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**MEMORANDUM**

**DATE:** 25 June 2012

**SUBJECT:** Reconciliation Memorandum on Review of *Procedures for the Derivation of Equilibrium Partitioning Sediment Benchmarks (ESBs) for the Protection of Benthic Organisms: Nonionic Organics*

**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Please find below my responses to the comments by the five external reviewers on this draft guidance document. For several of the comments, my co-author Dr. Susan Kane-Driscoll (Exponent, Inc.) contributed to the responses. The five 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. In particular, Reviewer #4 provided a series of constructive comments that changed the use of some key terminology and wording in the document (including the document's title and focus). Despite the quality 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. 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.

In the Responses below, revisions to the document have been made in red font on italicized text. For Reviewer #5, "Reviewer Response" is the reviewer's answer to specific questions asked as part of the formal review format. The "Editor Response" is my response to Reviewer #5 comments. For citations in this memorandum that refer to papers cited in the draft ESB document are not fully referenced. However, new citations not in draft ESB document are joined with brief references (e.g., Journal, Volume: Pages).

Please note the responses below are presented as they appeared in the preliminarily revised version of the document. With further revision of the document for clarity and continuity, the wording of the revisions shown below may change to some degree. However, it is unlikely any changes of substance recommended by the reviewers will be modified by later revisions of the document for clarity and continuity.

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

## Reviewer #1

Comment: The document reads fairly easily and from a technical standpoint, the document is fine. I don't really have any major comments. I'm on top of this literature and this report is quite good in citing and brings the things together on the passive sampling subject.

Response: -

Comment: I have few concerns about the document. Most importantly, EqP theory (assuming I understand it correctly) assumes that solids, dissolved organic carbon in the sediment interstitial water, and interstitial water (freely/truly dissolved chemical) are at equilibrium in the sediment. However, EqP makes no assumption about the magnitude of the partition coefficient among these phases but rather EqP theory is an assumption about the chemical having the same activity or fugacity in all three phases. As it has been applied, organic carbon normalization has been used in defining the partition coefficient, i.e.,  $K_{OC}$ . The text, in places, reads as if EqP assumes that the partition coefficient is  $K_{OC}$ . I strongly suggest that authors look very carefully at the text and make sure that this confusion does not exist nor is it implied.

Response: I contacted the reviewer by e-mail and we agreed no change was necessary.

Comment: The document seems to be missing text in Section 2.4 on the method, used by many investigators including Hawthorne et al. 2009, for measuring concentrations of chemicals in porewater. With this method, 1 g of sediment is diluted with 10 ml of water (volumes and masses are illustrative) and passive sampler is added to the mixture. In essence, one is making porewater. Discussion of this is very limited and it feels like more details are needed.

Response: The suggested citation for Hawthorne et al. (2009) has been included in Section 2.4.2 under the discussion of adding passive samplers to sediment-water slurries.

Comment: There is no discussion of uncertainties associated with any of the methods. Discussion of the uncertainties should be included in the document; maybe with the examples?

Response: This concern was expressed by several reviewers and text has been added through-out the document addressing this point (e.g., Section 1.5).

In response to the Charge Questions:

Front Matter:

Comment: The opening is acceptable and provides the reader with adequate background for this document.

Response: -

Comment: add  $f_{BC}$  to glossary

Response: The suggested text has been added to the Glossary:

*f<sub>BC</sub> Fraction of black carbon in sediment*

### Section 1: Introduction

Comment: Section 1.2, first paragraph: Are all of these items true or have you run into the issue I outlined above?

Response: I contacted the reviewer by e-mail and we agreed no change was necessary.

### Section 2: Procedures for deriving site-specific ESBs

Comment: Section 2.2: Some folks are using chromic acid digestion to remove diagenic carbon. Should this method be referenced?

Response: A sentence indicating other methods are used has been added to Section 2.2:

*Other methods are available for measuring BC but are less commonly used with contaminated sediments (e.g., chromic acid digestion, microscopic inspection).*

Comment: Section 2.3: Should you add some text stating how difficult this is to do with sediments?

Response: The following text was added to Section 2.3.1:

*Further, in general, eliminating and/or avoiding artifacts when centrifuging can be quite difficult experimentally.*

### Section 3: Examples

Comment: Table 3.1: page 3-6. I would remove “TUs”

Benzo[ghi]perylene	2.7	72	0.07
Total	257		9.3

Similarly for other locations in the tables.

Response: The “TUs” have been removed from relevant tables in Section 3.

### Section 4: Implementation

Comment: Yes, the tiered approach in the section is useful. However, I think you need to add the fact that even if concentrations are below ESBs for a group of chemicals, the samples could be toxic from other chemicals. Obviously, the flowchart does not work in this case.

Response: Text has been added to Section 4.2 clarifying the interpretation of Tier 3 from the flowchart:

*Finally, it should be recognized that if a whole sediment toxicity test finds significant toxicity, the cause or causes may be toxic chemicals other than those measured in Tiers 1 and 2.*

Comment: The suggestion that one measure concentrations in porewater instead of predicting concentrations in porewater is good.

Response: -

Section 5: References

Comment: The literature is sufficiently cited.

Response: -

## **Reviewer #2**

**Front Matter: *Foreword, Abstract, Table of Contents, Executive Summary, etc.***

Comment: The front matter is very well written and provides necessary information to the reader.

Executive summary first word: Replace ‘This’ with ‘The’

Response: Recommended change entered into text in the Executive Summary.

### **Section 1: *Introduction***

The introduction provides a concise and adequate background. Specific comments are:

Comment: Section 1.3 last sentence:

Here, and throughout the document the phrase ‘bioavailable concentration’ has been used which is very misleading. In most places ‘bioavailable concentration’ is simply replacing ‘freely dissolved concentration’. I would suggest removing the term ‘bioavailable concentration’ throughout the document and use a more specific term as appropriate for the situation.

Response: The entire document was reviewed and “bioavailable” replaced with “freely-dissolved” in instances where the latter was more appropriate.

Comment: The following sentence should be replaced with the suggested sentence

below: "...Further, in recent years, technologies have been developed which use EqP theory to measure the bioavailable concentrations of contaminants in sediments rather than attempting to estimate concentrations of bioavailable contaminants from sedimentbound concentrations" Replace this with: "Further, in recent years, technologies have been developed which directly measure freely dissolved porewater concentration of chemicals instead of estimating from sediment-bound concentrations."

Response: The reviewers comments were edited slightly and the following text added to Section 1.3:

*Further, in recent years, technologies have been developed which combine passive sampling and EqP theory to calculate the freely dissolved interstitial water concentrations of chemicals instead of estimating them from sediment associated concentrations.*

Comment: Section 1.4: Line 12: replace 'then' with 'than'

Response: Recommended change entered into text in Section 1.4.

## **Section 2: Procedures for Deriving Site-Specific ESBs**

This section provides a nice description of procedures. Specific comments:

Comment: Section 2.2: last sentence:  
Temperature should be 375 C not 275 C

Response: Recommended change entered into section 2.2.

Comment: Section 2.2.2. last sentence of first paragraph: Remove repetition of 'range of'

Response: Recommended change has been entered into the text in Section 2.2.2.

Comment: Section 2.2.2. last sentence: Another problem with the black carbon approach is that particle size of black carbon can have a major influence on K<sub>bc</sub>. Fine soot particles with large specific surface area can have an order of magnitude higher sorption capacity than a large particle of coke or charcoal, both registering high fBC values. Can cite: "The Role of Black Carbon in Influencing Availability of PAHs in Sediments. U. Ghosh. *Human and Ecological Risk Assessment*. 13, 276–285, 2007."

Response: Recommended change was added to Section 2.2.2:

*such as coal tar pitch, exhibit a range of partitioning behavior as well as the black carbon particle size affecting the magnitude of the K<sub>BC</sub> (Hong et al., 2003; Ghosh et al., 2003; Khalil et al., 2006; Ghosh, 2007; Ghosh and Hawthorne, 2010).*

Comment: Section 2.3.3. last sentence of first paragraph: Note: there is no 'non-bioavailable' interstitial water concentration. Bioavailability term should be used with reference to

sediment concentrations only throughout the document.

Response: The word “bioavailable” has been replaced with “freely dissolved” in Section 2.3.2. Also note, the original Section 2.3.2 (*Quantification of Dissolved and DOC-associated Nonionic Organic Contaminant Phases*) was deleted from the document. In the revised document, the former Section 2.3.3 is now Section 2.3.3.

Comment: Section 2.3.3. second paragraph: “*Even low KOW nonionic organic chemicals are known to bind to this material, causing a reduction in their bioavailability.*” Not sure what this means. High DOC in interstitial water is not going to reduce freely dissolved PW concentrations at equilibrium with sediment.

Response: A potential source of confusion in this section is that for this discussion the interstitial water has been already been isolated from the sediment matrix and consequently is no longer in an equilibrium system that includes the sediment. Under these circumstances, the presence of elevated dissolved organic carbon will affect the bioavailability of nonionic organic contaminants due to partitioning to the dissolved organic carbon. The following clarifying text has been added to Section 2.3.2:

*However, this approach is problematic and is not recommended because high concentrations of DOC can be present in isolated interstitial water.*

Comment: Same paragraph as above: “*Therefore, a liquid-liquid extraction of interstitial water would contain both the freely-dissolved and the DOC-associated chemical, overestimating the true bioavailable concentration.*” Again, inappropriate use of the term 'bioavailable'. Replace with: ...overestimating the true bioavailability of the compounds.

