Review

Deriving Sediment Interstitial Water Remediation Goals (IWRGs) at Superfund Sites for the Protection of Benthic Organisms from Direct Toxicity

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

The document is written in a way that a professional trained in environmental risk assessment will be able to fully understand and adopt the procedures outlined in the document. However, persons not familiar with sediment risk assessment will find it difficult to understand.

(2) Is the described methodology sufficiently clear to be performed by Superfund remediation project managers, risk assessors, and consultants for Superfund sites? If not, please provide suggestions on how clarity can be improved.

The document is sufficiently clear till section 4. Section 5 requiring the development of site-specific dose-response curves is a major departure and would require significant skills in sediment toxicology research experience to conduct adequately.

(3) Is the document missing any important concepts, sections, definitions, and/or text that should be provided in order to make the methodology truly implementable?

Yes, see detailed review below

(4) Are the illustrative examples for determining IWRGs complete enough to demonstrate how the IWRGs are derived?

Yes, these are excellent examples and provide sufficient guidance

(5) Is the methodology for deriving interstitial water remediation goals scientifically defensible?

Yes, and the guidance needs to state that more clearly.

(6) In implementing the methodology, site-specific K_{OC}s are used to convert the IWRGs on concentration basis in sediment interstitial water (µg/L) to concentrations in bulk sediment (µg/kg dry weight). Is the discussion of the K_{OC}s adequate? Is the discussion of the conversion from concentrations in interstitial water to bulk sediment adequate? Is the discussion of which K_{OC}s should be used in the conversions adequate?

Discussion of Koc is excellent and adequate.

(7) Passive sampling can be performed on any number of samples from a site; for example, on all samples where contaminants are measured in bulk sediment, on only the surface sediments, on the top and bottom of sediments cores, on the top and at the dredge depth of the sediments cores, on surface sediment and based of BAZ (biological active zone), or some other

arrangement. Currently, the methodology allows flexibility (makes no recommendation) on which samples are measured using the passive sampling technique and how those data are used in the conversion from interstitial water IWRGs to bulk sediment IWRGs. The extremes in this process are a) perform one passive sampling measurement and assume all sediments are the same across the location of interest (horizontally and with depth) or b) perform passive sampling on all samples and develop 3-D contour plots with depth based upon concentrations in the interstitial water. Should the methodology make a recommendation on this issue? If so, provide your recommendation.

It makes sense to leave the details of how the methodology is implemented to site-specific needs. For many sites I would imagine that the optimal sampling scheme will likely like somewhere between the two extremities outlined above.

(8) Section 5 provides information on comparing toxicity test results and developed IWRGs. Is this section sufficiently clear for the non-experts in toxicity testing and/or passive sampling?

This is the section I am most concerned about. Please see the last part of the review below.

Pg 6 last paragraph: At some point here or in the next section it may be helpful to make the distinction between total and freely dissolved concentrations (C_{free}) in interstitial water. For Kepone with a log K_{ow} of 5.4 or so, the two may not be very different for low DOC porewaters, but for higher K_{ow} compounds the difference becomes larger. The explanation of C_{free} provided in paragraph 3 of pg 8 needs to move up and we need to explain at the outset that Interstitial Water is really C_{free}.

Pg 8, para 2, line 8: This should be: "Since freely dissolved concentration in interstitial water corresponds to…

Pg 8, para 2 last 2 sentences. This is an excellent way to present the concept.

Pg8, para 2, last sentence: This sentence can be misleading. C_{free} is not the only bioavailable pool of the chemicals. Chemicals loosely associated with solids are also bioavailable as they are extractable in the gut and exchanges rapidly with C_{free}. I would suggest taking this sentence out.

Pg 10: '… it is presumed that their primary ecological risk would occur via accumulation and …..": True, but at contaminated sediment sites, exposure to higher trophic level organisms is influenced largely by C_{free} which controls exposure to fish through flux into overlying water and accumulation in benthic organisms (diet). So, with the right model, interstitial water concentrations can be used to perform calculations of uptake in fish and other higher trophic level animals. (See Fadaei et al. Environ. Sci. Technol. 2015, 49, 12405−12413)

Pg 11, line 6: should be 'sample' not sampling.

Pg 13, 2nd sentence: add: "Deuterated internal standards are added before introduction of a fiber to the isolated …"

Pg 13, line 3: "…the fiber is extracting some of the internal standards and dissolved contaminants…."

Pg 13, line 5 onwards should be: "The fiber is then thermally desorbed and analyzed for target contaminants. The dissolved concentrations are calculated based on the ratio of analytes to corresponding internal standards. This process creates an operationally defined form of C_{free} (i.e. interstitial water minus colloidal and dissolved organic matter precipitated by alum).

Pg 20, last 5 sentences: Excellent! This is exactly what I was hoping this would lead to.

Pg 23, Figure 4-1. There are several inconsistencies in this figure. I would suggest redoing this figure completely. Maybe best to use a simple flowchart. It is not clear what the captions mean for the boxes versus the arrows. If the arrows are actions and boxes are values calculated, these need to be consistently applied. The second arrow states the use of Equations 4-2, 4-3, and 4-4. But none of these equations yield concentrations in water in ug/L as indicated in the caption of the subsequent boxes.

Pg 24, paragraph 4: I am surprised to see no reference to organic matter types and presence of black carbon in the explanation of Koc variability. A brief mention of the role of BC and the challenge with different forms of BC in sediments will be helpful here.

