

***Peer Review Comments – Peter Landrum, Ph.D., Scientist
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Review of Methodology for Derivation of Pesticide Sediment Quality Criteria for the Protection of Aquatic Life

General Comments and Questions:

In reviewing this document I attempted to consider whether it was complete, clear, and the methods appeared to be appropriate. I also attempted to examine whether the authors conveyed a method that could be easily followed and was supported by clear method and theory. This document has three major deficiencies in my estimation and several minor ones that should be addressed prior to release. The three major deficiencies are as follows:

First, there should be a clear theory section that relates the methods for assessing bioavailability to the objective endpoint, acute or chronic. The state of the art today for bioavailability of sediment associated contaminants remains in flux and the methods available are all subject to uncertainties that have not been fully defined. Thus, this section will need to address theory, limitations of each method used to address bioavailability and an application section that indicates how the objective is to be applied/used. While the method recognized that bioavailability needs to be addressed and that there are several methods available to do this, there was not a clear description of each approach that will underlie the development of a sediment quality objective. In this case, the authors need to lay out the underlying relationship between exposure and the measures of bioavailability and the limitations of each method. For instance, organic carbon normalization has been used to account for differences in bioavailability and related to water quality values through equilibrium partitioning theory. In this theory, the route of exposure does not matter because the chemical activity is represented by the freely dissolved interstitial water concentration and one expects equal chemical activity in all phases at equilibrium. Thus, it becomes possible to relate water quality objectives to sediment concentrations (DiToro et al. 2002). [Note: all references refer to references used in the method paper unless they are new and will be added at the end of this document] It is also recognized that carbon normalization is not very reliable (USEPA 2012 a,b). Thus, the uncertainty of this approach needs to be acknowledged as a part of this theory section indicating that factors such as differences in the organic matter composition can affect the reliability of the prediction. Further, the actual approach for calculation of the sediment quality objective by this approach should be laid out in an equation with appropriate units. To follow up on the other methods, what needs to be done is to describe how each method of determining bioavailability will be used to lead to the

same sediment quality objective that is an objective with the same units. It will be important to ensure that the sources for data, e.g. polymer water partition coefficients for passive samplers, address not only the source but provides the suggested partition coefficients for this method. I was particularly disturbed that there was not a clear discussion of the different materials for use as passive samplers and the limits that are required to use these devices (SETAC held a workshop in November 2012 covering passive samplers. The papers associated with this workshop are to come out in IEAM in 2014. I will attach the literature review paper for your information which has been accepted and is in press, I also suggest you contact Dr. Thomas Parkerton (thomas.f.parkerton@exxonmobil.com) to get access to other accepted papers). Also, there was no clear description about how to use the Tenax extraction data. Tenax extractions for bioavailability are of two types, sequential extractions that lead to estimates of the different binding fractions and single point extractions where the amount extracted has led to relationships to bioavailability. This document has advocated the use of Tenax to address bioavailability and this theory section should lay out how the two types will be used and applied to lead to a common sediment quality objective. (Unfortunately, there is not a good review paper for Tenax extraction though I am working on one.) With this section, the reader should understand how each of the different approaches are to be used to help lead to a clear sediment quality objective.

Second, there was a general absence of propagation of error throughout the document to provide clear estimates of the uncertainty associated with the calculated objective. For instance, there was a call to calculate geometric means in several places in the document and then to use the mean as though it is a deterministic value. There is error associated with such a determination and that error needs to be propagated through the equation where it is used along with any other uncertainty of the parameters in the equation to produce a clear estimation of the uncertainty of the result. All of the toxicity measures have uncertainty associated with them and this uncertainty needs to be propagated as well through to the end result. There are well defined approaches for propagation of error and there should be an uncertainty section that describes the need for such application and how the uncertainty should be determined and applied in the document. Note, how uncertainty is incorporated in the regulation is policy but to have policy address that issue the science must supply the estimate.