Response: The text has been changed to the following in Section 2.3.2:

*over-estimating the true bioavailability of the nonionic organic chemicals.*

Comment: Section 2.3.3 third paragraph: Need to explain this better. What is the C18 SPE for? extraction of DOC or DOC-associated contaminants?

Response: The following descriptive text has been added to the third paragraph of Section 2.3.2:

*Solid phase extraction (SPE) using C<sub>18</sub> selectively isolates the freely-dissolved chemical on the column while the DOC-associated chemical passes through the column. The freely-dissolved chemical can then be eluted from the column with an organic solvent (Landrum et al., 1984; Ozretich et al., 1995). The application of this method depends on the DOC-associated concentration being operationally defined as the chemical passing through the column.*

Comment: Section 2.4.1: Paragraph 5 (SPME): The SPME method of Hawthorne et al. is a laboratory sampling technique for PW measurement that is very different from the equilibrium SPME approach when a SPME fiber is used much like a passive sampler.

Need to cite the new ASTM and USEPA methods for SPME here.

Response: To avoid the confusion the reviewer is referencing, the citation Hawthorne et al., (2005) has been removed from Section 2.4.1: Paragraph 5. In turn, Section 2.4.3 discusses the depletive sampling method the reviewer is describing and the ASTM (2010) method is included in the citations along with Hawthorne et al., (2005).

Comment: Section 2.4.2.1: section heading: “Inappropriate use of the term ‘bioavailable’. Not sure what is meant by ‘bioavailable concentration’. Replace with freely dissolved PW concentration.

Response: The term “Bioavailable” has been replaced with “Freely-Dissolved”.

Comment: Same section: “*Values for KPS-d are passive sampler specific and can be found in the literature*”: Would be appropriate to suggest confirming KPS-d values for the specific polymer used in a study

Response: Agreed, text as suggested by the reviewer has been added to Section 2.4.2.1:

*However, whenever viable, laboratory confirmation of literature-based  $K_{PS-d}$  values for a given polymer is recommended highly.*

### **Section 3: Example Calculations of Site-Specific ESBs**

Comment: The examples provided are illustrative and helpful for the potential user. The presentation can be improved with the suggestions below. One potential contradictory aspect of the example is that the two sediments were MGP-impacted matrices. MGP PAH contamination is typically associated with coal-tar source materials, and as such, the examples may be presenting data for a coal-tar NAPL contamination source while early in the document there is a disclaimer which states the following: “*The effects of petroleum and other non-aqueous phase liquids (NAPLs) on contaminant bioavailability are not considered in this document due to the lack of approaches, at this time, for accurately addressing their effects.*” I think it will be appropriate to explain the disclaimer further by stating that MGP industry NAPL sources such as weathered coal tar and pitch often behave as condensed phase carbons (especially after extensive weathering) and direct measurement of porewater concentrations for such source material impacted sediments may be possible.

Response: The reviewer makes a good point about manufactured gas plant (MGP) sites sometimes being contaminated with non-aqueous phase liquids (NAPLs) but that is not always the case. For Section 3.0 of the document, some of the information used to develop the examples was from a MGP site but not a site with known NAPLs present. Regarding adding more text to the disclaimer in Section 1.4, it is probably too early to make any specific statements in this guidance document about our ability to understand the effects of weathered coal tar and pitch on interstitial water concentrations of contaminants. We do not disagree with the reviewer that our

understanding is improving but believe it may be misleading at this point in time to add such text to this guidance document. No change was made to the document.

Comment: Equation 3-1: Suggest using Equation 2-2 first to calculate  $C_d$  and then use the same approach as in the 2-carbon model to calculate total toxic units. It will be easier for the practitioner to use similar approach for the calculation using the 1-carbon and 2-carbon models. The difference between the two models will be better understood if the  $C_d$  values for both methods are presented and can be compared.

Response: While it is agreed that Equation 2-2 could be used to calculate the toxic units in the one-carbon model and this would be more similar to the approach used in the two-carbon model, the example uses the current convention for calculating toxic units with the one-carbon model (i.e., organic carbon normalization of the sediment dry weight and effect concentrations). However, it is also agreed that showing the practitioner how to use the approach that does not use organic carbon normalization to derive toxic units could be very instructive and serve as a good introduction to the next section on the two-carbon model. Consequently, the following paragraph has been added to the end of Section 3.2.1:

*As noted above, the approach for using the one-carbon model followed the convention described in the earlier U.S. EPA ESB documents (U.S. EPA, 2003d; 2008) in which the dry weight PAH concentrations were converted to the organic carbon normalized concentrations ( $C_{OC}$ ) and then divided by the organic carbon normalized PAH-specific FCV to derive the  $ESBTU_{FCV}$ . An alternative approach and one more similar to the approach used in the two-carbon model discussed in the next section, is to calculate the  $C_d$  using Equation 2-2:*

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*The  $C_d$  value calculated for each PAH would then be divided by the  $C_{dPAHiFCVi}$  from Table 3-1 rather than the  $C_{OC,PAHi,FCVi}$  to derive the  $ESBTU_{FCVs}$ . The two approaches will result in the same number of toxic units for a given sediment but the approach using  $C_{OC,PAHi,FCVi}$  is currently more commonly applied in assessing sediments when using the one-carbon model.*

Comment: Section 3.2.2: “Note that the  $C_{dPAHiFCVi}$  is a different value than the  $C_{OCPAHiFCVi}$  used for calculating the one-carbon model based toxic units.” See previous comment. Use  $C_{dPAHiFCVi}$  for both carbon models.

Response: See response immediately above this one relative to Section 3.2.1.

#### **Section 4: Implementation of Site-Specific ESBs**

This section is very useful. Specific comments are listed below.

Comment: First paragraph: “..... the result may result in.....” Awkward, change to ‘.. the site may need to be cleaned up via ...’

Response: Agreed, the following text has been inserted into Section 4.1:

*“the site may need to be remediated via”*

Comment: First paragraph last sentence: This document presents 4 alternate methods of assessing Toxic Unit values, but does not necessarily demonstrate accuracy of the methods. Note: there is no direct comparison to a true toxicity end point in the examples provided.

Response: Agreed but that comparison is beyond the scope of this document. The primary objective of this document is to provide a summary of procedures for determining the freely dissolved concentration of nonionic organic contaminants in sediment interstitial water in order to derive interstitial water toxic units. More specifically, the examples provide an illustration of the calculations involved in the determination of interstitial water toxic units. This is a good suggestion but unfortunately matching toxicity data are not available for the two examples in the document. In previous ESB documents, examples were provided but did not necessarily also include matching toxicity data. No change made to text.

Comment: Second paragraph: *“Further, the two carbon model is not applicable to all nonionic organic chemicals for which ESBs are relevant; that is, the two carbon model should only be used with planar organic chemicals (e.g., PAHs).”* This statement is not correct. The 2-carbon model can be used for any hydrophobic chemical as long as the correct  $K_{BC}$  values are used.

Response: In principle, I agree with the reviewer. However, currently, many  $K_{BC}$  values are being estimated based on linear relationships derived from  $K_{BC}$  versus  $K_{OW}$  for PAHs and not for other classes of non-planar organic chemicals. The text has been modified here (Section 4.1) and earlier in the document (i.e., Section 2.2.2) to make the reviewer’s point while acknowledging the uncertainty that may exist for  $K_{BC}$  values for non-planar organic chemicals:

*Further, the two carbon model is applicable for all classes of nonionic organic chemicals assuming the appropriate  $K_{BC}$  values are used in the model calculations. Currently, many  $K_{BC}$  values are derived using linear free energy relationships between  $K_{BC}$  and  $K_{OW}$  for planar chemicals like PAHs but not non-planar compounds. As noted earlier, these  $K_{BC}$ s may not be appropriate for using with non-planar compounds and may result in elevated uncertainties in estimates of freely dissolved concentrations.*

In Section 2.2.2 the following text has been added:

*Further,  $K_{BC}$  should only be used for nonionic organic contaminants that are planar **and not non-planar chemicals unless the  $K_{BC}$ s were derived specifically for those non-planar chemicals (see discussion in Section 4).***

Comment: Figure 4-1: Tier 2: Replace “Site-Specific Bioavailability” with “Site-Specific Partitioning” to be more specific.

Response: A modified version of the recommended change has been added to Tier 2 of the Figure 4-1:

*Assessment of Chronic Toxicity based on Measurement of Freely Dissolved Interstitial Water Concentrations*

**Section 5: References**

Comment: The cited references are sufficiently comprehensive.

Response: -

**Reviewer #3**

Comment: The document describes an excellent strategy to formulate site-specific ESBs in cases where first tier EqP may grossly over- or underestimate the risk associated with non-ionic organic contaminants in sediments. The definitions, descriptions and organization of the document are clear and easy to follow. The inclusion of multiple tools in a tiered decision making construct should improve our ability to make prudent, science-based decisions concerning contaminated sediments. The authors should be commended for their part in developing and communicating this important work.

