

Charge to the Peer Reviewers of "Procedures for the Derivation of Equilibrium Partitioning Sediment Benchmarks (ESBs) for the Protection of Benthic Organisms: Compendium of Tier 2 Values for Nonionic Organics"

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? If not, what specific additions or deletions to this section would you suggest?

Overall, I think the front matter does an excellent job of presenting the preliminary information for this document. I think the consequences of deriving tier 2 ESB values is missing. As stated in the foreword, the ESBs do not serve as regulatory values and are for screening and advisory purposes only. In the last half of the Foreword the general term for ESBs is used, implying no distinction between tier 1 and tier 2 ESBs. If the EPA perceives that tier 1 and tier 2 ESBs will be used differently, I think this needs to be conveyed. If they are not considered different in their application then that point should also be made. A third possibility is that the EPA will be neutral and allow the user to decide the value of tier 1 versus tier 2 ESB values. Whatever the position, this distinction should be stated in the Foreword and also in the Executive Summary.

Section 1: *Introduction*

- 1) Does this section adequately describe the overall approach used to derive ESBs? Further, does it provide a sufficient overview of the approach used for the protection of benthic environments contaminated with the nonionic organic chemicals addressed in this document? What specific improvements to this section would you suggest?
- 2) Is the discussion of the types of ESBs and the outline of the document's contents useful? If you identify deficiencies, please recommend ways to remedy them.

The Introduction seems sufficient as an overview of the approach. It is clear that tier 1 ESBs are more rigorous than tier 2 ESBs. See my comment above regarding the application of tier 1 versus tier 2 ESBs and my recommendation for addressing the application of each ESB.

Section 2: *Derivation of Equilibrium Partitioning Sediment Benchmarks*

- 1) Does this section describe a sound scientific basis for selecting toxicity and K_{OW} values for the calculation of ESBs? Are the methods and logic clearly explained and scientifically justified?
- 2) Is there any aspect of the toxicity or chemistry of the nonionic organic chemicals addressed in this document that is relevant but not considered, and exactly what scientifically defensible suggestions can you recommend to overcome the limitations?

Overall I think that the method is well presented and the criteria for chemical and toxicity values are explained clearly. I think one oversight is the consideration of overlying water. For viable predictions from this model, one would have to assume that the organism received all of its uptake for a given contaminant from equilibrated porewater, infaunal prey, or bedded sediment where it resides. Many (if not most) benthic species ventilate overlying water and consume prey that are not in contact with the benthos. Overlying water and pelagic prey are usually not in equilibrium with the bedded sediment, which would violate the EqP assumption for this approach. This point needs to be addressed in the Section 2 and Section 3.5 (limitations).

I think Section 2 needs a discussion that deals specifically with confounding factors and how they would affect the results. This discussion may also be appropriate in Section 3.

I didn't see any mention of "adjustment factors" that were mentioned in the Introduction (Section 1.2).

Section 3: *Calculation of Equilibrium Partitioning Sediment Benchmarks*

- 1) Does the section describe a sound scientific basis for determining the adverse effects of the nonionic organic chemicals addressed? Do the tables and figures provide clear and useful information?

Over all, I think the scientific basis and explanation of the EqP approach is clear and well supported. I wouldn't say that this section describes the scientific basis for determining adverse effects for these compounds but that it provides an approach for converting predicted water concentrations and known values of water-based toxicity values to sediment concentrations.

- 2) Are there any relevant aspects of chemistry and toxicity that the section does not address

adequately, and exactly what would you suggest to overcome the limitations?

I would like to see a more detailed explanation of the correction using f_{solids} . From what I remember about f_{solids} , the values range from around 0.8 for sand to as low as 0.2 or so for clay dominated sediment. Given these values, the correction would appear to range from 0.25 to 4. Figure 3 shows a few examples for this correction; however, I couldn't read the symbols on the figure. While I am sure that the figure is useful, I think a small table showing how these factors would affect the final ESB for different types of sediment (mostly sand, sandy silt, silty clay, etc.) would be informative. Additionally, TOC is generally highly correlated with grain size because of the higher surface area of smaller particles, which are coated with organic carbon. Because the value for f_{solids} is a function of grain size, I think it would be appropriate to discuss how the correlation between f_{oc} and grain size would affect the results.

Eqn 3-5 contains the term " $f_{\text{oc}} \cdot K_{\text{oc}}$ ", which is just the K_p . I would guess this term was used instead of K_p because it's much easier to acquire values or model f_{oc} and K_{oc} . Looking at eqn 3-6, it seems circular that f_{oc} is used to convert $\text{ESB}_{\text{tier2}}$ to $\text{ESB}_{\text{tier2oc}}$ when eqn 3-5 includes f_{oc} to determine $\text{ESB}_{\text{tier2}}$. These equations are fine, but more explanation would ease any confusion.

3-5 Limitations. The section mentions mixtures only superficially. I think this document needs to take a stronger stand on mixtures. The additive nature of non-specific (narcosis) toxicants is generally accepted and I think the authors should say so. I think they should cite a few of the dozens of papers demonstrating additivity for this mode of action and provide the toxic unit approach equations for dose additive compounds. This was addressed in a little more detail (as a narrative) in section 4.2.5, but still fell short.

Section 4: Sediment Benchmark Values: Application and Interpretation

- 1) Are the ESB values discussed in this section supported by the information and analysis discussed earlier in the document?