Third, there is much use of toxicity values established by hypothesis testing such as NOEC and LOEC, recommended in this document. These values are not to be considered reliable measures of the effect of chemical on species. This method should only rely on clear dose (concentration) response relationships for determination of sediment quality objectives. The reasons for this are as follows: Values obtained through hypothesis testing do not describe the level of response in relation to dose. They are experimentally structured and could be very different depending on the selection of doses used in different experiments. They do not provide inference or establish causality for the toxicity of a particular compound. They are only a sign of difference from some control value. They are inordinately subject to confounding stresses that cannot be separated from the response to the chemical. They do not convey the extent of response and the associated

uncertainty in the value. Thus, they are not appropriate toxicological protocol for establishing the response of a compound to a toxicant. Toxicology is based on dose response and if it is not present in a toxicity test then there is reason to question the validity of the test and the likely presence of confounding factors. Criteria should be based on clear dose response not happenstance.

You use the term acceptable several times in the document and it needs to have a clear definition where used and applied. For instance, if data are to be deemed acceptable then the criteria to define acceptable should be part of the document. These criteria may be different depending on the specific item that is to be considered acceptable.

Questions

Is the way the method addresses bioavailability in accordance with the current state of research on this topic?

You have to do a better job of describing how you will incorporate each of the types of measures for bioavailability into your method. You can see my call for a theory section above, which would go a long way to establish how to use the different approaches to come up with a single sediment quality measure.

Are the ways of accounting for bioavailability included in the method scientifically valid. Are there additional technically valid ways to account for bioavailability that could be used?

You need to lay out in the theory section where the data comes from for the various methods listed and how it would be applied and lead to a sediment quality object with specific units. Also, how that objective will be related back to the bulk sediment collected in the field. It was certainly not clear how you would apply each type of approach to lead to a sediment quality objective. There also needs to be a portion of this that describes the limits for each approach based on their use in the literature. I am particularly concerned about your apparent understanding of the use of Tenax extraction. See my comment above about theory.

Will environmental regulators and researchers be able to use existing toxicity and monitoring data included in the method to check compliance or does the method require new techniques be used to generate new data?

There are limits in the existing data that will require new data in many cases. For instance, most folks do not measure the different types of carbon that have major impact on the binding of organic contaminants. At the very least, there should be measures of total organic carbon and black carbon. It is likely that even with this measure determination of freely dissolved interstitial water concentration will not be as accurate as desired because there are many types of organic matter that have different binding

properties. So at this point, I would suggest a method that measures the freely dissolved interstitial water concentration that reflects the chemical activity of the compound using passive samplers, which is not common in monitoring today and not used in toxicity testing today.

Is it clear how to evaluate studies by reading section 2.3 and appendix A (rating guides) and looking at tables 7-13?

I did not study these with detailed care but found the description very general for the most part and would suggest that you provide a logic guided example. I know you attempted to do this with the bifenthrin case study but it could have had more detailed descriptions of methods to lead a user through the thought processes required for the development of a sediment quality objective. I am particularly concerned with the rating tables 8-12, as I could not tell where the numerical values came from for evaluating studies or how to apply those values for a particular study. Thus, applying this method remains largely unclear.

Do the categories and point values assigned in tables 8-12 reflect the importance of the parameters to performing valid sediment toxicity testing?

You do not lay out the logic for the scores used or where the numbers come from. You need to make it more clear how these tables were set up and if this follows some specific regulation or criteria document that already exists how you applied those to this case for sediments. These seemed arbitrary to me as they were not described in detail. How do you know they are the correct values?

Is it clear how to prioritize and organize data by reading sections 2.4 and 2.5? Do the data prioritization and exclusion in the bifenthrin criteria derivation seem reasonable (Section 8.7)? This step plays a large role in determining which data are used to derive the criteria and the magnitude of the criteria.