Response: -

**Front Matter: Foreword, Abstract, Table of Contents, Executive Summary, etc.**

*Does this series of brief sub-sections provide an acceptable opening to the document and provide the reader with sufficient preliminary information for understanding the material that follows?*  
YES

*What specific additions or deletions to this section would you suggest?*

Comment: p. xii. Executive Summary. The last sentence limits the scope of this document to sediments with TOC > 0.2% and target non-ionic organics with log K<sub>ow</sub> > 2. Suggest stating this, along with any other critical limitations, earlier in the summary (e.g. 2nd or 3rd paragraphs).

Response: By convention in the ESB documents, this specific information has been included towards the end of the Executive Summary. However, to address the reviewer's comment, the information about TOC and K<sub>ow</sub> limitations has been moved to the end of the previous paragraph.

**Section 1: Introduction**

*Does this section provide adequate background on the Equilibrium Partitioning Sediments Benchmarks (ESBs) and explain the rationale for this site-specific ESB document?*  
YES

*What specific improvements to this section would you suggest?*

Comment: p.1-1, 1st para. It would assist the reader to list all non-ionic chemicals for which this document applies. If this is provided in Table 2-1, reference should be made in this section. If the listing in Table 2-1 is incomplete, a complete listing should be included.

Response: The text in this section indicates that the methods presented in the document are not limited for use the chemicals listed in Section 1.1 (i.e., in other ESB documents). To assist the reader, the following text has been added to Section 1.1:

*“(see Table 2.1 for a list of selected nonionic organic contaminants)”*

Comment: p.1-2, sec 1.3, 1st para. I am not sure the clause “...**which use EqP theory**...” is accurate and/or necessary.

Response: This text was modified in response to a comment by Reviewer #2. However, the statement that EqP theory is used remains because once the passive sampler has accumulated the contaminant of interest, EqP is used to calculate the dissolved phase concentration of that contaminant (i.e., a partition coefficient is applied).

Comment: p.1-2, sec 1.4, 2nd para. I would add two additional qualifiers to the last sentence “...scientifically complex **and costly**,...” and “... well qualified and experienced, **and when first order/tier assessment approaches do not result in a guideline exceedance**”.

Response: Agreed, the following similar text has been added to Section 1.4:

*Further, because these procedures can be **technically complex and sometimes costly**, it is important that they be conducted only by those who are well qualified and experienced, **and potentially only as a second-tier assessment approach (see Section 4)**.*

Comment: p.1-3, sec 1.5. The description of Data Quality Assurance is very brief, not specific and/or informative and hence is the weakest section in the Introduction. The accuracy and uncertainty associated with the various partition coefficients specified in this document are key to the success and veracity of site-specific ESBs. I would suggest adding in this section general guidance on minimum QA/QC provisions necessary for this approach to work, starting with accuracy, precision and expected uncertainty in critical parameters (K values). In contrast to chemical data such as bulk sediment chemistry, the validation of protocols for determining partition coefficients for passive sampling devices (PSDs) is trickier and has not been fully developed. Recommendations to guide and foster this development in a prioritized and systematic fashion (e.g. joint expert workshops; RFP solicitations) would be very useful.

Response: This is a very good point. Some aspects of the comment are probably beyond the scope of this ESB document, and previous ones, (e.g., minimum QA/QC provisions) but the following text has been added to Section 1.5 to encourage users to consider data quality assurance when using passive samplers:

*Data sources and manipulations used to generate black carbon-water and passive sampler-water partition coefficients (i.e.,  $K_{BC}$ ,  $K_{PS-d}$ ) presented in this document are discussed in detail in Section 2. Due in part to the relatively recent development and application of many of the passive sampling technologies as well as black carbon partitioning for estimating bioavailability, the magnitude of the accuracy, precision and uncertainties associated with these partition coefficients is not well known. Recent intensive evaluations of partition coefficients for solid phase microextraction (SPME), polyoxymethylene (POM), and polyethylene (PE) (DiFilippo and Eganhouse 2010, Endo et al. 2011, Lohmann 2012) are good examples of the types of analyses needed to parameterize these data quality assurance measures in the future. There is also a need to encourage the organization of expert workshops and funding of quality assurance-related research to provide guidance on these issues. For example, determining when contaminants have achieved equilibrium between the passive samplers and the dissolved phase is currently a critical challenge in the use of passive samplers. Further, as the number of values for  $K_{BC}$  and  $K_{PS-d}$  increase in the scientific literature some values may need to be retired and replaced with values that are more scientifically-sound and robust. Similarly, as new toxicological data and models become available (e.g., Di Toro et al. 2007; McGrath and Di Toro 2009), older data and models may need to be reassessed or removed from the data base. Further, the relationship between predicted toxicological effects and physicochemical parameters like  $K_{OW}$ , may also need to be reassessed, McGrath and Di Toro (2009), recently suggested to not use  $\log K_{OW}$  values greater than 6.4 to predict toxicological effects using the target lipid model, frequently used with narcotic chemicals, because of the uncertainties in the model's predictions above that  $K_{OW}$  value. Such a cut-off would affect five of the chemicals specifically discussed in this document (i.e., high molecular weight PAHs). At this time, this guidance does not recommend users to apply this cut-off but does want to make users aware of this type of discussion in the scientific literature. In contrast to the passive samplers, black carbon, and toxicological models, the accuracy, precision and uncertainties associated with other aspects of the procedures discussed in this document; for example, sediment and interstitial water instrumental analysis for contaminants and sediment characteristics (e.g., dissolved organic carbon (DOC)) are well understood and have been discussed elsewhere.*

## **Section 2: Procedures for Deriving Site-Specific ESBs**

*Does this section provide sufficient information about the derivation of conventional ESBs? YES*

*What specific improvements to this section would you suggest?*

Comment: p.2-2. Clarify what is meant by “(3) passive sampling of whole sediments and (4) interstitial waters. Subsequent definition of (4) appears to refer to interstitial waters after isolation from whole sediments (as described in sec 2.4.2). The Executive Summary (p.xii) uses different terminology (isolated interstitial water and interstitial water concentrations measured by PSDs).

Response: To make the text in the Executive Summary and Section 2.1.1 agree more closely, the following text has been added to the Executive Summary:

*This document includes examples that demonstrate the calculation of site-specific ESBs using various approaches including: a “two-carbon” model that estimates the concentrations of chemical in interstitial water by taking into account the influence of black carbon, direct measurement of chemical in isolated samples of interstitial water, and **deploying passive samplers in interstitial water and whole sediment.***

Comment: p.2-3, section 2.2. The authors state that BC is ubiquitous, but stop short of providing quantitative data from the literature to frame the range and nature of BC in sediments. For example, it would help the less informed reader to provide expected ranges for BC, or ratios of fbc/foc, in natural vs. impacted sediments. It would seem that the two-carbon model is not relevant nor useful when either of these two parameters is sufficiently low.

Response: The text in Section 2.2 does indicate that black carbon constitutes about 10% of sedimentary organic carbon of average sediments based on Middelburg et al. (1999). The following text has been added to indicate that at contaminated sites the amount of black carbon may exceed 10%:

*It is estimated that BC constitutes approximately 10% of sedimentary organic carbon **in ordinary sediments** (Middelburg et al., 1999). **In sediments from contaminated sites, the contribution of BC may exceed 50% due to the fossil-fuel related residues of historic industrial activity.***

Comment: p.2-3, section 2.2.1. It is not clear why a specific value “(n=0.6)” is included.

Response: The Freundlich exponent of 0.6 was applied based on its use in the reference Accardi-Dey and Gschwend (2002) for PAHs with log  $K_{OWS}$  between 4.00 and 5.50. Because the two-carbon model has been used most frequently with PAHs this value is reported as an example but the text indicates the Freundlich exponent value will vary depending on the contaminant. Text has been added clarifying the 0.6 is an example value:

***For example, to date, 0.6 has been used for PAHs with log  $K_{OWS}$  of approximately 4.00 to 5.50.***

*Does this section discuss the site-specific approaches in sufficient detail for someone unfamiliar with the methodologies to better understand the principles of how the site-specific tools operate and the type of information they produce?*

YES.

*What specific improvements to this section would you suggest?*

Comment: p.2-4, sec 2.2.2, last para. Empirical  $K_{bc}$  values are deemed “provisional” (i.e. they should be updated), but this also holds true for other K values, including  $K_{doc}$  (sec 2.3.3) and  $K_{psd}$  (sec 2.4.2.1; see also next comment). I would contend that this be expanded to qualify all critical K values; e.g. revisits and updates could be included as part of a continuing or “adaptive” QA/QC program (e.g. in sec 1.5).