I think the information on interpretation is sufficient; however the application sections are light. I did expect to see a discussion on potential regulatory and non-regulatory application. While, regulatory aspects are mentioned briefly in the foreword and introduction, Section 4 would be the place to provide more detail on potential application. Because I have not seen the document on tier 1 ESBs, I don't know how the EPA feels about ESBs in general as regulatory values. I think that should be addressed in

this document. For example, are tier 1 values also just for screening or are they going to be promoted as regulatory values. What about tier 2 values?

- 2) Are there any other aspects of these chemicals or this approach for deriving benchmarks for sediments that should be addressed?

One potentially important item that I think is missing here is the temporal factor. While only chronic values are used for ESBs (with actual FCVs or by converting FAVs to FCVs with ACRs), the protection offered by a chronic WQC versus that for an ESB may be different. The CCC for water is defined as the four day average not to be exceeded once every 3 years. Is this exposure guideline considered acceptable for species that have far less mobility and spend their entire life cycle just below the ESB compared to that expected for pelagic organism and the CCC? In the development of the CCC exposure time, wasn't it thought that pelagic species would not be exposed to the same concentration of water for extended periods of time?

Another temporal factor concerns steady state. Does the ESB account for compounds that may take longer to reach steady state than the duration of the chronic tests? Is a correction factor needed for those compounds expected to exhibit very long times to steady state?

Additional comments

Page 1-1. It should be noted that equilibrium between sediment and water will often not occur and that under these non-equilibrium conditions the route of uptake does influence the tissue concentration and hence the toxic response.

Page 1-2. The term "narcosis" is a poor descriptor of the process of non-specific (or baseline) toxicity. It would be advantageous to drop this term in favor of a more appropriate modifier.

Page 1-3. I am not sure I get number 1 ("numeric"). Would an ESB be anything other than numeric? How about noting that these ESBs are based on causal toxicity responses. This is an important distinction because this can't be claimed for other sediment toxicity guidelines.

Item number 5 (Protective of benthic organisms) may not be true. It really depends on the appropriateness of the biological responses and the species tested. Sublethal/chronic endpoints are often based on severe effects for a limited number of species.

Page 1-3 last para. "Adversely affect" is a subjective term. There may be adverse effects, especially for time periods beyond those used to determine the chronic values. Why not express ESBs as a "no effect" level? I think this is best accomplished by determining LOEC values and using safety/uncertainty factors to convert them to NOECs.

Page 1-5. Item 1. I don't see why a SPARC generated value is not required for tier 2 compounds. A Kow for almost any compound can be obtained with the SPARC program and the result is generally accurate. Why limit this requirement to tier 1 ESB values?

Page 2-3 section 2.3.2. para 1. *Along with the derivation of aquatic toxicity values using conventional techniques (see discussion above), narcosis theory was used to derive SCVs for chemicals determined to be primarily narcotic in their mode of action by ASTER (Russom et al. 1997).*

It would be more accurate to say that these compounds have no known specific mechanism of toxic action. The authors should also acknowledge that many compounds can act by a non-specific (narcosis) mode of action at high doses and by specific mechanisms at low doses. This may explain the disparate results reported in Table 3-1.

Page 2-4. I would rather not see the mean ACR used. Because ACRs range over a few orders of magnitude for some compounds and species, I would suggest using the 5th percentile (or lower) ACR. If only a few ACRs are available for a given compound, I think the lowest value should be used. If no ACRs are available and the ACR for several compounds is needed, I think the 5th percentile of all those ACRs would be a better choice to ensure that most species are protected. Therefore, instead of using a default value of 18, the 5th percentile ACR for all compounds for a specific mode of action should be determined and used as the "default".

Page 2-5 last para. I can't tell if these correlations are strong because the r^2 values are not shown. Given that these are log-log plots, it appears that the correlations are not strong.

Figures 2-2 through 2-5. Please supply the equations and r^2 values.

Page 3-11, bottom of first column. Therefore, the chemical must be associated with the sediment for a sufficient length of time for equilibrium to be reached.

I would restate as such,

Therefore, the sediment and water must be associated for a sufficient length of time for chemical equilibrium to be attained.

Page 4-3 2nd para. *In this approach, the contribution of each individual narcotic chemical to the toxicity of the overall mixtures is assessed by taking the ratio of the measured concentration of that individual chemical in the mixture by the corresponding single chemical ESB_{Tier2} value. This proportion is calculated*

Give the equation described here for simple additive mixtures. It's easier to understand an equation than to read a narrative that attempts to explain the relationship.

Page 4.3 bottom to top of 4-4. *For this reason, if a sediment shows toxicity but does not exceed the ESB_{Tier2} for a chemical of interest, it is likely that the cause of toxicity is a different chemical or chemicals.*

If there is toxicity and the ESB_{tier2} is not exceeded for a given toxicant, that toxicant can still be a contributor, along with other toxicants that are acting by dose addition.

Page 4-4. I would like to see DOC complexation addressed in greater detail here and in the section on limitations. Additionally, it is possible that [DOC] in porewater may be variable for a given f_{oc} , which would lead to potential differences in bioavailability for two sediments with the same f_{oc} and contaminant concentration. Therefore, direct measure of DOC would be preferred over modeling. If DOC must be modeled, this variability should be acknowledged as an uncertainty.

It seems that some of the points made in this document are redundant. For example, the text regarding partitioning when unusual components are present (e.g., hair, sawdust, hides, etc.) occurs in 3 places (Sections 1.2, 3.5, and 4.2.3). I think the detailed explanation for this phenomenon belongs in section 3.5. Section 4.2.3 should reference that section and section 1.2 is probably fine, but that text could be reduced.