As you can see from above, I would not include any data that is based on hypothesis testing for criteria development and you spend a lot of time indicating how those data should be incorporated. Your point “i” is one where this document does not provide any guidance about approach or limitations, see section on theory above. There is a general absence of propagation of error. There is also no indication of which data to exclude and what statistical test to use for that purpose.

Is it clear what information should be input in the toxicity data summary Table 14.

Yes

Are instructions in sections 3.4 – 3.7 describing how criteria are derived, clear and easy to follow.

The use of this approach is not within my expertise and while I read through it I did not study it for comment.

Does it make sense to derive two criteria for a given pesticide, one with a 10-d averaging period and one with a 28 d averaging period? Should only one criteria be derived? Please comment on the thoroughness, validity and completeness of the review and discussion in sediment 3.8.2. Are there any other considerations that should be included for determining criteria averaging periods?

It makes sense to derive a 10 d value because that is the type of data you have available, 10 d toxicity tests. To convert it to a chronic value is an estimate at best if there are no studies to compare to. The limitations of selecting a chronic value when no data for comparison are available should be spelled out including the uncertainty. You talk about averaging periods as though this were a water concentration. Sediments do not change in concentration as rapidly as water and would be expected to be more constant. The period should reflect the usual chronic test time frame.

Is the assumption of concentration addition reasonable for mixtures of pesticides in the same class?

Addition is reasonable for mixtures of pesticides of the same mechanism of action barring the understanding that compounds within the same mechanism of action can have different potencies because pesticides are generally specific acting. Because, the fit of each compound to the receptor for eliciting the toxicity can be different then simple concentration addition should not be considered reliable but toxic unit addition should be reasonable. As pointed out in the specific comments, you have neglected to consider independent action for mixtures when the mechanism of action is different among compounds. I strongly recommend that all concentrations be expressed on a molar basis to account for differences in molecular weight among toxicants.

Do you know of QSARs that could be used to estimate toxicity to other species, including threatened/endangered?

This is not something I can help with.

Are the bifenthrin criteria generated in section 8 protective of aquatic life, more specifically, are they neither unreasonably overprotective nor under protective?

The need to apply application factors instead of species sensitivity distributions for measured data leave the potential for requiring an over protective criteria. This becomes more likely if the numbers of data available are small thus the application factor larger. To help with this a formal uncertainty analysis would show that criteria with limited data for support would be more uncertain. Note: application factors are provided as deterministic values when in fact there should be uncertainty associated with them. This

again is a case of treating values as though they are deterministic when in fact they have associated uncertainty. Finally, any objective determined from this method should have an uncertainty range associated with it. What the regulators do with that range is policy but it should not be treated as a deterministic line in the sand value. Finally, in this example you achieve a set of values, acute and chronic, that seem overprotective based on the water quality data you report. This should be a flag that there are problems with the method and the particular application factors (see specific comments below).

Specific Comments: (Note I will send the original comment with the location of the comments detailed below so that you know where they belong in the document.)

Executive Summary 1st paragraph: I would change the description from criteria to objective. The reason is that criteria are a policy determined values and objectives are a science determined values.

Executive Summary 2nd paragraph: I would change the word porewater to interstitial water throughout the document. The water in question is really the water between sediment particles not what is in the pores or particles. In the SETAC workshop on passive samplers described above, there was a consensus that the term interstitial water should be used for sediment.

Executive summary 3rd paragraph: Define acute and chronic as used for this document.

Executive summary: There needs to be a theory section that outlines the methods, the units for the sediment quality objectives, and the application of the values.

Introduction paragraph 2: Based on my perusal of your references, you need to do a better literature search. I am adding a couple of references that you may find useful but it is clear that you should not claim that this reflects the latest available research.

Landrum, P.F., Robinson, S.D., Gossiaux, D.C., You, J. Lydy, M.J., Mitra, S., Ten Hulscher, T.E.M., 2007. Predicting bioavailability of sediment-associated organic contaminants for *Diporeia* spp. and oligochaetes. *Environ. Sci. Technol.* 41:6442-6447.

