REVIEWER 3
Response to charge questions:

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

The document could be reorganized to make the content more tractable to a wider audience.
First, I suggest focusing this guidance document on passive sampling of hydrophobic organics (see response to question 5 in regard to suggested options for how metals should be addressed).

Second, I recommend shortening the introduction chapter to cover objectives, background, types of passive samplers (LPDE, POM, PDMS) and deployments (in-situ and ex-situ options) and applications related to both assessing site risks as well as remedial efficacy.

I would then include an expanded chapter describing the principles of passive sampling of hydrophobic organic chemicals that would present all the relevant equations that can be applied regardless of polymer phase.

A revised outline of this "principles" chapter could be:

1. Stages of passive sampler operation (currently section 1.4)
    a. Potential use of biocides for ex-situ deployments (section 2.2.5)
2. Equilibrium passive sampling:
    a. Demonstrate equilibrium achieved
        i. Kinetic studies
        ii. Simultaneous deployment and comparison of polymers with different amounts/ sampling rates
    b. Provide negligible depletion extraction
        i. Selection of polymer to sediment ratio (currently addressed under POM chapter in 2.2.2 but this concept is generally applicable to all passive samplers)
3. Selection of $K_{polymer\text{-}water}$
    a. General considerations; need to reflect equilibrium conditions; need to specific polymer source and characteristics; discuss unit .. in case of POM/LPDE adopt mL water / g polymer in case of PMDS use mL water / mL PDMS
    b. General approaches
        i. Use of literature values
        ii. Use of estimated values derived from QSAR (i.e. Kow, ppLFERs)
        iii. Experimental determination based on published methods (could generalize discussion on POM currently presented in section 2.8)
    c. Correction of $K_{polymer\text{-}water}$ for temperature and salinity
4. Non-equilibrium sampling requirements:

    a. Concept of PRCs to correct for non-equilibrium conditions
    b. Selecting PRCs
    c. Loading PRCs including spiking quantity
    d. Chemical analysis of PRCs following deployment
    e. Appendix that describes in more detail the underlying equations and assumptions incorporated into the GUI that has been developed to analyze PRC data and compute Feq
5. Extraction and Instrumental Analysis
    a. General considerations applicable across polymers
6. Determination of method detection limits (currently 7.3.1 and 2.2.3)
    a. Analytical detection limits
    b. Mass of polymer
    c. Polymer-water partition coefficient
    d. Degree of non-equilibrium

The three subsequent chapters that follow would then focus on application of the theory and related equations presented in this chapter to passive sampling with each of the respective polymers, i.e. one chapter for POM, LPDE and PDMS.

These chapters should each have a consistent format and provide example calculations specifically relevant to passive sampling with the given polymer. For example, a common format that would link to the principles chapter described above would be:

1. Introduction
2. Sources and Characteristics (include polymer specifications and associated amounts or volumes that link to various commercial sources since these values are needed for normalization of analytical results and may not be obvious to many readers). If a specific source of polymer is recommended it would seem prudent to provide justification, e.g. for POM recommend only one supplier, why?.
3. Sampler Preparation
4. Exposure time and conditions for lab/field use
    a. General guidance on equilibrium vs on-equilibrium sampling options for polymer
    b. Example calculation of sediment to polymer ratio for ex-situ deployment
5. Equilibrium sampling
    a. Provisional $K_{polymer\text{-}water}$ for PAHs/PCBs and related QSARs (could have appendix with more detailed review of literature values for each polymer)
    b. Correction for temperature or salinity (if no data supporting correction state this for polymer as future need; if corrections available provide example calculation)
6. Non-equilibrium sampling
    a. Example application of GUI for determining Feq for this polymer
7. Extraction and Instrumental Analysis

    a. Polymer-specific considerations for this sampler
8. Method Detection Limits
    a. Example calculation for this polymer
9. Summary of pros/cons for current use of this polymer

The current QA/QC chapter could remain as a stand along section since it is applicable across polymers.

