32, “estimate” instead of “estimated”.	This text has been revised.
			Page 34: Here again, in the first column it reads, “Another approach if equilibrium is not assumed,...” a discussion of when equilibrium may or may not be assumed would be helpful. Assuming equilibrium in many/most PE or POM deployments would likely lead to under estimation of C_{free} .	Text has been added to this section indicating that Section 8 discusses the topic of this comment.
	2	Passive Sampling with Polyoxymethylene (POM)	Again, the writing style of this section is clear and easy to understand.	No response necessary.
			The equations contained in this section are clear and describe the important calculations for sampler preparation.	No response necessary.
			My only concern in this section is that the methods for cleaning POM for sampler preparation are different for cleaning the POM for measuring K_{POM} . This could be confusing to researchers just beginning to use POM samplers. Should a single best practice for pre-cleaning and preparing POM be recommended? The variability in extraction efficiency of POM using various solvents was investigated recently by Arp et al., <i>ETC</i> (2015). Their findings may be as important in this section as in the section 7.	Agreed, the text has been revised such that in both sections the POM is pre-cleaned with 50:50 acetone/hexane.
			One small note on section 2.3 Field Use. The last sentence mentions that POM samplers have been deployed by wading to station or by divers. They have also been deployed on weighted frames to sediments too deep to be accessed by divers (Fernandez et al. 2014)	Agreed; text has been added to this section addressing this comment and citing Fernandez et al. (2014).
			Last sentence of section 2.1, I believe the authors intend this to read “trapping of particulate matter”, instead of “trapping of particular matters”. This	This text has been revised.

			sentence appears to imply that particulate matter is likely to be trapped on LDPE samplers.	
	3	Passive Sampling with Polydimethylsiloxane (PDMS)	Again, the writing style of this section is clear and easy to understand.	No response necessary.
			Section 3.4 provides information on how to deploy the samplers and mentions that deployment time will depend on the thickness of the PDMS film, hydrophobicity of the target compound, and characteristics of the sediment. More guidance on how to determine the “specified length of time” for deployment would be useful. Is there a reference for how to estimate an appropriate length of deployment?	The author of this section was contacted and he recommended a reference to cite in the text. That reference (Lampert et al. 2015) has been added to the document.
			The equations contained in this section are clear and describe the important calculations for sampler preparation.	No response necessary
			At the end of the second column on page 49, vertical diffusion of contaminants along PDMS is mentioned. Is there a reference for this? Although I understand there is concern that this is a possibility, has anyone observed vertical diffusion along any of these passive samplers? Has it been modeled?	The author of this section was contacted about this comment and he reports that transport in the vertical direction is negligible compared to target contaminant movement in the horizontal plane.
			Philipp Mayer’s group (Technical University of Denmark) has published a lot of work using jars coated with PDMS layers of different thicknesses to measure C_{free} in sediment samples. It may be helpful to cite some of their work in section 3.2.	Text has been added to Section 3.1 of the document noting the technique developed by Mayer et al. as an additional method of interest when using PDMS.
			Minor note on Figure 3-1. When viewed/printed in black and white, there is not difference in contrast between the orange and blue section in the cross-section view of the SPME fiber.	A note to this effect has been added to the front matter ‘Notice’ section.
			Typo mid-way down second column on page 50, “PDME” should be “PDMS”.	This text has been revised.

	4	Passive Sampling with Low-Density Polyethylene (LDPE)	Again, the writing style of this section is clear and easy to understand.	No response necessary
			This section describes LDPE sampler preparation, deployment, and recovery in sufficient detail that someone would be able to follow the same methods. The authors might consider adding a note to section 4.4 describing how samplers can also be transported flat, between non-reactive no-flux sheets (glass or metal plates, or aluminum foil) for sectioning in the laboratory rather than in the field.	Text addressing this point has been added to this section of the document.
			Are the LFERs provided on page 60 (Eqns 4-1 and 4-2) recommended over the LFERs listed in Appendix B (Eqns B-1 to -4)? Perhaps the authors would consider mentioning that additional LFERs are available in Appendix B, and how much variability there is between the different calculated values.	Text addressing this point has been added to this section of the document with the suggestion to see Appendix B for alternative LFERs.
			No additional topics are recommended.	No response necessary
			No additional resources recommended.	No response necessary
			Small detail: at the top of the first column on page 54, sheet-metal screws are mentioned for connecting metal frames together. I believe, machine screws and bolts are actually used.	This text has been revised.
	5	Passive Sampling with Diffusive Gradient in Thin Films (DGT)	I do not have expertise in sampling using DGT. While I read this section, I do not feel I can reply to the charge questions for this section.	No response necessary
	6	Selection and Use of Performance Reference Compounds for Hydrophobic Organic Target Contaminants	Again, the writing style of this section is clear and easy to understand.	No response necessary
			This section does a great job of describing the nuances of selecting PRCs and PRC loading concentrations.	No response necessary

			Both equations are clear and easy to understand.	No response necessary
			The practice of loading PRCs to polymer from methanol:water solution is mentioned at the bottom of the first column on page 70 (section 6.2.3). It is often stated that the methanol:water swells the PE and that loading occurs more quickly. However, I don't believe I have ever seen data to back this up. Claims that PE can be loaded in hours would require molecular diffusion to occur within the PE at impossibly fast rates. My personal belief is that loading of PRC near the surface, without establishing an even distribution of PRC across the polymer thickness may lead to inaccurate calculation of fractional equilibration when PRCs are diffusing in two directions (toward the center of LDPE thickness and toward the exposed surface) during deployment. Perhaps the authors would consider editing the last sentence to note that the final soak in water should remove residual methanol and be sufficiently long to allow for diffusive distribution of PRCs across the PE thickness (a duration that can be modeled).	Text has been added to Section 6.2.3 indicating that the time necessary to load the PRCs into a passive sampling polymer such that they reach equilibrium can be estimated using diffusion modeling but requires some sophistication and acquiring assistance from one of the technical contacts listed in Table 1-3 is highly recommended. Requested information on removing residual methanol is stated in Section 6.2.2.
			No additional resources are recommended.	No response necessary
			Section 6.1: Near the bottom of this section (page 66, first column) the text reads, "(ii) follow the same kinetics as the target analyte". This would only be important for one method of using PRCs (matching each analyte with a PRC), which is not actually the method recommended in this document (using the GUI). An alternative for this text might be, "(ii) bracket the kinetics of target analytes".	Agreed; the text has been revised to address this comment.
			Near the bottom of the second column on page 66, the paragraph begins, " Most often PRCs are	Agreed; the text has been revised to address this comment.

			selected because they share similar log K_{OW} with the target". This may be a nuance, but it would also be important that the compound share similar diffusivities in polymer and sediment, which can be estimated from the molar volume or surface area.	
			Tiny typo: in the second to last line of the first column on page 71, "venders" should be "vender's".	This text has been revised.
	7	Extraction and Instrumental Analysis of Target Contaminants from Passive Sampling	Again, the writing style of this section is clear and easy to understand.	No response necessary
			Text Box 7-1 may actually provide too much detail. Instead of specifying sizes of vials and volumes of solvent, perhaps a rule-of-thumb ratio for polymer mass to solvent could be given. Alternatively, the size of the polymer for which this extraction procedure is designed could be specified in the title. Wrapping and freezing are mentioned throughout these steps. It might be more accurate to describe the steps as darkening and storing at -4°C. Step 8 refers to 60 ml vials, I believe these are the 100 mL vials. Step 9 calls for repeating steps 8 and 9. I believe that should read "7 and 8".	Agreed; the text has been revised in this section to address this comment including removing specific volumes.
			The one equation in this section is 7-1. This equation describes the calculation of method detection limits. It appears that this equation uses K_{PS} with units of $L_W L_{polymer}^{-1}$. Since these are different units than those used for K_{PS} in other sections of the document, the difference should be noted. Also, it would be worth noting that the detection limits calculated here correspond to equilibrium passive sampling. Using PRCs to	Agreed; the text has been revised to address the differences in passive sampler partition coefficient units and the effects of non-equilibrium conditions on the method detection limit (MDLs).