Yuping D, Landrum PF, You J, Harwood AD, Lydy MJ. 2012. Use of solid phase microextraction to estimate toxicity: I. Relating fiber concentrations to toxicity, *Environ. Toxicol. Chem.* 31:2159-2167

Yuping D, Landrum PF, You J, Harwood AD, Lydy MJ. 2012. Use of solid phase microextraction to estimate toxicity: II. Relating fiber concentrations to body residues, *Environ. Toxicol. Chem.* 31:2168-2174.

Mackenbach EM, You J, Mills MA, Landrum PF, Lydy MJ. 2012. Application of a Tenax Model to Assess Bioavailability of PCBs in Field Sediments. *Environ. Toxicol. Chem.* 31:2210-2216.

Yuping D, Landrum PF, You J, Lydy MJ. 2013. Assessing bioavailability and toxicity of permethrin and DDT in sediment using matrix solid phase microextraction. *Ecotoxicology* 22:109-117.

Summary phase 1 1st paragraph Line 4: See my comments above about the use of the term criteria.

Summary phase 1 1st paragraph line 18: Be specific about the assumptions you will incorporate into this method.

Summary phase 1 1st paragraph line 19: The use of SST would seem to have many of the limitations of an equilibrium method because of the variety of sediment compositions that could be employed. You need to specify the criteria that will be critical if you are to apply this approach including the need to measure the freely dissolved interstitial water concentration perhaps using a passive sampler.

Summary phase 1 1st paragraph last line: You need to spell out which uncertainties you are considering and how they will be determined.

Summary phase 1 second paragraph line 4: You need to be more specific about the term heterogeneous describing the types of binding phases of concern for organic contaminants.

Summary phase 1 2nd paragraph line 8: You need to be more specific about the “conditions” of importance for determining the objectives.

Summary Phase 1 2nd paragraph last sentence: Somewhere in here would be a good place to discuss the fact that the concentration in the interstitial water at equilibrium reflects the chemical activity of the contaminant in the sediment. It is this chemical activity that drives the extent of bioaccumulation, assuming equilibrium, and as such is independent of route of exposure.

Section 1.2.1 first line: There is a typo remove “0”

Section 1.2.2 line 5: It should be noted here that the active entity may be the transformation product as would occur with organophosphorous pesticides. However, the objectives are designed to reduce accumulation of the parent compound such that the transformation product would not accumulate to a toxic level.

Section 1.2.2. 2nd paragraph lines 6-8: Going back to a previous comment, you need to explain the relationship between the freely dissolved interstitial water concentration and bioaccumulation and the role of chemical activity. The explanation here is very weak and uninformative.

Section 1.2.2 3rd paragraph: This is a very superficial description of what takes place. There is a large difference in types of organic matter and substantial difficulty in determining the quantity and types present in a sediment and no good description for the dissolved organic matter types. At the very least this paragraph should include a notion that there are different types of organic matter and they have different partition coefficients. In particular, you need to discuss the

relative binding information e.g. dissolved organic matter is generally an order of magnitude less sorptive than solid phase organic matter and that solid phase organic matter such as soots, chars etc are about an order of magnitude more sorptive than natural organic matter after some diagenesis. You should also provide acceptable values for the partition coefficients for the different types of organic matter and not leave the reader to select the one they like.

Section 1.2.2 4th paragraph lines 9-10: How did these interstitial water concentrations based LC50 values compare with water exposure LC50 values and water quality values. You might indicate how comparable these were.

Section 1.2.2 5th paragraph line 2: You indicate that data generated from toxicity testing that incorporates bioavailability measures will be the most useful but you have not indicated yet what these measures will be and how they will be applied. You need to be more specific here. This would be less of a concern if you had a theory section above this part of the document. In fact, I would start a theory section right after the introduction.