(2) Does the document provide sufficient information for commercial analytical laboratories to begin to develop their own standard operating procedures for deploying, recovering and analyzing passive samplers as well as provide sufficient guidance for contacting experts in the field to ask questions.

As discussed in response to question #1, the current draft does not provide a consistent presentation of information across the different polymer types. Thus, the draft manual could be improved to help commercial labs better understand specific issues for deploying, recovering and analyzing the three specific types of polymers described.

I seriously question the merit of providing a list of "experts" upon which external parties can contact. First, is this a realistic expectation of these individuals? Second, are there potential conflict of interest concerns in specifying "preferred experts"? Third, this list of individuals will be of limited value in the future as new experts in the field emerge. Fourth, what objective process has USEPA employed to identify this list of experts (and how might this list discourage future cooperation with other experts not included). Lastly, if the objective of this guidance document is to provide the essential elements for developing acceptable SOPs for passive sampling methods by external parties does not the need to provide a list of experts to address questions somewhat undermine the purpose of this manual? I also have similar concerns with providing a "short" list of commercial labs capable of performing analyses on passive samplers. Surely, interested individuals can find out what commercial labs advertise these capabilities and the extent to which these labs have contributed to the field via external publications and publications. Thus, I would suggest that Tables 1-2 and Tables 1-3 be deleted.

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

No. I do not feel the present document explains sufficiently the theory and required calculations in a transparent manner. For example, it is not clear how type and configuration of the PS links to the amount (g of POM or LPDE) or volume (ul PDMS .. see below example in SERDP 2012 report) needed in various equations presented in the

document.

Fiber Designation	Inside dia. µm	Outside dia. µm	PDMS Volume (V) µL/m	PDMS L=V/Area(A) µm	Source
170/110	110	170	24.7	13.2	Polymicro
230/210	210	230	9.6	6.9	Fiberguide
1060/1000	1000	1060	29.2	97.1	Polymicro

In some cases units used in equations are not clearly defined or described. I would recommend using additional "break-out" boxes to highlight more "hands-on" examples of calculations for applying general principles to specific polymer types (e.g. see polymer-specific outline in response to question #1)

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

In my opinion, the inclusion of passive sampling methods for metals (i.e. DGT), which does not provide an estimate of Cfree that can be directly linked to sediment quality criteria or bioaccumulation prediction, should not be integrated into this guidance document. Rather this document should focus on passive sampling methods for hydrophobic organic chemicals where application in sediment management context is broadly recognized. This is consistent with the goal of this document to provide contract laboratories with the information needed to develop SOPs using PS methods.

In contrast, the utility of DGTs in the context of sediment management decision-making is evolving. Hence, it seems premature to be encouraging commercial labs to develop SOPs involving these techniques. I suggest either excluding PS of metals from this guidance document and instead developing a separate manual devoted to this topic in the future (ideally after DGT techniques are further optimized in sediment lab/field studies) OR including the present information as an appendix that highlights general concepts reflecting the current state of the science and need for further work in context of contaminated sediment assessment and management.

This is consistent with the consensus view from the SETAC Pellston workshop that application of PSMs for metals in sediments is still largely in a research mode of development.

The guidance document also seems to largely focus on non-equilibrium/in-situ PS but should provide a better balance to ex-situ/equilibrium sampling deployments as the later approach can be more practically applied. Ex-situ applications performed in an equilibrium sampling mode reduces cost and complexity of Cfree estimation by avoiding the need for

purchase, spiking, measurement and post data analysis of performance reference compounds. One particularly useful application of ex-situ equilibrium sampling is inclusion in laboratory sediment toxicity or bioaccumulation tests so that test endpoints can be linked to Cfree measurements. Further, recent work also shows promise of in-situ sampling with PDMS (Witt et al. 2013; Maruya et al. 2015) without inclusion of PRCs. Given the advantages of equilibrium sampling using fast, negligible depletion samplers, EPA should acknowledge and encourage the future development of such methods when possible.

