Laboratory, Field, and Analytical Procedures for using Passive Sampling in the Evaluation of Contaminated Sediments: User's Manual

Peer Review Charge Questions

Background Information:

While there is a distinct need for using passive sampling at contaminated sediments sites, there has not been definitive guidance on the laboratory, field and analytical procedures for using passive sampling at such sites. This document is intended to provide users of passive sampling with the guidance necessary to apply the technology to evaluate contaminated sediments. The document is not meant to be a series of standard operating procedures (SOPs) but should provide the information necessary for commercial analytical laboratories to develop their own SOPs. The contaminants discussed in the document include primarily polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and the metals cadmium, copper, nickel, lead and zinc. Other contaminants, including chlorinated pesticides and dioxins and furans, are also discussed.

The document is divided into ten sections, each discussing aspects of passive sampling including the different types of samplers used most commonly in the United States, the selection and use of performance reference compounds (PRCs), the extraction and instrumental analysis of passive samplers, data analysis and quality assurance/quality control, and an extensive list of passive sampling related references. In addition, the document has a set of appendices that discuss facets of passive sampling in greater detail than possible in the main document. In your review, please focus on the sections of the document listed in the **Focus Areas** below.

Focus Areas:

Sections: 1, 6, 7, 8, 9 and relevant appendices

Charge Questions:

As you read through the sections of this document that you have been asked to focus upon, please provide written responses to the best of your ability to the following questions. Additional comments and recommendations for improving this document and associated methodology are also welcome:

(1) Is the document written in a style that will be accessible for users with a range of educational and technical backgrounds?

- Yes

(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 contacting experts in the field to ask questions.

- 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.

- Introduction - 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 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.

- Introduction - 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.

- Introduction - 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.

- 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.

(3) Are the calculations described in the document sufficiently clear to be performed by users with a range of educational and technical backgrounds?

- Section 7- Calculation 7-1. I don't really understand it at all…but that includes the entire discussion in that section. See notes below.

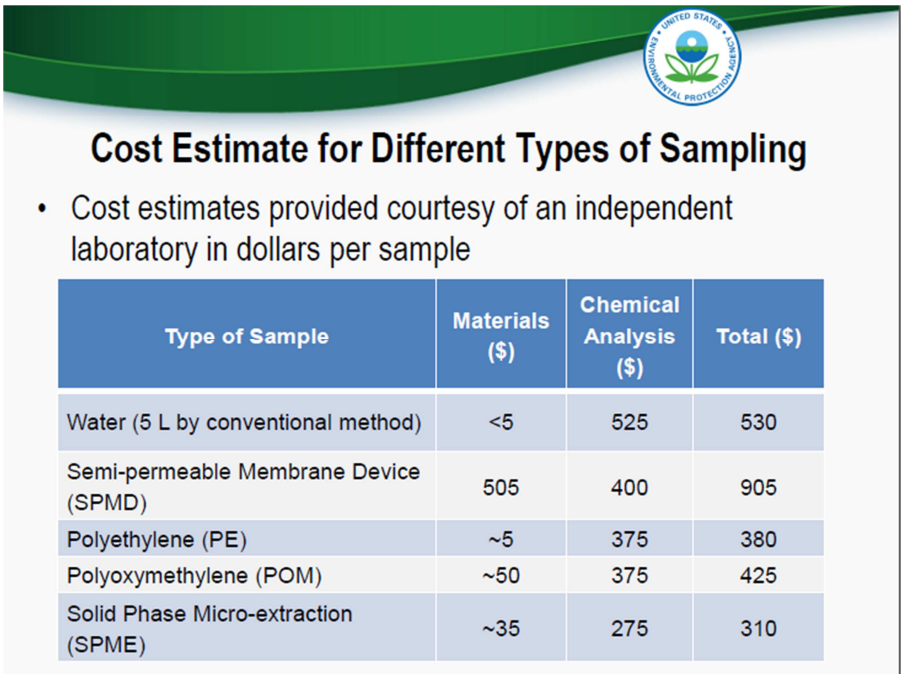
(4) Are there any topics related to passive sampling in the document that should be excluded? Are there topics that should be included but are not currently discussed?

- There are a lot of analytical details within this document. I believe that it is important in the introduction to emphasis 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).

- 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:
    - **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 shelf' support and there needs to be discussion in many areas.
    - **Media-** acquisition & handling, including choices of media, fabricating media for deployment & use of PRCs.
    - **Deployment of media –** handling of the media to get it to the site & QA/QC samples associated with it
    - **Retrieval of media-** handling of the media to get it to the lab & QA/QC samples associated with it
    - **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.

- Section 6- 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.



Cost Estimate for Different Types of Sampling

- Cost estimates provided courtesy of an independent laboratory in dollars per sample

Type of Sample	Materials ($)	Chemical Analysis ($)	Total ($)
Water (5 L by conventional method)	<5	525	530
Semi-permeable Membrane Device (SPMD)	505	400	905
Polyethylene (PE)	~5	375	380
Polyoxymethylene (POM)	~50	375	425
Solid Phase Micro-extraction (SPME)	~35	275	310

[Presentation from Matt Lambert EPA to Sediment Management Work Group 5/17/2013 copy of entire presentation attached; this is Page 12]. 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 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:

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 discussion on the scope of services. This is often time above and beyond the routine support a project manager provides to a project and an hourly 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 routinely 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 on the 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 Samples which would be defined by the program. Field Duplicates, Field Blanks, Matrix Spikes, and Matrix Spike Duplicates, as required by the method. [These laboratory and field QC samples would need to be created and deployed just like a field sample.]

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.

- 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 of spiking (and it is listed above as a QC samples) which has a cost implication to the project.

- Section 7- 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.

- Section 7- 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 SOP would then reflect what they would be handling on their end.

- 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.

- Section 7 – 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.

- Table 7-1 should be in the introduction of the Section7. 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.

- 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.

- 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 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.

- 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.

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.

- Section 7- Commercial laboratories will provide the project team with the analytical results calculated as 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.

- 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 laboratories which would have their MDLs developed to meet NELAP and other certifying body's requirements.

- 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

- 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 (Kpom). Is it really the intention of the document to allow laboratories to develop their own Kpom 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.

- 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?]

- **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.

- 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.

- 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.

- 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?

- 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?

- Section 9.1.10. The text in this section does not support the section title. Something is mixed up here.

- Appendix 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.

(5) Are there other resources that the document should list (e.g., additional passive sampling experts, laboratories performing passive sampler analyses, more case studies)?

- 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 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 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.

Please provide your written comments to Virginia Houk (Houk.virginia@epa.gov) no later than 18 September 2015. If you have any questions concerning the draft manual or the charge, please do not hesitate to contact me at 919-541-2815. We sincerely thank you for your input to our peer review process.