Section 1.2.2 5th paragraph line 8: You need to be more specific. Tenax has been used in two ways. First, Tenax has been used in sequential extractions to determine the rapidly desorbing fraction. Second, Tenax has been applied in single point extractions. You need to indicate how you will apply the approach. Again this should be covered in a theory section as discussed above and would not need to be reiterated here.

Section 1.2.2 5th paragraph line 9: Some caveat's should be mentioned here about how you will apply this carbon normalization. For instance, it is possible to determine black carbon and other carbon and then apply representative partition coefficients. Failure to account for black carbon is not state of the art at this time. Again this could be part of a theory section.

Section 2.1.2 1st paragraph line 2: This word "theism" based on my dictionary leads to a meaning that is not appropriate for the use. You need to clarify what you mean here.

Section 2.1.2 1st paragraph line 11: Why do you believe this is the appropriate representation? Also, where is the standard deviation? You need to represent the uncertainty in the values you use to determine your final value and propagate the error so the uncertainty in the final value is known. How such uncertainty is applied in the regulation is up to the regulatory community but scientists must present the uncertainty in any derived value. At this point you at least need to call for the determination of the standard deviation. As I commented above, there needs to be a clear uncertainty analysis and presentation for this document and this is one place where it can start.

Section 2.1.3.1.2 lines 2-3: You should consider my comment above about the use of endpoints based on hypothesis testing. At the very least in this document there should be a discussion about the limitations of such values and the general uncertainty this would represent if used for criteria determination.

Section 2.1.3.1.2 lines 4: LC50s etc should not be considered simple point estimates. They have uncertainty associated with them and good studies report both the 95% confidence interval and the best report the slope of the concentration response relationship to allow for other levels of response to be calculated. Here is another area where the document treats values that have substantial uncertainty as though they are deterministic values.

Section 2.1.3.1.5 line 4: If one is talking about sediment brief pulse exposures are not the most likely scenarios except where sediment is disturbed and affects the water column. If you have some specific scenarios in mind you need to expand this section and be more specific about where this is an issue. Generalities do not help the regulator. So while time is an important issue, it seems to me to be more of one of the issues of what is the minimum exposure at the maximum duration that leads to an effect. See Lee et al.

Lee, J-H, P.F. Landrum, and C-H Koh. 2002. Toxicokinetics and time-dependent PAH toxicity in the amphipod, *Hyalella azteca*. *Environ. Sci. Technol.* 36:3124-3130

Lee, J-H, P.F. Landrum, and C-H Koh. 2002 Prediction of time-dependent PAH toxicity in *Hyalella azteca* using a damage assessment model. *Environ. Sci. Technol.* 36:3131-3138.

Lee, J-H and Landrum, P.F., 2006. Development of a multi-component damage assessment model (MDAM) for time-dependent mixture toxicity with toxicokinetic interactions. *Environ. Sci. Technol.* 40:1341-1349.

Lee, J-H and Landrum, P.F, 2006. Application of a multi-component damage assessment model (MDAM) for the toxicity of metabolized PAH in *Hyalella azteca*. *Environ. Sci. Technol.* 40:1350-1357.

Section 2.1.3.3 1st paragraph last sentence: Another criteria that needs to be articulated is that the compound not be biotransformed. If it is biotransformed either in aquatic organisms or mammals it may not be an issue for wildlife or human health unless the biotransformation products are stable and toxic.

Section 2.1.3.4 1st paragraph lines 5-9: This is not true. This statement is a myth that reflects the failure to truly define route in most experiments and to rely on proportionality to suggest exposure. All one has to do to demonstrate this is have kinetics for water uptake and ingestion rates to show that such is not a true statement. (See Landrum, P. F. and J. A. Robbins. 1990. Bioavailability of sediment associated contaminants: A review and simulation model. *Sediments: Chemistry and Toxicity of In-Place Pollutants*. R. Baudo, J. P. Giesy and H. Muntau, Eds. Lewis Publishers, Chelsea, MI. Chapter 8, pp. 237-263). What is true is that the interstitial water reflects the chemical activity of the compound in the sediment at equilibrium, thus the uptake will be proportional to the interstitial water concentration. The fact that compounds have a proportionality to interstitial water concentration is not proof of route of exposure.