Response: I agree with the reviewer on the need to be prepared to constantly update partition coefficient values. As the text in Section 2.2.2 notes, the  $K_{BC}$ s were called provisional because the dataset used to generate them was very small ( $n = 17$ ) compared to most of the other partition coefficients used in the document (e.g.,  $K_{OW}$ ,  $K_{DOC}$ ). To clarify this point, the following text has been added to Section 1.5:

*Further, as the number of values for  $K_{BC}$  and  $K_{PS-d}$  increase in the technical literature some values may need to be retired and replaced with values that are more scientifically sound and robust.*

and to Section 2.2.2:

*As noted in Section 1.5, as the number of available empirical  $K_{BC}$  values increases, Equation 2-4 should be updated.*

Comment: p.2-10, sec 2.4.2.1 and Table 2-1. The  $K_{pdms}$  values generated from regression equation 2-11 (and listed in Table 2-1) are 0.5 log units on average lower than more recently published values, e.g. by Maruya et al. (2009) for fibers with a range of coating thickness (7, 30 and 100  $\mu$ m). Furthermore, these latter values are more similar to  $K_{ped}$  (see Table 2-1a below). Ensuring that all PSDs are carefully and correctly calibrated is a critical component for application in a decision making framework. One obvious reason for the higher  $K_{pdms}$  values is attainment of equilibrium via extended time series calibration experiments (up to 120 d), enhanced mass transfer via stirring, and closed mass balances that may not have been achieved in earlier calibration work. Improperly calibrated PSDs can result in biased measurements (positive or negative) that could lead to an erroneous categorization of sediments, hence the need for rigorous QA/QC screening of K values for PSDs (see previous comment on sec 1.5).

Table 2-1a. Recently reported  $K_{pdms}$  values compared to  $K_{ped}$ .

PAH	ESB	Maruya et al. (2009)	Mayer et al. (2000b) $K_{ped}$
phenanthrene:	3.58	3.90-4.32 3.98-4.01	4.21
fluoranthene:	4.18	4.26-4.69	4.75
benzo[a]pyrene	5.38	5.82-6.06	5.82

Response: This is a good observation. In addition, the Leslie et al., (2002)  $K_{OW}$  versus  $K_{SPMD}$  linear free energy relationship is based on only ten chemicals. We actively investigated the availability of a more statistically robust log  $K_{OW}$  versus log  $K_{SPME}$  linear free energy relationship to use in this document. Following an e-mail exchange with Reviewer #3, the linear free energy relationship developed by DiFilippo and Eganhouse (2010) (EST, 44:6917-6925) was used to derive  $K_{PDMS}$  values in this document:

$$\text{Log } K_{PDMS} = 0.83 \text{ log } K_{OW} + 0.07$$

This equation, which is based on a very robust  $K_{SPMD}$  dataset, has been substituted into the document as Equation 2-11. The linear free energy relationship for  $K_{POM}$  was also updated with

a larger data set (Endo et al. 2011) (EST, 45:10124-10132). The following equation has been substituted in the document as Equation 2.12:

$$\text{Log } K_{\text{POM}} = 1.01 \log K_{\text{OW}} - 0.60$$

Further, based on the e-mail exchange with this reviewer, the following text has also been added to Section 2.4.2.1:

*Several authors have reported that as  $K_{\text{OW}}$  increases, the relationship between  $K_{\text{PS-d}}$  and  $K_{\text{OW}}$  begins to demonstrate curvilinear behavior often at  $\log K_{\text{OWs}}$  of greater than 6.5 or 7.0. The result is that the  $K_{\text{PS-d}}$  decreases in value. Our understanding of why this behavior occurs is incomplete and research to better understand this phenomena is underway.*

Comment: p.2-5, sec 2.3.1, 2nd para. The authors should be commended for their detailed description of porewater isolation. However, the level of detail seems out of balance with other “how to” sections. Such detailed descriptions may be better placed in an Appendix, particularly if future revisions to this document and the same level of detail are envisioned for other approaches.

Response: Agreed, Section 2.3.1 has been edited to a level of detail similar to other parts of the document. The text in Section 2.3.1 has been edited as shown below:

*If performed with a minimum of artifacts, centrifugation without subsequent filtration results in an acceptable sample of interstitial water which can be used to make an accurate measurement of the freely dissolved concentration of nonionic organic contaminants in sediments (Adams et al., 2003). Substantial artifacts include the formation of dissolved and colloidal organic matter during interstitial water preparation and isolation which can result in an overestimation of interstitial water nonionic organic contaminant concentrations especially those with high  $K_{\text{OWs}}$ . The objective of centrifugation is to obtain interstitial water containing contaminants operationally defined as freely dissolved. Therefore, any combination of gravitational force (i.e., speed with effective radius) and time that settles the particles of greatest effective diameter to the sediment – interstitial water interface is acceptable. For example, a procedure applied by Lee et al. (1994) and Swartz et al. (1994) on marine sediments was shown to effectively reduce losses of organic contaminants to laboratory ware surfaces (Ozretich and Schults, 1998). The procedure also allowed for the chemical analysis of DOC (U.S. EPA, 2000) and total contaminant concentrations (i.e., freely dissolved fraction plus the fraction associated to DOC). Conversely, the total interstitial water can be sub-sampled for direct measurement of the DOC-bound contaminants (see Section 2.3.2).*

*Centrifugation of the sediment and sub-sampling of the interstitial water should be performed within two hours of each other to avoid complications from the potential formation of de novo particles caused by oxidation of reduced iron. It is clear that cleanly sampled interstitial water is important, as the presence of a particle of sediment, as noted above, could result in erroneously high concentrations; on the other hand, if the time periods before extractions are extended, include filtering and excessive sample handling, erroneously low concentrations would result because of contaminant sorption to laboratory ware surfaces.*

Comment: p.2-5, sec 2.3.3. To give an idea of what instrumental sensitivity is needed, it would be informative to provide a range of relevant FCV, SCV or other water-effects concentrations. Such values are provided for PAH in Table 3-1 (ranging from ~0.07 to 300 ug/L).

Response: Agreed, the following text has been added to Section 2.3.2:

*Regardless of the extraction method used, it is critical that the instrumental analysis can detect contaminant concentrations below the relevant FCV, SCV or other water-only effect concentrations (i.e., ~0.01 µg/L for the most toxic chemicals).*

Comment: p.2-6, sec 2.3.3. DOC is an important parameter whose estimated/measured value will impart error and influence categorization of a given sediment. Is it appropriate to specify standard methods, if they exist? Do these methods perform sufficiently for inclusion in this framework?

Response: Later in this section (2.3.2), a U.S. EPA guidance document for the analysis of DOC is cited (i.e., U.S. EPA 2000). No change made to text.

Comment: p.2-9, sec 2.4.1, 1st para. Suggest adding "...but can **be protected for deployment** in the field"

Response: The suggested text has been included in the document in Section 2.4.1:

*The fibers are fragile, but can be **protected for** deployed in the field (Maruya et al. 2009 ) and used to determine vertical profiles of contaminants in sediment (Lu et al. 2011).*

Comment: p.2-10, sec 2.4.2, 1st para. The uncertainty in concentrations corrected for non-equilibrium using PRCs should increase as the extent of equilibrium achieved decreases. For example, is it acceptable practice to correct for 10% equilibrium? 1%? Some discussion of appropriate or acceptable PRC correction factors/ranges would be useful.

Response: To provide some requested guidance, the following text has been added to Section 2.4.2:

*Guidance on the use of PRCs is still being developed but for losses of PRC less than 10% during a deployment, because of the uncertainties potentially associated with such low losses, those PRC data should not be used to adjust the equilibrium status of target chemicals.*

p.2-11, sec 2.5, 1st para. Is the solubility limit specified for low or zero ionic strength solutions? Do the authors see it fit to correct solubility for temperature or salinity, depending on the sediment application?

Response: The guidance the reviewer proposes is beyond the scope of the current document, the following clarification text has been added to Section 2.5:

*In deriving the IWTUs, the estimated interstitial water concentration of each contaminant ( $C_d$ ) is also compared to the limit of water solubility for that contaminant in deionized water.*

Comment: Table 2-1. What is the rationale for including compounds with  $2 < \log K_{ow} < 3$ , i.e. those that are marginally hydrophobic at best? The applicability of PSDs due to insufficient sensitivity would be an issue depending on the aqueous toxicity threshold (i.e. FCV, SCV), unless PSDs other than those described are developed and/or included.

Response: The chemicals listed in Table 2-1 are included to be consistent with the contaminants presented in other ESB documents (e.g., U.S. EPA 2003d, 2008). The following guidance has been added to Section 2.4.2.1:

*Note that for chemicals in Table 2-1 with partition coefficients less than  $\log 2.00$ , the use of PEDs, PDMS and POM-based passive samplers may not be effective because of weak partitioning to the polymers. For chemicals demonstrating this level of aqueous solubility, direct extraction and analysis of the interstitial water may be more effective.*

### **Section 3: Example Calculations of Site-Specific ESBs**

*Are the examples illustrative of the different types of results generated by the site-specific tools?*

YES

*Do the tables provide clear and useful information?*

YES

*Are there other examples or other aspects of the current examples that would better convey how to use the document and site-specific tools?*

Comment: A second set of examples for a non-planar organic (e.g. DDT, dieldrin, chlordane or non-planar PCBs) and how the different approaches converge (or not) would be illustrative.

Response: This is a good suggestion but it is beyond the scope of the document. The goal of the two examples is to illustrate the process used to calculate the interstitial water toxic units and the interpretation of this information for assessing the sediment's likelihood to cause toxic effects. Based on the consensus within the other reviewers as well as the same format used for examples in earlier ESB documents, the current example appears to be relatively successful. No change to document.