			calibrate samplers for non-equilibrium conditions effectively raises the detection limits.	
			See above, the effects of PRC corrections on the calculated detection and quantitation limits should be mentioned.	Please see the previous response immediately above.
			No other resources are recommended.	No response necessary
			Section 7.2.1 (page 74) contains several typos. It isn't clear to me how this should read.	Agreed; this text has been revised for clarity.
	8	Data Analysis: Calculation of C_{free} and C_{DGT}	Again, the writing style of this section is clear and easy to understand.	No response necessary
			The document does a great job stepping one through using the GUI for non-equilibrium sampling with LDPE. The screen shots are very helpful.	No response necessary
			Would the authors check equation 8-3. To my way of using f_{eq} , this equation would be calculating $1-f_{eq}$ (as in, a sampler with 25% of the PRC remaining after deployment is 75% equilibrated). Perhaps this is what is being called by the GUI, however.	This equation has been revised to clarify what is being calculated and entered into the GUI.
			No additional topics are recommended.	No response necessary
			No additional resources are recommended.	No response necessary
			In section 8.1, midway down the first column on page 86, is it necessary to assume that the samplers are fully equilibrated with organisms in the sediments?	For the purposes of the first assumption discussed in this section of text, the passive samplers is assumed to have achieved equilibrium with all phases in the environment around the sampler.
			I could not review Figure 8-1 as I couldn't make out the text.	The visual quality of Figure 8-1 will be improved to insure that it is readable upon viewing and printing. The problem with readability has to do with the low resolution pdf that was created and distributed to the

				reviewers. Text has been added to the Notice section instructing users to print the pdf with sufficient dots per inch (dpi) to insure readability.
	9	Quality Assurance and Quality Control, and Other Considerations	Again, the writing style of this section is clear and easy to understand.	No response necessary
			The document thoroughly describes the QA and QC considerations for using passive samplers.	No response necessary
			This section does not contain equations.	No response necessary
			No additional topics are recommended.	No response necessary
			No additional resources are recommended.	No response necessary
			The first sentence of section 9.1.11 at the bottom of the second column on page 97 should read "In 2013, LDPE...".	The '2011' date is accurate for the work discussed in the QAPP attached as Appendix G.
2	1	Introduction	Introduction - The introduction of the manual should discuss that the use of Passive Sampler for contaminated sediment sites is an emerging technology. And with this, it requires a collaborative working relationship with a laboratory develop an approach to support these projects and make the best decisions related to all the variables related to the sample preparation, sample handling and subsequent analysis and data reporting.	A subsection was prepared for this section to address issues related specifically to commercial laboratories based on comments reported by this reviewer.
			There is some information within this document for labs to develop their own SOPs for the preparation of the passive samplers. I perceive a disconnect between the current laboratories (which I assume to be researchers) and commercial laboratories. My working assumption is that this manual to provide the project team, including the commercial laboratories but not	The document authors agree with this statement. No response necessary.

			excluding researchers, with information to successfully execute passive sampling project.	
			I believe that the manual needs to state that the project team should default to the laboratory specific SOPs. There is a lot (too much) of very specific information in this document on analytical methods and the specificity provided in this document may not be the commercial laboratories standard which would be US EPA Methods. I suspect the specificity in this document represents the past execution of extraction/analysis for passive sampling materials and I am assuming in many cases by various universities, researchers and not commercial laboratories. Commercial laboratories will be trying to use many of their existing processes and methods to support the analysis of these materials, where they can and it is appropriate. Commercial laboratories can use different analytical techniques than were employed by researchers, since they have the technology available (GC/MS and HRGC/HRMS) and can provide a lower level of sensitivity.	Text has been added to a subsection of Section 1 on commercial laboratories to address this point.
			I would recommend that the user manual should state that the project team should develop a detailed project specification/statement of work for the project to work with a laboratory. This document should refer to the conceptual site model for the site and the project should be provided for discussion with the laboratory. The laboratory will be in a better position to support the project team if they know the overall goals of the project.	Text has been added to a subsection of Section 1 on commercial laboratories to address this point.

			From the laboratory perspective, the project team will make the determination on the appropriate passive sampling material and then work with the laboratory on the preparation of the material.	Text has been added to a subsection of Section 1 on commercial laboratories to address this point.
			I would recommend that within each of the sections of each passive sampling material, that within the section on preparation and laboratory use, it be specifically stated that each lab should have an internal SOP developed for the preparation of the passive sampling material. The specifications within this document are very detailed and laboratories may develop their own approach. The project team should be able to review the laboratories SOPs to determine if they meet their project goals.	Text has been added to a subsection of Section 1 on commercial laboratories to address this point.
			There are a lot of analytical details within this document. I believe that it is important in the introduction to emphasize that this is a reference/guidance document and not intended to be prescriptive in its use. Laboratories will create or default to their existing SOPs for support. For example, laboratories may use different solvents basis on their analytical method choice and unable to use the specified solvent listed in the document (PAHs and acrylonitrile).	Text has been added to a subsection of Section 1 on commercial laboratories to address this point.
			For a commercial laboratory to support this work, there are certain areas which are non-standard and should be addressed in the document. They are: o Project goals – There will need to be a discussion with the project team on their goals in order to support the project. This is not 'off the	Text has been added to a subsection of Section 1 on commercial laboratories to address this point.

			shelf' support and there needs to be discussion in many areas. - o Media- acquisition & handling, including choices of media, fabricating media for deployment & use of PRCs. - o Deployment of media – handling of the media to get it to the site & QA/QC samples associated with it - o Retrieval of media- handling of the media to get it to the lab & QA/QC samples associated with it - o Data Reporting – on a mass or concentration basis. From the laboratory perspective, these are the areas which need to be clear and discussed to appropriately execute the project and transition this support from project teams within a university setting to a commercial laboratory. The actual extraction and analysis of the media is the easy part.	
			Page 37. Patricia McIsaac name is spelled wrong. Please add Bruce Wagner at TestAmerica as an additional contact. Bruce.Wagner@TestAmericainc.com 865.291.3000	The misspelling was corrected and the name added to the table.
			The world of passive samplers is not too different, from an analytical perspective, in providing source testing analytical support (stack gas monitoring). In most cases, there is a media which is prepared by the laboratory, which is sent	The objective of the document under review is to provide guidance not specific SOP-like documentation. In addition, parts of this document are based largely on the noted

			to the field and then returned. There are specific methods for the media and specific spiking standards for the media. I have attached a copy of Method 23 for Dioxin/Furans as (check this out) (7/7/2016) an example. I don't know if the long term goal is to have standardization which would allow for the specific method development. I am aware of the ESTCP's SOPs on media preparation which have been very helpful and specific in the area which is nonstandard for commercial laboratories.	SERDP/ESTCP SOPs for specific passive samplers.
	2	Passive Sampling with Polyoxymethylene (POM)	Section 2.2.2 through 2.2.5. This section discusses the steps used for a laboratory to develop in-house partition coefficients for POM (K _{pom}). Is it really the intention of the document to allow laboratories to develop their own K _{pom} factors and not use standardized factors? We see a huge potential problem of data comparability if this is the case as well commercial laboratories don't develop partition coefficients.	In general, commercial laboratories are not expected to generate K _{PS} values unless specifically requested. For the most common target contaminants (e.g., PCBs, PAHs, DDTs), K _{PS} values are provided in the document. In those rare cases where a K _{PS} is not available, the commercial laboratory is recommended to contact a research facility for a value. This information is now discussed in the subsection on commercial laboratories.
	3	Passive Sampling with Polydimethylsiloxane (PDMS)	Section 3.3.2. The last paragraph regarding Deployment Blanks is very confusing and not clear at all. Is this intended on being a field blank? Which is then analyzed after the SPME are in the field? If no deployment blanks are used for samples which are analyzed immediately, how is immediately defined? [Commercial laboratories have holding time in which they have to analyze the samples. Are you recommending something like that?]	The noted text has been revised and clarified as follows: <i>All SPME insertion devices are marked during deployment to allow retrieval. This might include cording to surface-deployed buoys or cording run to a nearby shore. The samplers can be pushed into sediment by hand at easily accessible sites (e.g., onshore locations at low tide and</i>