Ingestion is more likely to have an impact on the elimination rate see Lotufo, G.R. and P.F. Landrum. 2002. The influence of sediment and feeding on the elimination of polycyclic aromatic hydrocarbons in the freshwater amphipod, *Diporeia* spp. *Aquat. Toxicol.* 58:137-149.

All the above being said, if the organism comes to equilibrium, that equilibrium will reflect the chemical activity of the system which is reflected by the interstitial water freely dissolved concentration.

Section 2.1.3.5 3rd paragraph: This section ignores the importance of different forms of carbon especially black carbon and the impact on bioavailability.

Page 24 lines 3-6: Here is another example of the determination of a geometric mean and not addressing the uncertainty represented by that determination.

Page 24 line 10: You need to indicate that measures of the freely dissolved concentration in interstitial water represents the chemical activity of the compound in the sediment.

Page 24 rest of page: The determination of the freely dissolved interstitial water concentration ignores the potential for multiple types of organic carbon. At the very least, you should lay out the issue and how to address it should data be available or the potential impact of not including different types of organic carbon on the estimate of the sediment quality objective. You also should have a clear propagation of error section for using the values you have both measured and obtained from the literature.

Section 2.2 lines 2-3: You state that sediment exposures are inherently chronic. However, you do not support this statement with logic or with citation. How do you define chronic for this document? I would agree that in the environment sediment exposures are chronic but in the lab they may not be depending on the length of exposure and the life span of the test species. Preface this with how you are going to define the terms and what the important variables are for this consideration.

Section 2.2.1 Equation 7: All equations of this type have error for the parameters a and b and result in a deterministic solution that also has uncertainty. Be certain that all uncertainty is acknowledged and quantitatively addressed.

Section 2.2.2 Reference to *Hyalella Azteca*: Note that recent publications recognize that *Hyalella* is really a species complex that contains several phylogenetic groups thus lumping data from multiple organizations suggests that you have included this in the determination of ACR. However, you should be careful to acknowledge this. See Weston et al. PNAS 110:16532-16537 (2013).

Page 26 lines 1-2: You recommend using the water acute to chronic ratios for sediments however this is not appropriate. The reason is that acute toxicity in aqueous exposures is often short term generally 4 d or less exposure while the acute exposures for sediments are 10 d generally. So and acute to chronic ratio for water would not represent the same ratio of exposures as found in sediments. Thus, the ratios for sediments would likely be lower than for water exposures.

Section 2.3.1 3rd paragraph line 2: Define relevant for the purposes of this document. What are the criteria?

Section 2.3.1 4th paragraph last sentence: Why would a site specific partition coefficient be better? It could have just as much error as any other determination and maybe more. You need to specify data quality for such determinations. Thus, there should be a section in this document about data quality. I understand your goal of accounting for differences in sediment composition issues, which have not been well discussed in the document. However, you need to specify quality in order for that to have a clear advantage.

Section 2.3.2 1st paragraph: Here again it would seem that there should be some discussion of uncertainty analysis for the data used and I would suggest that there should be some discussion of the appropriate application of that uncertainty for regulatory purposes.

Page 28 line 14: How does one month ensure equilibrium? You might suggest some criteria that should be established to ensure this condition. Or at least support your statement with a citation that would be applicable to compounds with physical chemical properties in the range of interest.

Section 2.4 a,b,c,e: See my notes above about the limitations for considering the use of hypothesis derived end points.

Section 2.4 i: You have not, to this point in the document, put together a description of how to apply different approaches to address bioavailability and their application. See my comments on the need for a theory section.

Section 3.3 line 2: Is there some reason to focus on the 50% response measure. It would seem to me that you would want to focus on a 5 or 10% response level.