### **Section 4: Implementation of Site-Specific ESBs**

*Is the tiered approach described in this section useful as an example of how to implement the use of site-specific ESBs?*

YES

Comment: The tiered strategy proposed in this document makes very good sense. However, it should be noted that uncertainties in PSD measurements, due to non-standard calibration and/or implementation procedures, could impart as much if not greater error than 1st tier (i.e. 1- or 2-carbon EqP models) estimations. A concerted effort to provide standardized calibration parameters (e.g. K values in Table 2-1), implementation procedures and/or data interpretation guidance for PSDs should be undertaken to minimize the uncertainty associated with PSD sediment porewater measurements.

Response: Please see previous responses to Review #3 relative to quality assurance concerns in Section 1.

Comment: p.4-1, sec 4.1, 2nd para. Modify to read "...analysis of contaminated **bulk** sediments for a suite...."

Response: The following text has been added to section 4.1:

*Currently, the analysis of **whole or bulk** contaminated sediments for a suite of nonionic organic chemicals is less expensive than performing a similar analysis for passive samplers, such as SPME, PEDs or POM.*

## **Section 5: References**

*Is the cited literature sufficiently comprehensive?*

YES.

Comment: A recent review article on the utility of PSDs for contaminated sediment management cited below would be a good addition in supporting statements made in Section 2.

Maruya KA, Landrum PF, Burgess R, Shine J. 2010. Incorporating contaminant bioavailability into sediment quality assessment frameworks. *Integrated Environ Assessment Management* DOI:10.1002/ieam.135.

Response: Agreed, the suggested reference has been added to Section 2.

## **Reviewer #4**

### General Comments

Comment 1: This document describes approaches for quantitatively assessing the bioavailability of non-ionic organic chemicals in field contaminated sediments. Given the importance and cost implications of decisions related to the management of contaminated sediments, the Agency is applauded for progressing guidance for this purpose.

Response: -

Comment 2: The document is sometimes verbose and repetitive and would benefit from a critical review of the text to be more concise. For example, the executive summary could be condensed and improved by explaining why (initial chemical assessment) and how (EqP theory) national ESBs have been derived; the advantages that national ESBs provide (addresses substance-specific causality, incorporates sediment organic carbon which is one important factor known to modulate bioavailability, simple to apply in practice); and recognition of the limitations of national ESBs in accurately quantifying site-specific bioavailability under field conditions. These points then provide the logical incentive for this work which translates into better sediment management decisions at sites. It could then be stated that this document describes three approaches for addressing bioavailability, discuss the advantages and limitations of these approaches and provides several practical examples to illustrate use.

Response: The purpose and scope of this document is to provide guidance on assessing contaminated sites using recently developed tools for determining the freely dissolved concentrations of nonionic organic contaminants. Further, in terms of structure, the document is intended to be an extension of the previously published Equilibrium Partitioning Sediment Benchmarks (ESBs). Therefore, the format of the current document is designed to be similar to the previous ESB documents. In this comment, the reviewer provides several interesting and good recommendations for the contents of a different document or review article discussing the use of the conventional one-carbon EqP model versus the approaches discussed in this document.

It should be noted that as a result of revising the document to address this reviewer's later comments, as well as the other reviewer's comments, some of the specific comments discussed above were incorporated into the revised document. However, many of the recommendations provided in the comment above are beyond the scope of the current ESB document.

Comment 3: The title and terminology used throughout this document is misleading and should be modified to more accurately reflect the objectives of this effort and avoid confusion with previous USEPA guidance. The proposed document does NOT provide procedures for deriving equilibrium partitioning benchmarks. Rather, the guidance describes advances in models and measurements for improving estimation of freely dissolved concentrations in sediment interstitial water. These procedures offer the opportunity to provide an improved technical basis to quantify the site-specific bioavailability of non-ionic organic chemicals to benthic organisms than is currently afforded by national ESBs. Thus, this effort focuses on improved exposure characterization NOT benchmark development. Water quality criteria (defined in terms of FCVs and SCVs) represent the actual site-specific benchmarks that are applied in this guidance without modification from earlier EPA work. Thus, the use of the term "site-specific ESBs" is confusing and should be dropped. Similarly, the use of the "general" EqP approach/model is inconsistent with previous EPA guidance. Rather it is recommended to use "EqP model" to refer to the model used for derivation of national ESBs (one-carbon model) and refer to the two carbon model as the modified EqP-BC model.

Response: The reviewer makes several good points in this comment. First, the draft document emphasizes the determination of the freely dissolved concentrations of nonionic organic chemicals in sediment interstitial waters and the document does not provide a tabulation of

“new” FCVs or SCVs for deriving ESBs. Second, in this document, the measured or estimated freely dissolved interstitial water concentrations are divided by the FCV or SCV (or other relevant water-only toxicity value) to generate the sediment interstitial water toxic units and do not derive sediment benchmarks in the same way as is performed in a one-carbon model ESB (i.e., based on organic carbon normalized sediment concentrations). Finally, the site-specific terminology is not appropriate for the procedures used in this document. To address these points, the document’s title has been changed to the following:

*Equilibrium Partitioning Sediment Benchmarks (ESBs): Procedures for the Determination of the Freely Dissolved Interstitial Water Concentrations of Nonionic Organics for the Protection of Benthic Organisms*

Further, the use of “site-specific” in the document has been removed and replaced with text emphasizing the determination of the freely dissolved concentrations of nonionic organic chemicals to derive interstitial water toxicity units. *This is a major change to the terminology and focus of the document.* Use of other terminology including “general EqP” and “two-carbon model” is appropriate and was not changed in the document.

Comment 4: The authors propose three methods for estimation of freely dissolved concentrations for consideration in higher tier sediment assessments involving non-ionic chemicals: 1). application of a modified EqP-BC model; 2) measurement of "total" contaminant and DOC concentrations in interstitial water 3). measurement of freely dissolved concentrations in interstitial or whole sediment using passive sampling devices (PSDs). However, the document fails to provide sufficient comparison of the advantages and limitations of the different techniques. Further, a key issue that is not addressed is the absolute and relative uncertainties associated with the proposed methods. One important consideration relates to the uncertainty that is associated with equations 2-4, 2-8, 2-10, 2-11 and 2-12. However, no indication is provided on the variance associated with these relationships. Further, the domain of applicability (number of compounds, compound classes and Log K<sub>ow</sub> range used in development of these relationships) is not discussed.

Given the lack of an appreciation of the uncertainty in the proposed methods, its hard to judge if the examples presented in section 3 showing a reduction in toxic units to below one provides convincing evidence that no adverse effects are expected.

Response: First, a table (Table 2-4) comparing the different approaches for determining the freely dissolved concentrations has been added to Section 2. Relative to the chemicals relevant to this document, in Table 2-1 several chemicals are listed. Further, the document discusses the broad range of chemicals that may be used with the ESBs, including the methods discussed in this document, in the last paragraph of the Executive Summary (e.g., log K<sub>ow</sub> ≥ 2.0). Finally, the examples are meant primarily to guide the document user in understanding the sources of data, performance of the actual calculations, and interpreting the data.

Relative to uncertainties, as noted earlier in response to Reviewer #1, text discussing uncertainty has been added to Section 1.5 and uncertainties associated with the methods are noted throughout the document.

Comment 5: Since the objective of this document is to provide guidance for applying the approaches described it would be helpful to provide a summary of FCVs that reflect the current state of the science rather than citing values that are outdated, e.g. SCVs developed in the 1990s under various initiatives. Further, in some cases different FCV/SCVs for the same compound will create confusion regarding which values should be used as benchmarks (in absence of guidance often the lowest value will be selected regardless of the underlying technical basis).

For chemicals that act via a narcotic mechanism, the target lipid model can be used to establish mode-of-actions based FCVs using the equation:

$$\log(\text{FCV}) = \log(\text{CTLBB}_{5\text{th}}) - 0.936 \log(\text{Kow}) - a_0 - \log(\text{GMACR})$$

Where CTLBB<sub>5th</sub> is the 5th percentile of the distribution of critical target lipid body burdens obtained using the target lipid model, a<sub>0</sub> depends on chemical class and GMACR is the geometric mean acute to chronic ratio that is derived from empirical data (DiToro et al. 2007 ET&C 26:24; McGrath & DiToro 2009 ET&C 28:1130).

Response: This is a good point and reflects the likelihood for toxicological values to change as time goes by, more (and possibly better) data is collected, and models improve. Throughout this document, users are encouraged to apply the current FCVs and SCVs or other relevant water-only toxicity values. To address the reviewer's point, the following text has been added to Section 2.1:

*These concentrations can then be used with current ESBs and other relevant water-only toxicity value. For example, as recently discussed by Di Toro et al., (2007) and McGrath and Di Toro, (2009), the target lipid model used to calculate the FCVs for PAHs (U.S. EPA, 2003d) can also be modified to calculate "mode of action" based FCVs. The mode of action FCV considers the 5<sup>th</sup> percentile of the distribution of the critical target lipid body burdens using the target lipid model, a chemical class variable, and an empirically-derived geometric mean acute to chronic ratio.*

Comment 6: A more in-depth discussion of the methods used for DOC and BC determination including precision, accuracy and potential bias of specific test protocols as well as the expected range of these parameters in field sediments is needed. These two parameters are the key site specific input parameters for the models described and thus warrant more attention.