				<i>shallow creeks). Deployment blanks (also considered a field blank) can be shipped to the field but not deployed, to assess possible sources of contamination to the samples on site or during shipping. For SPME, the deployment blanks should be processed (i.e., transferred to vials and solvent added) at the time of deployment. A field blank can also be used for retrieval. No retrieval field blank is needed if the samplers are processed on site immediately after retrieval.</i>
	6	Selection and Use of Performance Reference Compounds for Hydrophobic Organic Target Contaminants	Providing analytical costs for these projects can be challenging. Much of the discussion on the use of passive samplers, there has been an underlying tone that it is inexpensive or less expensive than generating pore water and its subsequent analysis. The reality is that actual passive media itself and the analysis of the passive sampling material are not expensive. The costs are associated with the laboratory project manager participating in project design, cost associated with the PE acquisition, cleaning and preparation, the cost of the PRC standards, the labor in spiking the passive sampling material, the cost of verification of the spiking the PRC, field and laboratory quality control samples are significant. For each field sample deployed, there are many quality assurance/quality control samples which need to be discussed, evaluated and potentially deployed	A table has been added to a new subsection of Section 1 on commercial laboratories based on reviewer's comment. The table lists new costs that need to be considered by commercial laboratories when starting to perform passive sampling. Including an actual cost model is beyond the scope of the document.

			as well. One field samples does not equal just one analytical sample. I would suggest developing a costing model/ check list so that the project team understands all the details which are required in the costing for the project. For example: (see table below): <table><tr><th>Scope of Services</th><th>Comment</th></tr><tr><td>Laboratory Project Manager for Project Design</td><td>Many times, the project team requires a senior project manager/technical director at the laboratory to support the discussi on the scope of services. This is often time above and beyond the routine support a project manager provides to a project and an hou rate for the senior technical person has to be considered.</td></tr><tr><td>Passive Sampling Acquisition &Cleaning</td><td>There is a cost of supplies and labor for the preparation of the material, even if it includes placement in various field placement devices.</td></tr><tr><td>Cost of PRC Spiking Solutions</td><td>The cost of the 13-C labeled or D- labeled PRCs can be very expensive, especially if these are compounds which are not routine used by the laboratory</td></tr><tr><td>PCBs Congeners</td><td>Up to hundreds of dollars for each PRC compound</td></tr><tr><td>Dioxin/Furan</td><td>Up to thousands of dollars for each PRC compound</td></tr><tr><td>Pesticides</td><td>Up to hundreds of dollars for each PRC compound</td></tr><tr><td>PAHs</td><td>Up to hundreds of dollars for each PRC compound</td></tr><tr><td>PRC Spiking Labor Cost</td><td>There is labor and supply cost for spiking the passive sampling material</td></tr><tr><td>Verification of PRC Spiking Verification samples</td><td>There is the additional analytical costs to verify the PRC spiking or passive sampler</td></tr><tr><td>Analytical Cost of Passive Samplers Field sample Field duplicate Method blanks Matrix Spikes Matrix Spike Duplicates Deployment blanks Retrieval blanks</td><td>This would include any Quality Control/Quality Assurance Sample which would be defined by the program. Field Duplicates, Field Blanks, Matrix Spikes, and Matrix Spike Duplicates, as required b the method. [These laboratory and field QC samples would need t created and deployed just like a field sample.]</td></tr></table> In many cases, we have found that the project teams were not anticipating these additional costs or understanding the magnitude of these costs in their engineering cost estimate. Section 6 or an additional section should address the cost implications associate with the PRCs, field QC and all the other matrix specific QA/QC requirements.	Scope of Services	Comment	Laboratory Project Manager for Project Design	Many times, the project team requires a senior project manager/technical director at the laboratory to support the discussi on the scope of services. This is often time above and beyond the routine support a project manager provides to a project and an hou rate for the senior technical person has to be considered.	Passive Sampling Acquisition &Cleaning	There is a cost of supplies and labor for the preparation of the material, even if it includes placement in various field placement devices.	Cost of PRC Spiking Solutions	The cost of the 13-C labeled or D- labeled PRCs can be very expensive, especially if these are compounds which are not routine used by the laboratory	PCBs Congeners	Up to hundreds of dollars for each PRC compound	Dioxin/Furan	Up to thousands of dollars for each PRC compound	Pesticides	Up to hundreds of dollars for each PRC compound	PAHs	Up to hundreds of dollars for each PRC compound	PRC Spiking Labor Cost	There is labor and supply cost for spiking the passive sampling material	Verification of PRC Spiking Verification samples	There is the additional analytical costs to verify the PRC spiking or passive sampler	Analytical Cost of Passive Samplers Field sample Field duplicate Method blanks Matrix Spikes Matrix Spike Duplicates Deployment blanks Retrieval blanks	This would include any Quality Control/Quality Assurance Sample which would be defined by the program. Field Duplicates, Field Blanks, Matrix Spikes, and Matrix Spike Duplicates, as required b the method. [These laboratory and field QC samples would need t created and deployed just like a field sample.]	
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		Section 6.2.5 Is always required to analyze a non-deployed passive sampler to confirm the spiking concentrations? We would call this a verification	Yes – this type of sample will always need to be analyzed when using PRCs. This type of sample is																							

			of spiking (and it is listed above as a QC samples) which has a cost implication to the project.	included in a new table (9-1) in Section 9 responding to similar comments by this reviewer.
	7	Extraction and Instrumental Analysis of Target Contaminants from Passive Sampling	Calculation 7-1. I don't really understand it at all...but that includes the entire discussion in that section. See notes below. This section seems to be a rehash of what has happened in the past and not a vision on how to execute work in the future. In working on projects, we recommend the project team to start with the end in mind. In this case, what is the level of sensitivity which you are looking to achieve for which compound of interest on this project? Once, that is known, then we recommend that project teams look at the available sampling material, discuss placement options and then we look at the material. With the material selected, size and mass, then we can start to look at the areas of sensitivity needed and method selection. In some cases, we can discuss more than one method selection, cost implications and then the selection can be made. It would be helpful if the project team had a check list or a flow diagram to start the discussion, and this could be tied into the costing discussion as well. I would find it useful if there was a summary of how each of the passive samplers would be received at the laboratory [each of the passive sampling section has something], so that the field staff would know what is required of them and the laboratory would provide them the necessary bottles/equipment and they would know how the samples would be received. The laboratories	In response to this comment and others by the reviewers, the text describing this equation has been expanded to improve clarity. The goal of this section is to provide the document user with guidance on how to extract and analyze passive samplers. Much of the content of this section is meant to inform the user that passive samplers are not very different from other environmental media that they have routinely extracted and analyzed in the past. The reviewer's comment addresses investigation design and organizing work flow which is beyond the scope of this document. Text is has been added to Section 7.1 summarizing the requested information: <i>Ideally, the POM and LDPE passive samplers will arrive refrigerated at the analytical laboratory in glass jars generally in coolers. The size of the</i>