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

Different sources of silicone rubbers are provided in Smedes et al. 2009 including the J flex-form upon which provisional recommended $K_{polymer\text{-}water}$ for PDMS is based. Given the limited use of this PDMS source in the US an additional compilation of empirically derived $K_{polymer\text{-}water}$ for selected PAHs and PCBs from other commercial sources of PDMS should be compiled and contrasted with the recommended $K_{polymer\text{-}water}$ values. Some key references include Reible et al (2012) [PAHs with Polymicro/Fiber guides]; DiFilipo & Eganhouse (2010) [PCBS/PAHs multiple PDMS sources] and Reible & Lufto (2008).

Temperature dependence of Kpdms-water has been reported by Reible et al. 2008 (Polymicro and Fiber Guide fibers) and Jonker et al 2015 (Altec PDMS sheets). The later paper also addresses salinity corrections. Theses references should be summarized and included in the PDMS chapter.

It is also suggested to provide an example calculation of detection limits using thermal desorption of PDMS versus conventional solvent extraction to highlight the great potential to increase method sensitivity while avoiding use of solvents and potential loss of more volatile constituents (e.g. naphthalene).

Given that SPARC is no longer publically available and not supported by USEPA (versus EPIWIN), the use of this model to estimate log Kow values for use in QSARs may present a barrier for practical use. If the reliability of Log $K_{polymer\text{-}water}$ - Log Kow relationships are not significantly reduced using EPIWIN Log Kow values, EPA may wish to reconsider using these values as inputs to these predictive models.

I suggest replacing the last case studying involving metals/DGT (see response to #1) with an example of ex-situ deployment for analysis of hydrophoobic organics since all of the other case studies involve field studies, in-situ deployments. As previously highlighted, a useful example would be ex-situ measurements of Cfree to support interpretation of lab toxicity or bioaccumulation tests with contaminated site sediments. Maruya et al. 2015 provides a recent example but other data from specific projects that are publically available, but not yet published, would be a good candidate as an ex-situ case study.

With regard to POM, the recent critical review from Arp et al 2015 should be incorporated into the manual.

References:

Arp et al. 2015 Review of polyoxymethylene passive sampling methods for quantifying freely dissolved porewater concentrations of hydrophobic organic contaminants, Environmental Toxicology and Chemistry 34: 710–720

Difilippo, E. L.; Eganhouse, R. P. (2010). Assessment of PDMS-water partition oefficients: Implications for passive environmental sampling of hydrophobic organic compounds. Environ. Sci. Technol. 2010, 44, 6917−6925.

Jonker,MTO, SA van der Heijden, M Kotte, F Smede (2015). Quantifying the Effects of Temperature and Salinity on Partitioning of Hydrophobic Organic Chemicals to Silicone Rubber Passive Samplers, Environ. Sci. Technol. 49, 6791−6799

Maruya et al. (2015). A passive sampler based on solid phase microextraction (SPME) for sediment-associated organic pollutants: Comparing freely-dissolved concentration with bioaccumulation Chemosphere 137 192–197.

Reible, D.D., G. Lotufo (2008), Lab Demonstration Plan-Summary and Results, ER-0624 Demonstration and Evaluation of Solid Phase Microextraction for the Assessment of Bioavailability and Contaminant Mobility, Report to ESTCP.

Reible DD, Lotufo G, Skwarski A, Lampert D, Lu X (2012) Demonstration and evaluation of solid phase microextraction for the assessment of bioavailability and contaminant mobility, final report. ESTCP Project ER-200624. Environmental Security Technology Certification Program, Arlington

Smedes, F.; Geertsma, R. W.; Van Der Zande, T.; Booij, K. (2009). Polymer-water partition coefficients of hydrophobic compounds for passive sampling: Application of cosolvent models for validation. Environ. Sci. Technol. 43 (18), 7047−7054.

Witt et al. (2013). Passive Equilibrium Sampler for in Situ Measurements of Freely Dissolved Concentrations of Hydrophobic Organic Chemicals in Sediments, ES&T 47:7830-7839.