Response: It is agreed that DOC and BC are important parameters. However, the level of detail the reviewer is requesting is beyond the scope of the current document. The document cites some of the dominant literature addressing these parameters. To clarify that this document is not a methods manual, the following text has been added to Section 1.6:

*Finally, the focus of this document is to provide the reader with an overview of the current approaches for determining the freely dissolved concentrations of nonionic organic chemicals in sediment interstitial waters. The document is not intended to serve as a methods manual. In the different sections of the document, relevant scientific literature is cited to provide the reader with more in-depth information.*

Comment 7: The proposed strategy for implementation in section 4 needs to be revised

(I) First, the statement that the tiered approach needs to balance environmental protection with cost is incorrect. The use of the proposed modeling / measurement tools for refining bioavailability predictions using EqP should be used when organic carbon normalization of bulk sediment data indicates non-ionic contaminants are present at concentrations that may cause impairment to benthic life. The inclusion of higher tier methods to address bioavailability will generally increase costs since conventional bulk sediment analysis are a required pre-requisite. However, the incremental costs of including higher tier methods should logically be considered. For example, inclusion of BC determinations at sites known or expected to exhibit elevated PAH contamination could be included in sampling and analysis plans for collection conventional bulk sediment chemistry data with little added costs (assuming a standard protocol for BC determination is provided, see earlier comment). The availability of site-specific BC data could then be used in the modified EqP-BC model to determine if predicted reductions in bioavailability are sufficient to warrant, more costly targeted follow-up studies to measure and confirm that interstitial concentrations of PAHs deviate significantly from EqP assumptions. However, applying the modified EpP-BC model is not straightforward since an iterative calculation procedure is required. Thus, the additional costs of data analysis would need to be factored into project costs. I think the point that needs to be conveyed is that the strategy adopted should balance the need for improved characterization of bioavailability with cost considerations.

(II) Second, I do not agree that the use of toxicity tests as a final third tier (Figure 4-1) provides a sound technical basis for verifying findings in the first two tiers. First, sediment toxicity tests maybe confounded by other measured or unmeasured stressors complicating the interpretation of causality. Second, the FCVs used as the basis for interpreting estimates of freely dissolved concentrations are intended to be protective of sensitive benthic organisms from chronic effects whereas sediment toxicity assay may not correspond to this level of protection. Thus, while sediment toxicity tests of field samples can play a role in developing a weight of evidence evaluation for contaminated sediment assessment these tests do not verify methods described in this document. In summary, I recommend that tier 3 in Figure 4-1 be deleted. Further, the general conclusion that sediment toxicity testing is the most accurate way to assess the adverse effects of sediment contaminants ignores potential variables that can confound lab to field extrapolation (e.g. water exchange rates) and undermines the concept of a weight of evidence evaluation using chemistry, toxicity and benthic community survey data in decision-making.

Response: These are all goods points but the tiered approach discussed in Section 4 of the document is intended to be a recommendation. Further, the other reviewers found the proposed approach valuable and also provided constructive comments that have been incorporated into the document. Reviewer #4's last point, in the second part of the comment (II), is very good; that is, the need to emphasize the weight of evidence approach. The following text has been added to Section 4.2:

*Finally, in a recommended weight of evidence sediment assessment, toxicity testing should not be used in exclusion of other lines of evidence including chemistry, bioaccumulation and benthic community analyses. It is highly recommended that the data generated in Tier 3 of the proposed*

*tiered approach be informed by lines of evidence in addition to chronic toxicity testing. This consideration emphasizes the merits of a weight of evidence approach when performing contaminated sediment assessments.*

Comment 8: The discussion on passive samplers in section 2.4 is welcomed as these techniques provide a sensitive, promising approach to addressing bioavailability of non-ionic chemicals. It would be helpful to restructure this section by first describing the general theory of PSD using different sampling formats (equilibrium sampling, kinetic sampling, ex-situ vs in-stu) and required data/assumptions needed for generating valid results using these approaches before going into the specific different sampling formats (e.g. POM, PDMS, LDPE, etc). For example, it would be useful to explain key equations and variables that determine time to equilibrium (e.g. PSD surface-volume ratio, substance Log Kow) and detection limits (e.g. Kpsd-water and PSD volume). Providing at least some preliminary recommendations on minimum requirements for accepting data using PSDs is needed to foster broader use and acceptance of these techniques. For example, if PSDs are being used in a manner that assumes equilibrium is attained, evidence should be provided to demonstrate this assumption is met under the sampling conditions that are being employed. One simple way to demonstrate this assumption is met is to equilibrate the sample with the same PSD but with different surface to volume ratios (and hence sampling rates) and confirm concentrations are not significantly different.

A table comparing key parameters relevant to use of different commercially available PSDs would also be helpful.

Response: The first paragraph of this comment includes several very good types of information that would be useful for understanding the data generated by passive samplers. However, the level of detail required to include this information is beyond the scope of this document and other scientific literature is available that addresses these comments. These sources are cited in the References section (e.g., Vrana et al., 2005; Huckins et al., 2006; Seethapathy and Gorecki, 2008). In contrast, a table (Table 2-4) and supporting text comparing the passive samplers as well as the other methods for determining interstitial water concentrations has been added to Section 2 of the document:

***Table 2-4. Advantages and disadvantages of approaches for determining interstitial water concentrations of nonionic organic contaminants***

<i>Approach</i>	<i>Advantages</i>	<i>Disadvantages</i>
<i>One-Carbon EqP Model</i>	<ul style="list-style-type: none"> <li>· <i>Standard methods and guidance document available to commercial laboratories</i></li> <li>· <i>Partition coefficients (e.g., <math>K_{ow}</math>, <math>K_{oc}</math>) and uncertainties available in the scientific literature</i></li> </ul>	<ul style="list-style-type: none"> <li>· <i>Simplistic model of NOC partitioning in sediments</i></li> <li>· <i>May over-estimate <math>C_a</math></i></li> </ul>
<i>Two-Carbon EqP Model</i>	<ul style="list-style-type: none"> <li>· <i>More complete model of NOC partitioning in sediment</i></li> <li>· <i>Method for <math>f_{BC}</math> determination</i></li> </ul>	<ul style="list-style-type: none"> <li>· <i>Limited information for partition coefficients (e.g., <math>K_{BC}</math>)</i></li> </ul>

	<i>for commercial laboratories is available</i>	<i>and their uncertainties available in the scientific literature (especially for non-planar NOCs)</i> <ul style="list-style-type: none"> <li>· <i>Uncertainty in the measurement of <math>f_{BC}</math></i></li> <li>· <i>May under-estimate <math>C_d</math></i></li> </ul>
<i>Direct Measurement</i>	<ul style="list-style-type: none"> <li>· <i>Direct determination of <math>C_d</math></i></li> <li>· <i>Partition coefficient (e.g., <math>K_{DOC}</math>) and related uncertainties available in the scientific literature</i></li> </ul>	<ul style="list-style-type: none"> <li>· <i>Large amounts of sediment required</i></li> <li>· <i>Physical manipulation of sediment may alter <math>C_d</math></i></li> <li>· <i>Methods are not standardized or available to commercial laboratories</i></li> </ul>
<i>Passive Samplers</i>		
<i>Polyethylene Devices (PED)</i>	<ul style="list-style-type: none"> <li>· <i>Inexpensive and rugged sampling technology</i></li> <li>· <i>Growing acceptance in scientific literature and in practical use</i></li> <li>· <i>Laboratory and field deployments possible</i></li> </ul>	<ul style="list-style-type: none"> <li>· <i>Increasing amount of information on partition coefficients (e.g., <math>K_{PED}</math>) and their uncertainties available in the scientific literature</i></li> <li>· <i>Determination of sampler equilibrium is an area of research</i></li> </ul>
<i>Solid Phase Microextraction (SPME)</i>	<ul style="list-style-type: none"> <li>· <i>Inexpensive sampling technology</i></li> <li>· <i>Growing acceptance in scientific literature and in practical use</i></li> <li>· <i>Laboratory and field deployments possible</i></li> </ul>	<ul style="list-style-type: none"> <li>· <i>Increasing amount of information on partition coefficients (e.g., <math>K_{PDMS}</math>) and their uncertainties available in the scientific literature</i></li> <li>· <i>Determination of sampler equilibrium is an area of research</i></li> <li>· <i>Fibers are fragile and require protective covering when used</i></li> </ul>
<i>Polyoxymethylene (POM)</i>	<ul style="list-style-type: none"> <li>· <i>Inexpensive and rugged sampling technology</i></li> <li>· <i>Growing acceptance in scientific literature and in practical use</i></li> <li>· <i>Laboratory and field deployments possible</i></li> </ul>	<ul style="list-style-type: none"> <li>· <i>Increasing amount of information on partition coefficients (e.g., <math>K_{POM}</math>) and their uncertainties available in the scientific literature</i></li> <li>· <i>Determination of sampler equilibrium is an area of research</i></li> </ul>

*Based on the discussion in this section of the document, Table 2-4 summarizes a selection of the advantages and disadvantages of each approach for determining interstitial water*

*concentrations.*

Comment 9: I don't agree that the discussion of PSD experience does or should be focused only in North America (page 2-8). Many of the citations provided refer to work outside NA.