			SOP would then reflect what they would be handling on their end.	jars will depend on the objectives of the investigation but will likely range from 20 mL to four liters in volume. The PDMS passive samplers, in the form of SPME fibers, will also arrive at the analytical laboratory in glass jars refrigerated but because of the SPME's small size, the jars will most often range in volume from 2 to 20 mL. For POM, LDPE and PDMS, the storage/transport jars should use clean foil as a lid liner (not a plastic polymer). The POM and LDPE films and SPME fibers can be processed in the field by the addition of organic solvent to the glass jars holding the retrieved passive samplers. This initiates the extraction and reduces the loss of volatile target contaminants during transport and storage. <u>It is extremely critical to confirm that vials and jars are firmly sealed and that solvent will not leak during transport.</u> If the samplers require extensive cleaning at the laboratory, they should not have solvent added to them in the field. In addition, if the passive sampler cannot be processed in the field or upon arrival at the laboratory (which is recommended), they should be stored at or below 4.0 °C in the dark until processing can be started. After recovery, the DGT samplers should be rinsed with deionized water prior to placement in a clean plastic bag. A few drops of deionized water should be added to the interior of the bag to maintain moist conditions and
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				<i>prevent drying. When the DGT samplers arrive at the analytical laboratory they should be refrigerated (~4.0 °C) in the dark in the same plastic bag (but not frozen).</i>
			On page 80, there is a narrative on method selection. I would suggest adding a table with method options and provide some summary information / guidance on method selection.	A new table (7-1) has been added to this section summarizing the extraction and analytical methodologies.
			This section jumps into a discussion on extraction /analysis without an overview/summary of extraction/analytical methods available for the program. I would suggest a summary table of options rather than such detail.	As noted above, a new table (7-1) has been added to this section summarizing the extraction and analytical methodologies.
			Table 7-1 should be in the introduction of the Section 7. This can be part of the summary table I referred to above. Also, the extraction methods should be listed as well as the analytical methods. Extraction methods should not be overlooked. In some of the HRMS methods, they are a part of the method.	As noted above, a new table (7-1) has been added to this section summarizing the extraction and analytical methodologies.
			Text Box 7-1, 7-2, 7-3 are very detailed. I believe most commercial laboratories know how to extract this media. It is important to specify how the media should be handled (Text Box 7.3, Step 1). That is the difference from a standard solid and a special program. And this detail should be reflected in the laboratories SOP on handling passive samplers.	A table has been added to Section 7.1 providing an overview of the extraction and analytical methods as requested by this reviewer in the comments above. The detailed text boxes (7-1, 7-2 and 7-3) have been retained and their legends revised to indicate that they are examples of extraction procedures.
			I think it would be helpful if there was a list/table of historical methods, [can reference the work done] listing each of the passive sampling	This is an interesting comment but beyond the scope of this user's manual.

			material which has been used, as well as a discussion of other methods as well.																					
			The document excludes some other analytical techniques which would be used to support the analysis. For example there are High Resolution GC/MS Methods which are a very viable option for passive sampler to achieve low reporting limits. For Chlorinated Pesticides, EPA Method 1699 is a HR/MS method and for PCB Congeners EPA Method 1668A is available for all 209 Congeners. I would also suggest adding EPA Method 1613 for Dioxin/Furan analysis as well. I am not suggesting that HRMS methods are the only option for the passive sampler but they should be added into the discussion as an option. These methods are commercially available. Much of the initial research used available analytical options within the various universities which in most cases did not include HR/MS technology.	The U.S. EPA Method 1699 has been added to Table 7-1 (previously Table 7-2). The other methods mentioned in this comment were already listed in this table.																				
			In Section 7.3 There should be some additional specification related to PCB analysis. There are a few options for PCB analysis and the document isn't clear. <table border="1"><thead><tr><th>Nomenclature</th><th>Method Choice</th><th>Analytical Technique</th><th>Comments</th></tr></thead><tbody><tr><td>PCB Aroclors</td><td>SW 846 Method 8082</td><td>GC/ECD</td><td>Choice of 7 or 9 Aroclors</td></tr><tr><td>PCB Homologs</td><td>SW 846 Method 8270/ EPA Method 608</td><td>GC/MS</td><td></td></tr><tr><td>PCB Congeners</td><td>SW 846 Method 8082</td><td>GC/ECD</td><td>Short list of Congeners, list in method does not reflect risk</td></tr><tr><td>PCB Congeners</td><td>EPA Method 1668A</td><td>HRGC/HRMS</td><td>Can report up to 209 congeners as well as Total PCBs.</td></tr></tbody></table>	Nomenclature	Method Choice	Analytical Technique	Comments	PCB Aroclors	SW 846 Method 8082	GC/ECD	Choice of 7 or 9 Aroclors	PCB Homologs	SW 846 Method 8270/ EPA Method 608	GC/MS		PCB Congeners	SW 846 Method 8082	GC/ECD	Short list of Congeners, list in method does not reflect risk	PCB Congeners	EPA Method 1668A	HRGC/HRMS	Can report up to 209 congeners as well as Total PCBs.	Some of the additional information listed in the table cited in this comment have been added to the text in Section 7.3; specifically, information about PCB analyses.
Nomenclature	Method Choice	Analytical Technique	Comments																					
PCB Aroclors	SW 846 Method 8082	GC/ECD	Choice of 7 or 9 Aroclors																					
PCB Homologs	SW 846 Method 8270/ EPA Method 608	GC/MS																						
PCB Congeners	SW 846 Method 8082	GC/ECD	Short list of Congeners, list in method does not reflect risk																					
PCB Congeners	EPA Method 1668A	HRGC/HRMS	Can report up to 209 congeners as well as Total PCBs.																					
			Commercial laboratories will provide the project team with the analytical results calculated as	To make the information in this section of the document as broadly																				

			discussed and agreed upon. The results will be expressed as on a mass basis or on a concentration basis. The laboratory will not be providing any Log Kow reference values nor making any calculations based on any Log Kow values which may be provided by the project team. Therefore, if section 7 is to focus on just the commercial laboratory portion of the program, I would suggest removing this information from the tables. I believe that university laboratories, with the project teams may include this in their data tables, but certainly a commercial laboratory would not. Page 80 makes reference to detection limits being reported with Kow, and that would be the project team and not the commercial laboratory.	useful as possible to as many users as possible, the log K_{ow} values listed in the tables have not been removed. Text has been added to the subsection on commercial laboratories in Section 1 to include recognition of how data will be quantified to insure C_{free} can be calculated.
			Section 7.3.1 – The terms Instrument Detection Limit, Method Detection Limit, PQLs, Detection Limits--- this entire section is confusing and seems to have a mismatch of terms. Commercial laboratories will have Method Detection Limits [MDLs] established for solid matrices which then they would have reporting limits based on these MDLs. In most cases, we would just be treating these matrices as any other solid matrix and our QA/QC procedures already have the information required. Our calculated results would be based on the mass of the material extracted. [High Resolution/Mass Spec methods are different since they are isotope dilution methods and therefore, they have EDLs rather than MDLs]. I find this entire section really really confusing and assume that it is based on university support (where they don't have routine MDLs/RLs) unlike commercial	The merits of this recommendation were considered but the text will remain in this part of the document and will not be moved. Some users of the document may find this information applicable and having it near the other methods valuable.

			laboratories which would have their MDLs developed to meet NELAP and other certifying body's requirements.	
			Analyze immediately needs to be defined in days. Laboratories define holding times per methods. If we treated these passive samplers as a solid sample, many of the holding times for GC / ECD such as Method 8081 for Pesticides, GC/MS methods such as Method 8270 for PAHs, the holding time would be defined as 14 days. Some of the HRMS methods, the holding time is defined as 1 year. A shorter holding time often have an increased cost impact to the project as well.	A discussion of the terms "immediate" and "immediately" has been added to the subsection on commercial laboratories in Section 1 to clarify what they mean relative to passive sampling.
	9	Quality Assurance and Quality Control, and Other Considerations	Section 9- Quality Assurance / Quality Control section should be much earlier in the document. By placing at the end, it seems to be an afterthought. This area can introduce cost into the program as well. I would recommend at summary table of the QA/QC samples that are available and recommended. Much of this QA/QC documentation should be addressed in the laboratories SOP as well as in the QAPP.	This section will remain in its current location. A brief introductory section of text has been added to the beginning indicating that this discussion is not exhaustive and is intended to allow research and commercial laboratories flexibility when preparing their standard operating procedures (SOPs). A summary table of quality assurance/quality control measures has been included to this section.
			Section 9.1. Field Blanks do not seem to be adequately defined. How are they different than a Deployment Blank? Are they the same? Is there a different process for deploying and retrieval to the lab? Should they be spiked with the PRCs? Is there a time frame in which these samples need to be analyzed within the lab from receipt? Immediately upon arrive is not defined. This also has cost implication for the project.	The summary table added to this section based on the comment above provides more descriptive information on field, deployment, retrieval and trip blanks. Information has also been added on whether or not they should include PRCs. As noted in response to a prior comment, text has been added to the subsection on commercial laboratories in Section 1