Section 3.4.1 page 26 line 2: See my previous comment about the *Hyaella* existing as a species complex with different characteristics depending on source. There are several papers now in the literature about this issue and it should be raised and discussed in the method.

Section 5.2 first line: You suggest that endangered species are particularly sensitive to stressors. You need to supply a citation to support this statement. Species may be threatened or endangered for many reasons but that does not specifically make them sensitive to toxicants and if they are sensitive not necessarily to all toxicants.

Section 6.1 third paragraph: Your recommendation to use a level 1 fugacity model is not necessarily representative of a specific environment particularly the dynamic environment of the delta. Thus, higher level more specific models should be recommended and used that address site specific conditions

Section 6.1 third paragraph line 10: You make a statement that if site specific conditions are used in the level 1 model and no exceedances are found then no further analysis is required. It seems that this needs to be supported by citation or that the statement needs to be toned down. I agree that exceedances are unlikely but it should not provide a pass for further analysis if there is a problem.

Section 6.2 second paragraph second sentence: I disagree with this sentence. Both acute and chronic criteria should be examined. This is the case because benthos often come to steady state within 10 d, the typical acute test period, and some even more quickly. Thus, there is potential to pass the compound up the food chain at a higher level. You need to better justify your statement.

Page 66 BSAF discussion: BSAF values have the difficulty that they are quite variable and are not always an accurate representation of the bioaccumulation. This is the result of differing partition coefficients with different types of organic matter. At a minimum this limitation should be discussed and the potential impact discussed.

Section 7.1 second paragraph: You provide two concentration levels that are not supported by citation. I presume you mean this to be an example of the statement of the criteria but that is not completely clear.

Section 7.2 first line: You call for discussion of the uncertainty of the derived objectives but you have provided no guidance on how to do this in the document. As I stated in the major issues for this document there should be a formal section on uncertainty analysis and error propagation. All derived objectives should have uncertainty limits provided.

Section 7.2 second paragraph: This statement is not supported. It seems to me that interstitial water concentrations determined from partition coefficients and SPME or other passive samplers would lead to a better estimate of freely dissolved interstitial water concentrations than many other measurement techniques. You need to support your statement with a citation of an example.

Section 7.3: When addressing comparisons to other criteria, you need to say something about the need to adjust for the issue of bioavailability which most other criteria do not address.

Section 8.2: First sentence: Provide all the information in an appendix. This document should stand independently and the user should not have to search to get the information necessary to follow the method.

Section 8.3 second sentence: Since this is an independent document from the water quality document, then you should lay out all the calculations for the example. You may want to do that in an appendix but it should be provided. Regulators should not have to go searching for data to follow the example.

Section 8.3 second paragraph: The term acceptable should be defined as indicated above. The K_{oc} is subject to substantial variation based on the specific sediment characteristics and this limitation needs to be considered in the example. How will this be addressed, particularly since you advocate its use in the next sentence?

Section 8.3 last paragraph: Again do not make the reader search for the information. I again suggest that all the details for this example and the calculations be put in an appendix then you can refer to the appendix for the details.

Page 72 first paragraph first sentence: It would have been good to get the data and determine the relationship and permit calculation of LC10 or other appropriate value instead of an NOEC which is meaningless, that is the value will likely depend on the experimental design and the concentrations chosen for testing.

Page 72 first paragraph third sentence: Your comments on the NOEC is exactly why such values should not be considered reliable.

Page 73 first paragraph third sentence: Provide a summary of the reasons for excluding the data here.

Acute BSQC calculation: This is a big factor and could easily result in an over protective condition. Consider, how sensitive *Hyalella* and chironomids are and would these species be at the lower end of a typical species sensitivity distribution if the exposures were in water. In other words, is there some way to be certain that this large an application factor is required. In addition, it would seem that there should be some uncertainty associated with these factors but again such information is missing and not applied. The further division by 2 adds another layer

of protection that may lead to an overprotective condition. The validity and uncertainty of these factors need to be discussed in the body of the method.