Response: The intent of this document is to provide guidance to the user community in North America (i.e., especially, the United States). Therefore, with regard to passive samplers, the focus is on the samplers used most commonly in North America. The cited literature does include research from outside North America but primarily on the types of passive samplers used in North America. No change to document.

Comment 10: To increase practical application of this guidance, it would be particularly helpful to clarify recommendations on selection of a PSD strategy rather than referring the reader to primary literature (page 2-9).

Response: Discussion within Section 2 and the information in Table 2-4 provides suggestions for selecting a type of passive sampler, the discussion is not comprehensive, because that's beyond the document's scope, but it does serve as guidance.

Comment 11: I suggest an added section on further research needs be considered. The development/standardization of reliable, cost-effective measurement and modeling methods to gain consensus and reduce uncertainty in  $K_{psd}$ -water coefficients across different classes of non-ionic chemical classes would be one such recommendation.

Response: Based on previous reviewer' comments, this type of discussion has been included in Section 1.5. However, more text has been added to Section 4, re-emphasizing the importance of some areas of research for improving the reliability and reducing the uncertainty associated with the approaches discussed in this document:

### **4.3 Research Needs**

*As discussed in Section 1.5, there remain several areas of research and development for the approaches for determining interstitial water concentrations discussed in this document. Most of these areas involve making a better measure of or reducing the uncertainty associated with the array of partition coefficients used in these approaches (e.g.,  $K_{BC}$ ,  $K_{PED}$ ,  $K_{PDMS}$ ,  $K_{POM}$ ). A second area is improving the measurement of black carbon in sediments. Currently, the commonly used version of this measurement involving the removal of inorganic and NSOC (Gustafsson et al., 1997) has been shown to be highly variable in inter-laboratory comparisons (Gustafsson et al., 2001). In addition, for the passive samplers, it is critical to develop improvements in the methods for the determination of when equilibrium between nonionic organic chemicals in the interstitial water and the passive sampler has been established.*

Comment 12: In summary, the draft guidance document advances USEPA's efforts to apply the latest scientific advances to improve risk-based decision-making related to contaminated sediment management. However, the current draft has a number of shortcomings that will limit consistent and practical use of the guidance provided. Thus, this document should be

significantly revised to address the above concerns before publication.

Response: As noted in the cover memorandum, this reviewer provided a series of significant comments that altered the terminology used in this document as well as the document's focus. Specifically, this report went from being considered a guidance document for deriving site-specific ESBs to a guidance document for determining sediment interstitial water concentrations of nonionic organic chemicals. Although some of the reviewer's comments were beyond the scope of this document, the change in terminology and focus constitute substantial revisions.

## **Reviewer #5**

### **Front Matter: *Foreword, Abstract, Table of Contents, Executive Summary, etc.***

Does this series of brief sub-sections provide an acceptable opening to the document and provide the reader with sufficient preliminary information for understanding the material that follows? What specific additions or deletions to this section would you suggest?

Reviewer Response: Yes, the front matter seems to adequately introduce the remainder of the document. I feel that the information presented in the Foreword, Abstract, and Executive Summary seems a bit redundant. I also think the discussion of the methodology that is to be presented is pretty vague. Perhaps there could be a very brief summary of the methodology in the Abstract.

Editor Response: As noted earlier, the format used for composing the Foreword, Abstract, and Executive Summary is the same as was used for composing other ESB documents in this series. To provide some more detail on the methodology within the context of the Abstract, a section of the Abstract has been rewritten:

*These procedures allow for the more accurate determination of the freely dissolved and potentially bioavailable concentrations of nonionic organic chemicals. These concentrations are used with final chronic values (FCVs), secondary chronic values (SCVs), or any relevant water-only toxicity value to derive the interstitial water toxic units.*

### **Section 1: *Introduction***

Does this section provide adequate background on the Equilibrium Partitioning Sediments Benchmarks (ESBs) and explain the rationale for this site-specific ESB document? What specific improvements to this section would you suggest?

Reviewer Response: Yes, the introduction seems appropriate.

Editor Response: -

### **Section 2: *Procedures for Deriving Site-Specific ESBs***

Does this section provide sufficient information about the derivation of

conventional ESBs? What specific improvements to this section would you suggest?

Reviewer Response: The section is well organized and provides an adequate description of the conventional approach. Little guidance is provided on the values to be used for  $K_{OC}$  in the body of the document. I think that at least a few of the conventional  $K_{OC}$  correlations with octanol-water partition coefficients should be included.

Editor Response: To address this comment, the following sentence advising readers to review other ESB documents that discuss the derivation of  $K_{OC}$  more thoroughly was added to Section 2.1.1:

*and organic carbon-water partition coefficient ( $K_{OC}$ ) (L/Kg OC) (for more discussion of selecting  $K_{OC}$ , see U.S. EPA 2003b,cd, 2008), Equation 2-1 can be rewritten as:*

Does this section discuss the site-specific approaches in sufficient detail for someone unfamiliar with the methodologies to better understand the principles of how the site-specific tools operate and the type of information they produce? What specific improvements to this section would you suggest?

Reviewer Response: I think this section is generally well-written and appropriately detailed. In Section 2.4.2.1, some relationships for determine pore water concentrations from passive samplers are presented. These equations assume equilibrium between the passive sampler, sediment organic carbon, and pore water as stated elsewhere in the section. I think the section should emphasize that equilibrium may not be instantaneous, and some correction for kinetic effects may need to be applied (i.e., these equations do not provide all the necessary information to determine an ESB and should not be construed as such). A brief discussion of the differences in equilibration time for the three materials would also be useful.

Editor Response: Currently, Section 2.4.1 provides a brief discussion of the equilibration behavior of PEDs, SPME and POM. Also, in response to an earlier reviewer, additional text has been added to Section 2.4.2 discussing measures for addressing contaminant disequilibria between the sampler and dissolved phase. To remind the reader that passive sampler data may need to be adjusted for disequilibria, the following text has been added to Section 2.4.2.1:

*As discussed in Section 2.4.2, there may be the need to adjust  $C_{PS}$  if the passive sampler deployment was insufficient in duration to achieve equilibrium conditions (Fernandez et al., 2009b).*

### **Section 3: Example Calculations of Site-Specific ESBs**

Are the examples illustrative of the different types of results generated by the site-specific tools? Do the tables provide clear and useful information?

Reviewer Response: The examples are illustrative and the tables provide useful information. A

have a few suggestions. It might be helpful to show one example for each of the calculations using a selected compound and then put those values in the tables to reinforce the methodology. I think that it is important that the document provide clear examples or else it will not be employed by practitioners. In 3.1 it might be easier to restate the names of the variables such as “ $f_{OC} = \text{fraction OC} = 0.032$ ” just for clarity, perhaps with each variable on a separate line. The equation used to calculate  $C_d$  from  $C_{OC}$  needs to be shown in 3.2.1. I’m have a mixed opinion of the “ $i$ ” subscripts everywhere. I realize why they are there but there are so many parameters I’m not sure it’s necessary to say “ $C_{di}$ ” instead of just “ $C_d$ ” for example. The “ $i$ ” subscript could be used just for the summation equations ( $i = \text{the PAH of interest}$ ).

Editor Response: Including an illustration of each calculation in the examples is likely to become too cumbersome. In previous ESB documents, the example format used in this document was proven to be fairly successful in conveying how to perform the calculations. For clarity,  $f_{OC}$  and  $f_{BC}$  have been more explicitly stated in parentheses in Section 3.1:

*The concentration of total PAHs is 39.4  $\mu\text{g/g}$  dry weight, the TOC is 3.2 % ( $f_{OC} = 0.032$ ), the BC is 0.3 % ( $f_{BC} = 0.003$ ), and interstitial water DOC is 5 mg/L.*

In response to an earlier reviewer, text has been added to Section 3.2.1 discussing how  $C_d$  can be calculated using Equation 2-2:

\_\_\_\_\_

which is equivalent to the following expression:

\_\_\_\_\_

This equation has been added to the text in Section 3.2.1. Finally, the  $i$  subscript notation is used when necessary to be consistent with previous ESB documents.

Are there other examples or other aspects of the current examples that would better convey how to use the document and site-specific tools?

Reviewer Response: I think putting the equations used to calculate the values in the tables before each table, and an example calculation for one compound (as stated above), would make it easier for someone unfamiliar with the methodology and the parameter definitions to follow. It seems like the passive sampler example should at least have the caveat that equilibrium has been attained and that it’s not likely this behavior would be seen in the field.

Editor Response: Please see the editor’s response above regarding the addition of example calculations to the document. The following text has been added to Section 3.3.2 to let the reader know equilibrium has occurred:

*For this example, the use of PRCs loaded in the PED demonstrated the target contaminants had*

*achieved 100% equilibrium between the sampler and freely dissolved phase. For actual deployments, it is critical to understand the equilibrium status of the samplers before performing the calculations below.*

#### **Section 4: Implementation of Site-Specific ESBs**

Is the tiered approach described in this section useful as an example of how to implement the use of site-specific ESBs?