				addressing when samples need to be processed.
			Section 9.1.2. Isn't it assumed that analyte free reagents will be used throughout analysis? Why would a Field Solvent Blank be required?	This blank should capture any contamination occurring in the field when solvent is being added to the vials containing the recently retrieved passive samplers.
			Sections 9.1.3 & 9.1.4. Very confusing sections. Is the working assumption that the extraction of the material will be taking place when the passive sampler is place in a solvent vial?	Yes – the solvent in the vials will initiate the extraction of the target contaminants and remaining PRCs (if being used) in the recently retrieved passive samplers.
			Section 9.1.10. The text in this section does not support the section title. Something is mixed up here.	The sections 9.1.8, 9.1.9 and 9.1.10 each discuss specific aspects of the quality assurance related to a specific organic contaminant passive sampler (e.g., POM, PDMS and LDPE). Specifically, Section 9.1.10 discusses the accuracy of the measurements made by LDPE with reference to studies published in the scientific literature. The section title and content do support one another.
	Appendices	E	The introduction of DOD QSM guidelines for these technologies is unexpected. We do not believe that QSM criteria should be applied to an emerging market in my opinion. The use of project specific QAPP criteria is more appropriate. I believe that is what was executed in the example QAPP.	The DOD QSM guidelines are intended as examples and are not meant to be followed or required. Language has been added to the document and appendix to clarify that the DOD QSM guidelines are examples.
3	1	Is the document written in a style that will be accessible for users with a range of	The document could be reorganized to make the content more tractable to a wider audience.	This reviewer has provided an excellent and comprehensive review of the draft document but the extent and nature of the comments are well

		educational and technical backgrounds?	First, I suggest focusing this guidance document on passive sampling of hydrophobic organics (see response to question 5 in regard to suggested options for how metals should be addressed). Second, I recommend shortening the introduction chapter to cover objectives, background, types of passive samplers (LPDE, POM, PDMS) and deployments (in-situ and ex-situ options) and applications related to both assessing site risks as well as remedial efficacy. I would then include an expanded chapter describing the principles of passive sampling of hydrophobic organic chemicals that would present all the relevant equations that can be applied regardless of polymer phase. A revised outline of this “principles” chapter could be: 1. Stages of passive sampler operation (currently section 1.4) a. Potential use of biocides for ex-situ deployments (section 2.2.5) 2. Equilibrium passive sampling: a. Demonstrate equilibrium achieved i. Kinetic studies i. Simultaneous deployment and comparison of polymers with different amounts/ sampling rates b. Provide negligible depletion extraction i. Selection of polymer to sediment ratio (currently addressed under POM chapter in 2.2.2	beyond the scope of the current document. Specifically, the comments recommend a thorough reorganization of the document. However, the format of the document was agreed upon by the authors during the development phase.
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			but this concept is generally applicable to all passive samplers) 3. Selection of $K_{\text{polymer-water}}$ a. General considerations; need to reflect equilibrium conditions; need to specific polymer source and characteristics; discuss unit .. in case of POM/LPDE adopt mL water / g polymer in case of PMDS use mL water / mL PDMS b. General approaches i. Use of literature values i. Use of estimated values derived from QSAR (i.e. K_{ow}, ppLFERs) i. Experimental determination based on published methods (could generalize discussion on POM currently presented in section 2.8) c. Correction of $K_{\text{polymer-water}}$ for temperature and salinity 4. Non-equilibrium sampling requirements: a. Concept of PRCs to correct for non-equilibrium conditions b. Selecting PRCs c. Loading PRCs including spiking quantity d. Chemical analysis of PRCs following deployment e. Appendix that describes in more detail the underlying equations and assumptions incorporated into the GUI that has been developed to analyze PRC data and compute F_{eq} 5. Extraction and Instrumental Analysis a. General considerations applicable across polymers 6. Determination of method detection limits (currently 7.3.1 and 2.2.3) a. Analytical detection limits b. Mass of polymer	
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			c. Polymer-water partition coefficient d. Degree of non-equilibrium The three subsequent chapters that follow would then focus on application of the theory and related equations presented in this chapter to passive sampling with each of the respective polymers, i.e. one chapter for POM, LPDE and PDMS. These chapters should each have a consistent format and provide example calculations specifically relevant to passive sampling with the given polymer. For example, a common format that would link to the principles chapter described above would be: 1. Introduction 2. Sources and Characteristics (include polymer specifications and associated amounts or volumes that link to various commercial sources since these values are needed for normalization of analytical results and may not be obvious to many readers). If a specific source of polymer is recommended it would seem prudent to provide justification, e.g. for POM recommend only one supplier, why?. 3. Sampler Preparation 4. Exposure time and conditions for lab/field use a. General guidance on equilibrium vs on-equilibrium sampling options for polymer b. Example calculation of sediment to polymer ratio for ex-situ deployment 5. Equilibrium sampling	
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			a. Provisional $K_{\text{polymer-water}}$ for PAHs/PCBs and related QSARs (could have appendix with more detailed review of literature values for each polymer) b. Correction for temperature or salinity (if no data supporting correction state this for polymer as future need; if corrections available provide example calculation) 6. Non-equilibrium sampling a. Example application of GUI for determining F_{eq} for this polymer 7. Extraction and Instrumental Analysis a. Polymer-specific considerations for this sampler 8. Method Detection Limits a. Example calculation for this polymer 9. Summary of pros/cons for current use of this polymer The current QA/QC chapter could remain as a stand along section since it is applicable across polymers.	
	2	Does the document provide sufficient information for commercial analytical laboratories to begin to develop their own standard operating procedures for deploying, recovering and analyzing passive samplers as well as provide sufficient guidance for	As discussed in response to question #1, the current draft does not provide a consistent presentation of information across the different polymer types. Thus, the draft manual could be improved to help commercial labs better understand specific issues for deploying, recovering and analyzing the three specific types of polymers described. I seriously question the merit of providing a list of “experts” upon which external parties can contact. First, is this a realistic expectation of these individuals? Second, are there potential conflict	The document has been prepared to provide a consistent presentation of the three types of passive samplers most commonly used in North America (four samplers if DGTs are included). These descriptions are presented individually for each passive sampler type in Sections 2, 3, 4 and 5. Further, whenever possible, to unify the discussion, sections of the document provide a combined description of how several of the samplers are handled for a

		contacting experts in the field to ask questions.	of interest concerns in specifying “preferred experts”? Third, this list of individuals will be of limited value in the future as new experts in the field emerge. Fourth, what objective process has USEPA employed to identify this list of experts (and how might this list discourage future cooperation with other experts not included). Lastly, if the objective of this guidance document is to provide the essential elements for developing acceptable SOPs for passive sampling methods by external parties does not the need to provide a list of experts to address questions somewhat undermine the purpose of this manual? I also have similar concerns with providing a “short” list of commercial labs capable of performing analyses on passive samplers. Surely, interested individuals can find out what commercial labs advertise these capabilities and the extent to which these labs have contributed to the field via external publications and publications. Thus, I would suggest that Tables 1-2 and Tables 1-3 be deleted.	given topic area. For example, Sections 6, 7, 8 and 9 address PRCs, extraction and analytical chemistry, data analysis, and quality assurance for all of the samplers, respectively. Regarding the merits of listing experts and commercial laboratories for document users to contact. This comment reflects a difference in the philosophy of the dissemination of new technologies to the user community. The alternative approach to what is used in the draft document and what is being recommended by the reviewer is to simply state that there are people who have accrued expertise in using passive samplers and that there are commercial laboratories that can be hired to perform passive sampling. But that later approach dictates not providing any of that information to the user community. This approach leaves it up to the user community to identify the experts when they have technical questions and locate the commercial laboratories when they want to have work performed with passive samplers. The role of federal organizations like the U.S. EPA and SERDP/ESTCP is to provide as much technical assistance and transfer as is possible to the user community of new technologies.
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				There is a risk, we agree, of recommending specific technical experts and commercial laboratories because of the appearance of favoritism and bias. To address this concern, text has been added to Tables 1-4 and 1-5 indicating the tabulations provided are not exhaustive. Further, this document is not intended to be the last word or final source of guidance on passive sampling and it will have achieved ultimate success when the document is unnecessary because it, along with the work of others in the field, have made passive sampling so common place and routine that the document is no longer needed for guidance.																							
3	Are the calculations described in the document sufficiently clear to be performed by users with a range of educational and technical backgrounds.	No. I do not feel the present document explains sufficiently the theory and required calculations in a transparent manner. For example, it is not clear how type and configuration of the PS links to the amount (g of POM or LPDE) or volume (ul PDMS see below example in SERDP 2012 report) needed in various equations presented in the document. <table><tr><th>Fiber Designation</th><th>Inside dia. µm</th><th>Outside dia. µm</th><th>PDMS Volume (V) µL·m</th><th>PDMS L=V/Area(A) µm</th><th>Source</th></tr><tr><td>170/110</td><td>110</td><td>170</td><td>24.7</td><td>13.2</td><td>Polymicro</td></tr><tr><td>230/210</td><td>210</td><td>230</td><td>9.6</td><td>6.9</td><td>Fiberguide</td></tr><tr><td>1060/1000</td><td>1000</td><td>1060</td><td>29.2</td><td>97.1</td><td>Polymicro</td></tr></table> In some cases units used in equations are not clearly defined or described. I would recommend	Fiber Designation	Inside dia. µm	Outside dia. µm	PDMS Volume (V) µL·m	PDMS L=V/Area(A) µm	Source	170/110	110	170	24.7	13.2	Polymicro	230/210	210	230	9.6	6.9	Fiberguide	1060/1000	1000	1060	29.2	97.1	Polymicro	The level of detail requested in this comment is beyond the scope of the current document. In revising the document, a renewed effort has been made to insure all
Fiber Designation	Inside dia. µm	Outside dia. µm	PDMS Volume (V) µL·m	PDMS L=V/Area(A) µm	Source																						
170/110	110	170	24.7	13.2	Polymicro																						
230/210	210	230	9.6	6.9	Fiberguide																						
1060/1000	1000	1060	29.2	97.1	Polymicro																						