Chronic BSQC calculation: In this calculation you are applying an additional factor that is treated as a deterministic value and as stated above may be too large for the relationship between 10 d mortality data and other chronic endpoints because of differences in exposure conditions in sediment versus water from which the application factors were derived.

Section 8.10.1 first paragraph third sentence: Converting back and forth from OC normalized concentrations to interstitial water concentrations and then back to OC concentration will increase the potential uncertainty. You need to discuss this in the body of the method.

Section 8.10.1 first paragraph fourth sentence: Where do you expect site specific partition coefficients to come from? Be more specific. What is acceptable methodology for such determinations? What is acceptable data quality for these values?

Section 8.10.2 first paragraph: See my comments on mixture issues above and incorporate more detail here for the example.

Section 8.10.2 third paragraph: You discuss PBO but to my knowledge no one monitors for this compound in environmental monitoring studies. We also do not know its environmental fate that I am aware of. You need to say more about this here.

Section 8.10.2 fourth paragraph: While nano materials may be important in water exposures, they are likely not of consequence for sediments as they become just part of the sediment particles. Carbon nano tubes for instance simply add to the organic carbon for partitioning. Petersen, E.J., Pinto, R.A., Landrum, P.F., Webber, W.J. Jr., (2009). Influence of carbon nanotubes on pyrene bioaccumulation from contaminated soils by earthworms. *Environ. Sci. Technol.* 40: 4181-4187.

Section 8.11.1 second paragraph: You compare your calculated value to an acute toxicity value for Hyalella and suggest that there is a difference. However, the uncertainty associated with both values would suggest that they are not statistically different. This paragraph is a misleading paragraph because you do not consider uncertainty. The issue of uncertainty should be fully discussed and carried through the method and the example.

Section 8.11: Considering all the methods you are using including inappropriate application factors would suggest that your calculated values are overprotective.

Section 8.11.2: You should not be applying your values for bifenthrin to fish! Fish are known to rapidly biotransform compounds and so should not be susceptible to pyrethroids as insects and aquatic invertebrates with less biotransformation capability.

Section 8.11.2 Last paragraph: If you have a water quality objective of 0.6 ng/L and you are advocating a sediment interstitial water quality value that is 0.005 ng/L you have demonstrated that your method leads to an over protective condition. It is unlikely that sediment dwelling organisms are substantially more sensitive than overlying water dwelling organisms. This over protection likely results from limited data and inappropriate application factors among other issues. It would likely be better to apply the data from the water to set the limit for sediment

interstitial water. Also, if you allow the overlying water to be at this high level compared to your sediment value you will likely have a difficult time reaching an acceptable sediment value.

Section 8.12.1: See last comment on comparison of criteria.

Section 8.12.2: Bifenthrin should bioaccumulate but will likely not biomagnify due to biotransformation. You need to consider biotransformation. I would guess that only the invertebrates will bioaccumulate much of the compound once biotransformation is considered. This paragraph does not consider biotransformation which is why bifenthrin is not a particular hazard to most species.

Table 7 is out of order because the values needed to characterize a study have not yet been provided.

Tables 8-12: The source of the scores and the method to apply the scores to studies is not provided. How were the scores established and how are managers to apply the information from studies to determine a score.

Figures: All abbreviations need to be provided in the figure legend.

References:

USEPA 2012a. Guidelines for Using Passive Samplers to Monitor Organic Contaminants at Superfund Sites. http://www.epa.gov/superfund/health/conmedia/sediment/pdfs/Passive_Sampler_SAMS_Final_Camera_Ready_-_Jan_2013.pdf

USEPA. 2012b. Equilibrium Partitioning Sediment Benchmarks (ESBs) for the Protection of Benthic Organisms: Procedures for the Determination of the Freely Dissolved Interstitial Water Concentrations of Nonionic Organics. http://www.epa.gov/nheerl/download_files/publications/RB%20ESB%202012final_2.pdf