Reviewer Response: Yes, it is useful, although at this point it is unclear to me how the black carbon and pore water measurement methods are to be applied in this process. The recommendation seems to be not to use the black carbon model or the interstitial water methods. If they are not to be applied, then why are they presented? I understand the difficulty in that the use and interpretation of black carbon data and interstitial water concentrations requires substantial expert knowledge (e.g. to recognize and correct passive sampler data that is not at equilibrium). There should be some guidance on when they may be appropriate, or as I would suggest, that they are some of the most effective tools available but should be caveated in that the data is difficult to collect and interpret properly.

Editor Response: This section (4.1) of text has been revised to indicate more explicitly that the black carbon and direct interstitial water measurements can be used in the tiered approach. However, the text has also been edited to explain why the passive sampler based approaches are preferred. Frankly, the black carbon and direct interstitial water measurements have been included in the document for completeness. If these alternative approaches were not included, it is very likely the document would be criticized for their exclusion. Further, as the reviewer notes there are also uncertainties associated with the passive sampler based measurements of the freely dissolved interstitial water concentrations. Consequently, in some instances, for example, a reader may want to estimate the freely dissolved concentration using the two-carbon model or make a direct measurement of interstitial water contaminants to verify the passive sampler measurement:

*Further, the two carbon model is applicable for all classes of nonionic organic chemicals assuming the appropriate  $K_{BC}$  values are used in the model calculations. Currently, many  $K_{BC}$  values are derived using linear free energy relationships between  $K_{BC}$  and  $K_{OW}$  for planar chemicals like PAHs but not non-planar compounds. As noted earlier, these  $K_{BC}$ s may not be appropriate for use with non-planar compounds and may result in elevated uncertainties in estimates of freely dissolved concentrations. Similarly, the collection of sufficient sediment interstitial water for direct measurement of contaminants continues to include significant artifacts and requires the additional chemical analyses that may not always be cost effective (e.g., DOC, interstitial water).*

and in Section 4.2:

*However, given the uncertainty around the  $K_{BC}$  values currently available in the scientific literature as well as the measurement of  $f_{BC}$ , the use of passive samplers in Tier 2 is*

*recommended over the two carbon model. In addition, as discussed above, because of the continued difficulties and costs associated with collecting interstitial water, a similar recommendation is made for using a passive sampler based measure to generate interstitial water toxic units rather than a direct measurement of interstitial water (Section 2.3).*

## **Section 5: References**

Is the cited literature sufficiently comprehensive?

Reviewer response: The literature citations are appropriate.

Editor response: -

Other reviewer comments

Reviewer comment: Page xii, the last sentence “These ESBs apply only to sediments having  $\geq 0.2\%$  total organic carbon by dry weight and nonionic organic chemicals with  $\log KOWs \geq 2$ ” was not addressed in the body of the document.

Editor response: This language is consistent with previous ESB documents. No change to text.

Reviewer comment: Page 1-2, line 2, double “between”

Editor response: Text in Section 1.2 has been corrected and the extra “between” deleted.

Reviewer comment: Page 2-4, on what compounds were Eqn 2-4 based?

Response: To provide more detail, the following text has been added to this section (2.2.2):

*... this document recommends using the relationship developed by Driscoll et al. (2009) for 17 PAHs:*

Reviewer comment: Page 2-5 “In general, centrifugation without subsequent filtration results in the most accurate concentrations of nonionic organic contaminants in interstitial water from contaminated sediments.” First, this sentence needs reference. I actually do not agree that this is the case since the processing associated with centrifugation seems to generate significant colloidal matter (e.g. DOC) and increase strongly colloidally associated contaminants (e.g.  $\log Kow > 6$ ). We have numerous examples where even centrifugation at high g results in interstitial concentrations (based upon total concentration) for strongly hydrophobic compounds (e.g.  $\log Kow > 6$ ) that are much higher than by more direct methods (e.g. low energy/flow displacement of interstitial water from sediments). Admittedly this is not a problem with moderate and low hydrophobicity contaminants. For the strongly hydrophobic compounds, flocculation or filtration may be necessary to avoid unrealistically high concentrations of contaminants. Admittedly, filtration and flocculation MAY make things worse in that it could reduce the amount of colloidally associated contaminants below what is actually observed in the interstitial water. In summary, I would state that centrifugation without filtration results in a conservative

measure of interstitial water concentrations but that it may strongly overpredict interstitial water concentrations for very hydrophobic compounds that are strongly associated with colloidal matter that might be generated by the sediment processing.

Finally, I would add that the statement implies (when considered with the rest of the document) that if you wanted to use interstitial water concentrations to indicate effects such as bioaccumulation or toxicity that you should use the centrifuged interstitial water concentrations. I would disagree with this in that I believe that research suggests that the freely dissolved concentration is the more direct indicator.

Editor response: The text in Section 2.3.1 the reviewer describes has been revised to reflect some of the noted concerns and a reference has been included:

*If performed with a minimum of artifacts, centrifugation without subsequent filtration results in an acceptable sample of interstitial water which can be used to make an accurate measurement of the freely dissolved concentration of nonionic organic contaminants in sediments (Adams et al., 2003). Substantial artifacts include the formation of dissolved and colloidal organic matter during interstitial water preparation and isolation which can result in an over-estimation of interstitial water nonionic organic contaminant concentrations and potential bioavailability especially those with high  $K_{OWs}$ .*

Section 2.33 of the document, discusses how to address some of the reviewer's concerns; for example, (1) adjusting for dissolved and colloidal organic carbon using  $K_{DOC}$  to consider the presence of organic carbon in the sediment interstitial water and (2) interpreting interstitial water data correctly to recognize that the use of "total interstitial water" as being equivalent to the "freely dissolved interstitial water" concentrations of nonionic organic chemicals is erroneous.

Reviewer comment: Page 2-6, Equations 2-6 and 2-7 had better be introduced in front of method 1 to determine freely dissolved water concentrations because the premise of the method one is that for low molecular weight compounds,  $K_{DOC} \cdot DOC$  is small and can be neglected. However, when  $C_{DOC}$  is large, the product can be high even  $K_{ow}$  is small, which will be clearly demonstrated by Equations 2-6 and 2-7.

Editor response: The text in Section 2.3.3 has been revised to discourage readers from using Method 1 when directly measuring interstitial water:

*However, this approach may be problematic and is not recommended because high concentrations of DOC can be present in isolated interstitial water.*

The order of the methods (i.e., 1, 2 and 3) has not been changed.

Reviewer comment: Page 2-10, Information such as applicable contaminants or  $K_{ow}$  ranges for correlations in Eqns 2-10 to 2-12 is needed before using these correlations.

Editor response: Table 2-1 provides a preliminary list of applicable contaminants and the range of log  $K_{OWs}$  is equivalent to values  $\geq 2.00$  as noted in the *Executive Summary*. No change to

text.

Reviewer comment: Page 3-2, in this sentence “Because  $C_d$  appears on both sides of Eqn 3-2, an iterative approach must be used to solve for  $C_d$ ”, Eqn 3-2 should be 2-3

Editor response: The suggested correction has been made to the text.

Reviewer comment: Table 3-1, suggest listing the water concentrations estimated from one-carbon model to compare with the estimations from two-carbon model.

Editor response: For the one-carbon model in the examples, the  $ESBTU_{FCVS}$  are calculated using the carbon normalized sediment concentrations and carbon normalized effect concentrations. Consequently, the freely dissolved concentrations based on a one-carbon model are not explicitly calculated. In response to another reviewer’s comment, text has been added to Section 3.2.1 showing readers how to calculate the dissolved concentration but there was no intent to include those calculations in the examples.

Reviewer comment: Page 3-4, please give an example of planar compounds or other guidance for the practitioner

Editor response: The following text has been added to Section 3.4:

*Consequently, at this time Equation 2-4 should not be used for non-planar nonionic organic chemicals; for example, DDTs and their degradation products, and ortho-substituted PCBs (also see Table 2-1).*

Reviewer comment: Page 4-1, “Currently, the analysis of contaminated sediments for a suite of nonionic organic chemicals is less expensive than performing a similar analysis for passive samplers, such as SPME, PEDs or POM.” Basis or Reference? If reference was not available, an estimate of cost needs be provided to draw this conclusion. I could basically agree with the statement since there are limited sources for using and analyzing the passive samplers but there are certainly limitations to the statement. For example, bioassays via conventional analysis or with the addition of passive samplers I would suggest are identical in cost. Laboratory analysis of collected samples with passive samplers trade off tumbling sediments for a period of time with much more extensive sample processing by conventional analyses. In either case, the problem is that there are not many people trained in use of the technology as opposed to any inherent cost issues. I would prefer that the document recognize that since the situation has changed dramatically in the past few years and will change more in the next few years.

Editor response: The statement about cost is based on estimates for the analysis of passive samplers versus a standard analysis on contaminated sediments. Further, as the reviewer points-out, and Section 4.1 also notes, the lack of laboratories performing chemical analyses on passive samplers and the limited amount of guidance on how to conduct the analyses results in the prices being elevated for the few laboratories doing that type of work. It is agreed that the cost of analyses on passive samplers will decrease with time and Section 4.1 indicates this point. No

change to the text.