			using additional “break-out” boxes to highlight more “hands-on” examples of calculations for applying general principles to specific polymer types (e.g. see polymer-specific outline in response to question #1)	equations include a definition of the units.
	4	Are there any topics related to passive sampling in the document that should be excluded? Are there topics that should be included but are not currently discussed?	In my opinion, the inclusion of passive sampling methods for metals (i.e. DGT), which does not provide an estimate of C_{free} that can be directly linked to sediment quality criteria or bioaccumulation prediction, should not be integrated into this guidance document. Rather this document should focus on passive sampling methods for hydrophobic organic chemicals where application in sediment management context is broadly recognized. This is consistent with the goal of this document to provide contract laboratories with the information needed to develop SOPs using PS methods. In contrast, the utility of DGTs in the context of sediment management decision-making is evolving. Hence, it seems premature to be encouraging commercial labs to develop SOPs involving these techniques. I suggest either excluding PS of metals from this guidance document and instead developing a separate manual devoted to this topic in the future (ideally after DGT techniques are further optimized in sediment lab/field studies) OR including the present information as an appendix that highlights general concepts reflecting the current state of the science and need for further work in context of contaminated sediment assessment and	In the process of developing this document, the DGT methodology was incorporated. We agree that the DGT method does not provide a C_{free} value comparable to the C_{free} provided by the passive samplers used with hydrophobic organic contaminants (this is noted in Sections 1 and 8). However, in order to provide a complete overview to users of the passive samplers applied with hydrophobic organic contaminants and metals, including the DGT section is necessary. In response to this comment, a statement has been added to the beginning of Section 5: <i>Users of this document should be aware that the DGT technology is not as established as the passive sampling technology for the hydrophobic organic contaminants. The inclusion of the DGT methodology is provided in this document for completeness in presenting the primary passive sampling technologies used in North America and to make the document</i>

			management. This is consistent with the consensus view from the SETAC Pellston workshop that application of PSMs for metals in sediments is still largely in a research mode of development. The guidance document also seems to largely focus on non-equilibrium/in-situ PS but should provide a better balance to ex-situ/equilibrium sampling deployments as the later approach can be more practically applied. Ex-situ applications performed in an equilibrium sampling mode reduces cost and complexity of C_{free} estimation by avoiding the need for purchase, spiking, measurement and post data analysis of performance reference compounds. One particularly useful application of ex-situ equilibrium sampling is inclusion in laboratory sediment toxicity or bioaccumulation tests so that test endpoints can be linked to C_{free} measurements. Further, recent work also shows promise of in-situ sampling with PDMS (Witt et al. 2013; Maruya et al. 2015) without inclusion of PRCs. Given the advantages of equilibrium sampling using fast, negligible depletion samplers, EPA should acknowledge and encourage the future development of such methods when possible.	<i>user aware of the DGT approach while also recognizing that the technology is continuing to mature.</i> New subsections in Sections 2, 3, 4 and 5 have been added that specifically address <i>ex situ</i> and <i>in situ</i> deployments. In addition, a brief portion of text has been added to Section 6 discussing the potential promise of PRC-free <i>in situ</i> PDMS-SPME deployments.
	5	Are there other resources that the document should list (e.g., additional passive sampling experts, laboratories	Different sources of silicone rubbers are provided in Smedes et al. 2009 including the J flex-form upon which provisional recommended K_{polymer-water} for PDMS is based. Given the limited use of this PDMS source in the US an additional compilation of empirically derived K_{polymer-water} for selected PAHs and PCBs from other commercial sources	Additional text has been inserted into Appendix B indicating that other alternative K_{PDMS} values could be found in the citations recommended by this reviewer.

		performing passive sampler analyses, more case studies)?	of PDMS should be compiled and contrasted with the recommended $K_{\text{polymer-water}}$ values. Some key references include Reible et al (2012) [PAHs with Polymicro/Fiber guides]; DiFilipo & Eganhouse (2010) [PCBS/PAHs multiple PDMS sources] and Reible & Lufto (2008). Temperature dependence of $K_{\text{pdms-water}}$ has been reported by Reible et al. 2008 (Polymicro and Fiber Guide fibers) and Jonker et al 2015 (Altec PDMS sheets). The later paper also addresses salinity corrections. Theses references should be summarized and included in the PDMS chapter. It is also suggested to provide an example calculation of detection limits using thermal desorption of PDMS versus conventional solvent extraction to highlight the great potential to increase method sensitivity while avoiding use of solvents and potential loss of more volatile constituents (e.g. naphthalene). Given that SPARC is no longer publically available and not supported by USEPA (versus EPIWIN), the use of this model to estimate log Kow values for use in QSARs may present a barrier for practical use. If the reliability of Log $K_{\text{polymer-water}}$ - Log Kow relationships are not significantly reduced using EPIWIN Log Kow values, EPA may wish to reconsider using these values as inputs to these predictive models.	Text has been added to Appendix C addressing the substance of this comment and the new information suggested for discussion. Text has been added to <i>Section 7.2.2 Extraction of PDMS</i> highlighting the potential increase in instrumental sensitivity and reduction in organic solvent usage when applying the thermal desorption technique. In addition, text was added indicating that more volatile target contaminants may be lost using this technique. An example calculation was not included. To respond to this very good comment, the following text has been inserted in Section 7.3.1: <i>In addition, SPARC is no longer available free of charge. Consequently, it may be unrealistic for all users to operate this estimation software. Another source of physicochemical parameters, like K_{OW}, is the U.S. EPA's EPI Suite software (https://www.epa.gov/tsca-screening-tools/epi-suite).</i>
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			I suggest replacing the last case studying involving metals/DGT (see response to #1) with an example of ex-situ deployment for analysis of hydrophobic organics since all of the other case studies involve field studies, in-situ deployments. As previously highlighted, a useful example would be ex-situ measurements of C_{free} to support interpretation of lab toxicity or bioaccumulation tests with contaminated site sediments. Maruya et al. 2015 provides a recent example but other data from specific projects that are publically available, but not yet published, would be a good candidate as an ex-situ case study. With regard to POM, the recent critical review from Arp et al 2015 should be incorporated into the manual. <u>References:</u> Arp et al. 2015 Review of polyoxymethylene passive sampling methods for quantifying freely dissolved porewater concentrations of hydrophobic organic contaminants, Environmental Toxicology and Chemistry 34: 710–720 Difilippo, E. L.; Eganhouse, R. P. (2010). Assessment of PDMS-water partition coefficients: Implications for passive environmental sampling of hydrophobic organic compounds. Environ. Sci. Technol. 2010, 44, 6917–6925.	<i>estimation-program-interface). This program can be downloaded free of charge, is gaining usage by the passive sampling community, and represents a viable alternative to using SPARC.</i> The fifth case study on DGT passive sampling has been retained in the document but a sixth case study has been added that discusses an <i>ex situ</i> passive sampler deployment in combination with a bioaccumulation study. The Arp et al. (2015) was cited in Section 2 of the document. All of these citations have been included in the document (or were already present).
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			Jonker,MTO, SA van der Heijden, M Kotte, F Smede (2015). Quantifying the Effects of Temperature and Salinity on Partitioning of Hydrophobic Organic Chemicals to Silicone Rubber Passive Samplers, Environ. Sci. Technol. 49, 6791–6799 Maruya et al. (2015). A passive sampler based on solid phase microextraction (SPME) for sediment-associated organic pollutants: Comparing freely-dissolved concentration with bioaccumulation Chemosphere 137 192–197. Reible, D.D., G. Lotufo (2008), Lab Demonstration Plan-Summary and Results, ER-0624 Demonstration and Evaluation of Solid Phase Microextraction for the Assessment of Bioavailability and Contaminant Mobility, Report to ESTCP. Reible DD, Lotufo G, Skwarski A, Lampert D, Lu X (2012) Demonstration and evaluation of solid phase microextraction for the assessment of bioavailability and contaminant mobility, final report. ESTCP Project ER-200624. Environmental Security Technology Certification Program, Arlington Smedes, F.; Geertsma, R. W.; Van Der Zande, T.; Booij, K. (2009). Polymer-water partition coefficients of hydrophobic compounds for passive sampling: Application of cosolvent models for validation. Environ. Sci. Technol. 43 (18), 7047–7054. Witt et al. (2013). Passive Equilibrium Sampler for in Situ Measurements of Freely Dissolved Concentrations of Hydrophobic Organic Chemicals in Sediments, ES&T 47:7830-7839.	
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4	Front Material	Abstract	Page 6 – revise the estimated cost for Hudson and for addressing sediments nationally. The last estimate I saw for Hudson put the cost at \$2.25 billion. Gary Klawinski is the EPA program manager and could provide the best estimate and best document to cite. I don't know of any recent national analysis of costs to remediate sediments, but I can think of 3 sites that will likely cost over \$1 billion, many more that will hit several hundred million.	A new estimate of the Hudson River Superfund site remediation is 1.5 billion dollars. This new information has been added to the text. Also, revised text to indicate total costs were in the tens of billions of dollars.
	1	Introduction	1. Writing style/audience friendly – This section is appropriate for an audience of remedial contractors and analytical laboratories, and it's a good summary/history of the development of passive samplers. 2. Sufficient information – yes 3. Calculation Descriptions – These descriptions are well done and as simple as you can make them. 4. Topics to include/exclude – In Section 1.6 .1, HOCs – the focus is largely on the relationship to toxicity and bioavailability. Consider adding a paragraph to point out how this information might be used, such as in baseline & long term monitoring, as an input to a fate and transport model, or for design of remedial options. For example, Passive samplers provide a monitoring mechanism that is closely related to uptake by organisms, but are	No response necessary. No response necessary. No response necessary. No response necessary. A paragraph and table (Table 1.2) have been added to the text to address this comment.