Pg 24, last line: replace 'with' with 'which'

Pg 32: I have several major concerns with this entire section:

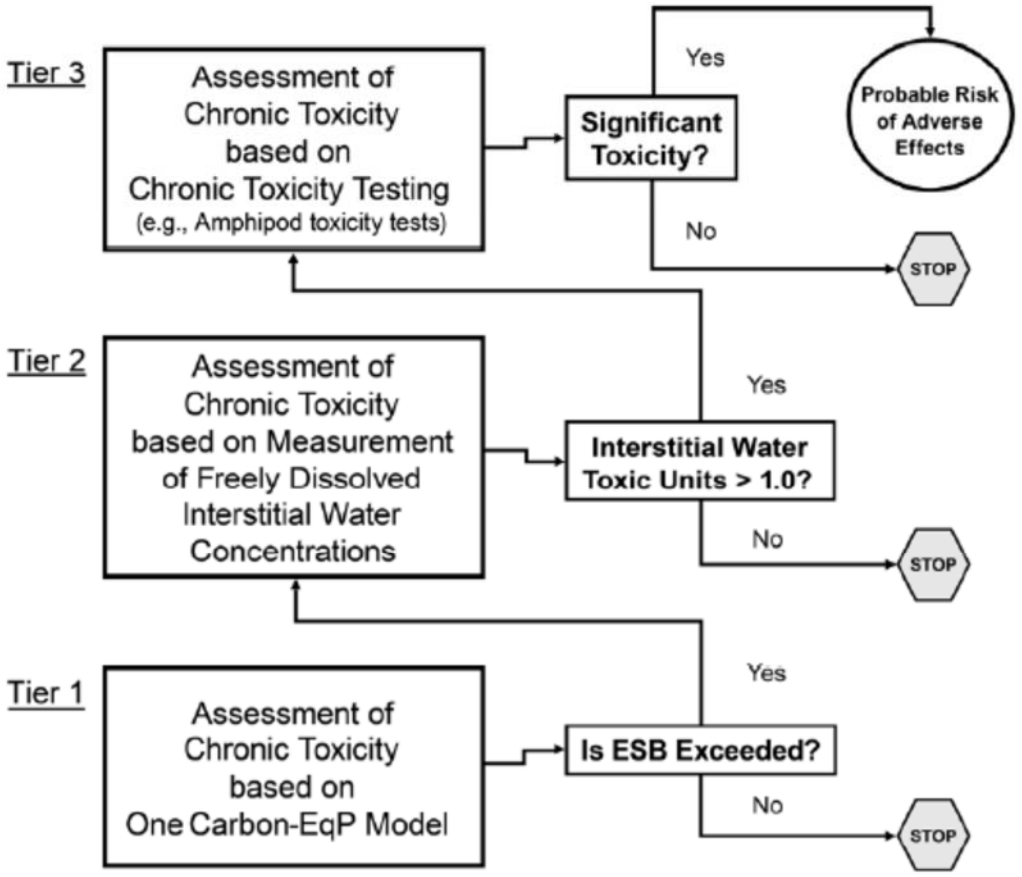
1) Are sediment toxicity studies always required at every Superfund site? Note that that the IWRG approach is also helpful in many site assessments outside the Superfund program where actual sediment toxicity assessments will not be performed. The way this guidance is written, it appears that without the consistency evaluation with site toxicity data, the IWRG approach is not defensible.

2) Pg 37, lines 7-8: Sounds like the goal here is to obtain a full dose-response curve. However, it is quite possible for a site to have no toxicity associated with the target chemicals.

3) Pg 37, first paragraph, last sentence and remaining text: This does not make sense. It appears that EPA is proposing an approach that it is not confident of and requiring the user to demonstrate consistency for each site. That sounds like further research for every site! This was not the spirit of the original ESB document where calculated porewater concentrations could be used to determine the extent of potential toxicity for a range of chemicals.

An user should not have to develop chemical dose response curves for site-specific sediment toxicity. Rather, the user should be able to use this guidance to determine to what extent a chemical or class of chemicals is potentially responsible for sediment toxicity. The idea of site-specific toxicity confirmation proposed in this guidance is a major departure from past ESB guidance. For example in the 2012 ESB document (EPA/600/R-02/012), a tiered approach to risk assessment is proposed (as shown in Figure 4-1 copied below). An user could use the measured C_{free} to make a tier 2 assessment if sediments were toxic or not and whether to move to tier 3 and further refine the assessment with actual toxicity studies. I would strongly suggest maintaining continuity with the tiered structure of risk assessment as done previously

Figure 4-1. Schematic of proposed tiered approach for implementing the use of the freely dissolved interstitial water concentrations of nonionic organic chemicals (based on Burgess, 2009).



Pg 39, section on method replication: This section on replication is vague. Need more specifics here. Some RI/FS efforts are taking the replication of porewater similar to what one would do for sediment samples – duplicates for every 10 or 20 samples. Most sediment samples are measured once. There is a reference here to eight replicates for each sample as in the

standard tox studies. This would be an absolute overkill and waste of effort. I would rather suggest performing more sediment samples than do 8 replicates of each. We should have a good sense of how replicable passive sampling is and provide a more specific suggestion here. In my experience, passive sampling is inherently more precise than typical biological response measurement.