			not affected by salinity, temperature, oxygen, non-CERCLA related pollution, etc. - Section 1.6.2, Metals – This leaves me thinking why bother using DGTs at all. The end of that section states “DGT measured metals provided valuable information on metal speciation, distribution, and flux that is important for quantifying exposure and, more specifically, bioavailable concentrations.” I think it would be good to expand on this, perhaps even provide an example of the use of DGT data. 5. Any additional resources – The navy has an interactive matrix called ISRAP (http://www.israp.org/) that helps RPMs sort out appropriate monitoring tools for different purposes/environments/contaminants. It covers PE and SPME’s, as well as a variety of other monitoring tools. It’s a good tool for understanding how passive sampling would fit into a monitoring program. That might be good to have listed somewhere, though maybe an appendix would be the best place. 6. Other comments – - Table 1.1 probably requires a caveat - “mention of company names or trademarks does not constitute an endorsement by EPA...” unless that’s included elsewhere. - Section 1.7, pg 34. The first two sentences of the following quote are confusing because the preceding text is already discussing	The authors believe it is important to retain the sections on DGT. Text has been added orienting the reader to Case Study 5 which is an example of using DGT at a contaminated sediment site. Two sentence were added to Section 1 highlighting the use of the on-line ISRAP tool with the passive sampling user’s manual. No response necessary. This statement is present in the Notice section. This section of text has been edited to clarify the point.
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			the choice of K values to use for this particular method. "Another evolving area for passive sampling is the approach used for calculating the C_{free} concentration for the target contaminants. As discussed in Section 8, one can assume that equilibrium has been achieved between the target contaminants and environmental phases (e.g., water, particulates, colloids), and C_{free} can be calculated using a KPS. Another approach, if equilibrium is not assumed, is to use performance reference compound (PRC) data to adjust the non-equilibrium passive sampler concentration (CPS non-eq) data for equilibrium conditions." I would edit this such that it is the beginning of a new paragraph and it begins "A common but evolving approach for passive sampling is to assume that equilibrium has been achieved..."	
	7	Extraction and Instrumental Analysis of Target Contaminants from Passive Sampling	1. Writing style/audience friendly – good 2. Sufficient information – good. The text boxes and tables are particularly useful. 3. Calculation Descriptions – for equation 7.1, it's not clear if V_s is the total volume of solvent for the extraction, the volume of solvent injected in the GC, or the volume of solvent after being reduced. Otherwise, it's a good description. 4. Topics to include/exclude – none 5. Any additional resources – none 6. Other comments –	No response necessary. No response necessary. The description of the equation has been clarified to better explain the variables. No response necessary. No response necessary.

			- Section 7.2.1, pg 74 – typos in the text make it illegible. - Text box 7.3, pg 78 – just looking to clarify the extraction times – the first extraction is for >12 hours, the 2nd, 3rd, and 4th extraction are for >10 minutes while agitating? What’s the reasoning behind this method? Why not agitate the first extraction, and is 10 minutes enough for the remaining extractions?	Text revised based on Reviewer #1 comment. The author of this section was contacted and asked to respond to this comment. He indicated that because of the overwhelming volume of organic solvent relative to polymer mass, the extraction procedure as described is capable of extracting nearly all of the target contaminants from the LDPE.
8	Data Analysis: Calculation of C _{free} and C _{DGT}	- Writing style/audience friendly – good - Sufficient information – yes - Calculation Descriptions – good - Topics to include/exclude – - It may be worth discussing the use of two samplers of different thicknesses to determine if equilibrium has been reached. Admittedly, it’s easiest to do this ex situ, but it is a simple and robust method to check for equilibrium and it has been done in situ. - Also, the intro in section 8.1, pg 86, states “This assumption can be based on previous experience with the passive sampler, the deployment site, or the design of the passive sampler investigation.” I might add as an example that one way to appropriately incorporate time to equilibrium in the design would be to do a small time series test.	No response necessary. No response necessary. No response necessary. No response necessary. Text has been added to Section 8.1 discussing the use of multiple thicknesses and time series to determine when equilibrium conditions have been achieved. See the response immediately above this one. Text has been added to this section to address the comment.	

			- Section 8.2, pg 87 – Perhaps we should include a discussion of who is responsible for these calculations. I think many RPMs would assume that the laboratory does it, but I think in many cases this is something that should fall to the contractor. Also, it's implied that the standard analytical QA/QC associated with the EPA methods should be done before anything is calculated, but perhaps it should be explicit that the Cfree calculations come after that. - Section 8.4, pg 93 – any case studies of DGT use? I think that the case studies are sufficiently useful that they should be a chapter of their own, rather than an appendix. 5. Any additional resources – none 6. Other comments – - Section 8.1, pg 86 – We can place the GUI's somewhere on this website: http://www.epa.gov/superfund/health/conmedia/sediment/index.htm. Unfortunately, there were some issues with the recent move to a new web platform, and this site is not fully operational. I can put the GUI's on the list to be added, but it may be a while before we can publish them to the site. - Figures 8.1 – 8.5 are difficult to read due to the pixilation.	Responding to this comment is beyond the scope of this document. Potential content for an implementation document. Case Study #5 is focused on DGTs. The document authors disagree with the reviewer, the case studies will remain in the appendices. No response necessary. No response necessary. No response necessary. Responded to this comment based on a similar comment by Reviewer #1. Text has been added to the Notice section to print the pdf with
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			▪ Explain the pros and cons of forcing the regression through an intercept of 1 (as allowed in the GUI, Figure 8-2). ▪ Section 8.3, pg 93 – where is Figure 8-17?	sufficient dots per inch (dpi) to insure readability. Responding to this comment is beyond the scope of this document. Potential content for an implementation document. The figure cited should be Figure 5-1 not 8-17. The text has been revised.
9	Quality Assurance and Quality Control, and Other Considerations	1. Writing style/audience friendly – good 2. Sufficient information – good 3. Calculation Descriptions – none 4. Topics to include/exclude – ▪ Sections 9.1.8 – 9.1.10, pg 96-97 – The section on specific QA/QC for POM focuses on the need to use the same type of POM as was used to measure the K_{POM} values that you're using, a thickness of 76um or less, and a solvent of hexane-acetone. Why aren't there similar considerations for PDMS or PE? Are these polymers that much more consistent? I see that appendix A notes some differences between manufacturers of different PDMS. That should be discussed here as well. ▪ Section 9.2.2, pg 98 – Is there a recommended method for measuring the DBL?	No response necessary. No response necessary. No response necessary. No response necessary. Comparable text has been added to the quality assurance sections addressing each type of passive sampler and emphasizing the importance of using the same thickness and batch of polymer for deployments and determination of partition coefficients. Table 1-1 provides information on commercial sources of the polymers. The author of this section was contacted and text has been added to the document addressing ways for	

			5. Any additional resources – none 6. Other comments – none QAPP Passive Sampling for Persistent Organochlorine Pollutants (POPs) in the Water Column of the Palos Verdes Shelf (2013) This is a useful example. I would add a line to the introductory text stating “This QAPP is for passive sampling of surface water, however it is broadly applicable to porewater sampling as well.” Also, it might be useful to have a second example QAPP where passive sampling was used as a dose-metric for toxicity tests, or at least where passive sampling was done ex situ.	estimating the thickness of the diffusion boundary layer (DBL). No response necessary. No response necessary. Agreed; Text emphasizing the water column sampling has been added. In addition, a second interstitial water passive sampling QAPP-like document (i.e., specifically, a Sampling and Analysis Plan (SAP)) has been included in Appendix G. An unsuccessful effort was made to locate an <i>ex situ</i> QAPP to include in the document.
5 & 6		Specific Comment	We have many concerns about this technology as it is adopted by commercial labs, outside of our comfort zone which has generally involved successful analyses by academia. Many lessons learned on the Portland Harbor/11E application of the technology with MIT should be exhibited/discussed here (callout/case study box?). Phil or I can provide the 11E passive sampling report which details commercial lab problems experienced which need to be captured. Uncertainties alleged by the Hawthorne paper (attached) should be noted and addressed in some fashion. Though he is an author on this document, it is not apparent how these concerns were addressed. Frankly, the paper raised	Responding to this comment is beyond the scope of this document. Potential content for an implementation document. Responding to this comment is beyond the scope of this document. Potential content for an implementation document.

			anxiety levels when presented at the Battelle 2015 conference on the part of my less inclined to try passive sampling RPM colleagues, so the more these issues can be addressed directly, the better.	In addition, many of the issues raised by Hawthorne et al. (2015) are addressed through-out this document (e.g., selecting reasonable partition coefficients).
			We would like to reiterate our concern that in Figure 1-5, the likelihood of vandalism of the sampling array is high. We have experienced sample loss that risked the overall study being undertaken when surface buoys have been deployed, and arrays tampered with and/or stolen. As stated in section 3.3 “running to shore” is an option, and in our collective 5 decades of sampler deployment, far preferable when possible to limit vandalism. Subsurface buoys are another technique that should be considered if tag-lines to shore are not feasible.	Text has been added to Sections 1, 2, 3, 4 and 5 on ways to avoid vandalism of field deployed passive samplers.
			Information should be further explored on adjustments needed to account for temperature and salinity in highly modified systems, e.g. higher than normal groundwater discharge temperatures on the west coast due to abnormally low rainfall/snowpack and groundwater systems contaminated by salt from manufacturing impacting partitioning coefficients beyond what might normally be expected. Appendix C should go into more detail on practical considerations, such as variability within feet of passive sampler placement that warrants measurement of temperature and salinity at the time of sampler placement and retrieval via a real time instrument such as a hydrolab pumping porewater to the surface via tubing/piezometer to	Responding to this comment is beyond the scope of this document. Potential content for an implementation document. Text has been added to Section 1 recommending users contact the technical experts in Table 1-4 in situations beyond those discussed in this document.

			ensure these parameters are appropriately bracketed and uncertainties minimized.	
			A reference should be included that “Diver health and safety concerns for deployment of samplers in contaminated waters are beyond the scope of this guide. Please contact the Environmental Response Team and/or Region 10 dive unit expertise centers in polluted water diving for more information.” I can provide a web site, papers, or other contact information as needed, but the document as written leaves this issue wide open—it would be helpful to give RPMs some indication that this is a serious health and safety issue and point them in the right direction to get example HASPs, dive plans, and other assistance. Many publications on such considerations are included here: http://yosemite.epa.gov/r10/OEA.NSF/investigations/divepubs	Agreed; text on diver health and safety has been added to Section 1.
			Additional deployment QA/QC measures should be appreciated in this guide. For example, for co-located grab samples and core samples, is a particular sequencing of sample design preferred to ensure pore spaces being sampled by the passive media are undisturbed?	Responding to this comment is beyond the scope of this document. Potential content for an implementation document.
	3	Passive Sampling with Polydimethylsiloxane (PDMS)	3.3.2 “Retrieval by divers or remotely by pulling on an attached line has been demonstrated at multiple field locations and is easy to implement in all environments.” This is a gross misrepresentation. There are many environments where diver based deployment is anything but easy. Suggested revision, “If surface based retrieval is not feasible, diver based retrieval will be necessary, which involves special considerations including appropriate PPE usage.	Agreed; the text has been revised and new text added to this section recommending consultation with divers if it is necessary to have divers deploy or recover passive samplers.

			Consulting with EPA experts on diver based deployment and retrieval is recommended.”	
	4	Passive Sampling with Low-Density Polyethylene (LDPE)	Biofilms are discussed in 4.4 relative to analysis, but not for other impacts. It would be helpful if the guide could address biofilm impact (or not) on equilibrium timeframes, if any. This should cross reference a recommendation to load PRCs at all stations to control for variable uptake of target contaminants.	Agreed; text has been added to Section 6 recommending the use of PRCs to consider the effects of biofilms and fouling on attaining equilibrium.
	Appendices		Case study #2. Please add “EPA scientific divers placed and retrieved PSR samplers to ensure proper placement and quality of the retrieved sample.” It would also be appropriate to note here that EPA divers were substantially involved in the sampling and analysis plan at PSR to ensure sample retrieval. In this example, EPA divers were instrumental in having samplers deployed on transects which were not visible from the surface, thereby ensuring sample integrity.	Text emphasizing the diver’s contributions to the project have been added to the <i>Site Narrative</i> section of this case study.
			Case study #2. Please include a photo of samplers being deployed at PSR. (EPA r10 diver...) “EPA scientific diver Brent Richmond takes a surface grab sample co-located with an SPME passive sampler at the PSR site. Photo by Sean Sheldrake, USEPA.”	Suggested photograph and figure legend added to Case Study #2 in Appendix F.
			I would suggest adding the attached photo (img 1424) with credits to the final document in case study #3 “EPA scientific diver Brent Richmond places an SPME passive sampler at the Wyckoff Superfund Site to assess cleanup effectiveness. Photo by Sean Sheldrake, USEPA.”	Suggested photograph and figure legend added to Case Study #3 in Appendix F.
			For case study #4 at United Heckathorn, please credit the 2013 deployment having been designed	Text emphasizing the diver’s contributions to the project has been

			and conducted by USEPA Environmental Response Team scientific divers.	added to the <i>Site Narrative</i> section of the case study.
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