Reviewer: John P. Knezovich, PhD
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Review of the Draft Report: Methodology for Derivation of Pesticide Sediment Quality Criteria for the Protection of Aquatic Life. Phase II. Method Development and Derivation of Bifenthrin Sediment Quality Criteria (October 2013)
Authors: Tessa L. Fojut, Martice Vasquez, Kelly Trunnelle, and Ronald S. Tjeerdema

The subject report describes the derivation of a methodology for deriving pesticide sediment quality criteria (SQC) for the protection of aquatic life in the Sacramento and San Joaquin River basins of California. The derived methodology, which is named the University of California Davis Sediment Methodology (UCDSM), was subsequently used to derive sediment criteria for bifenthrin. This methodology is largely based on prior work by this group, which was reviewed previously, has since been published[1], and is referred to in the subject report as the University of California Davis Methodology (UCDM).

Overall, the current report was found to be a comprehensive treatment of factors that determine the bioavailability and toxicity of contaminant in sediments. Although it is stated that the methods are being derived specifically for the Sacramento and San Joaquin River basins, no data or discussion of its relevance to these watersheds is included in the report. As presented, the report provides methods that could be applied to any freshwater system.

At the request of the authors, this review was focused on answering the following twelve questions:

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

The authors have done a good job describing the factors that control the bioavailability of contaminants in sediments. This review could be improved by including a discussion of the potential for food web transfer. As written, the report does not specifically adress this route of exposure, which can be significant for bottom-feeding organisms (e.g., catfish, carp).

2. *Are all of the ways of accounting for bioavailability included in the method (and listed below) scientifically valid? Are there additional technically valid ways to account for bioavailability that could be used?*

    a. OC-normalized sediment concentrations
    b. DOC-normalized porewater concentrations
    c. Directly measured freely dissolve porewater concentrations (via SPME or Tenax)

[1] P.L. Tenbrook *et al*. The University of California-Davis methodology for deriving aquatic life pesticide water quality criteria. *Rev Environ Contam Toxiciol* **209**: 1-155 (2010).

Each of the approaches listed above has merit as well as limitations. The scientific basis for each method is sound; however, each method is limited by a lack of specific knowledge of sediment chemistry. For example, each method will be influenced by the amount and type of organic material contained in sediment or freely dissolved in porewater. The OC and DOC methods can account for the amount of organic material, but do not account for differences in organic matter composition that will also influence contaminant partitioning and bioavailability. Specifically, it is possible that a chemical bound to different sediments with identical concentrations of organic matter may exhibit different levels of bioavailbility. Although such differences may be slight, they do limit the accuracy of such methods. Accordingly, each method is an attempt to account for the fraction of sediment-bound chemical that is likely to be "most" available to aquatic organisms as a result of partitioning. In addition, while the use of measured, dissolved porewater concentrations of a chemical will provide a good measure of a compound's availability via water exposure, it cannot adequately account for exposure by other routes (e.g., sediment ingestion).

Overall, these methods provide the best currently available analytical approaches for assessing chemical bioavailability in sediments. The use of solid-phase extraction techniques has particular merit as this approach lends itself to standardization. This is the most appropriate approach to use until methods that account for site-specific differences in sediment and organic matter chemical composition can be developed. Such methods are not currently available.

3. *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 that new techniques be used to generate new data?*

This question asks about the utility of existing toxicity and monitoring data. However, it appears that the intent of the question is whether the assessment methods outlined in this report will be useful to regulators and researchers. The short answer is, yes, this method will have direct usefullness. It is a logical extrapolation of methods already in use and promulgates sound data analysis methods and assessment tools. It is based in large part on methods currently in use to collect data that will be required for its implementation.

The proposed method is constrained by current techniques and available data. This is a statement of fact and not a criticism because any method must be based on information and data available at the current point in time. More importantly, the method does not require that new techniques be developed in order for it to be implemented. However, this method can be readily adapted to incorporate new techniques and approaches for determining chemical bioavailability as they are developed and validated.

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

Section 2.3 describes methods for physicochemical and ecotoxicity data evaluation. This section reads like a discussion of methods and stops short of providing prescriptive directions for implementation. This section would be improved by an introductory

paragraph that describes the overall data evaluation approach and the steps required for its implementation. If the intent of this report is to define methods that can be used in a consistent manner, then this section should be revised in such a manner that the user can follow a step-by-step approach for implementation.

Tables 7-13 are generally clear and should be linked in a more explicit way to the implementation of the method. On page 31 it is stated that, "The list of components to be documented for an ecotoxicity study used to derive or support BSQC is presented in Table 13." However, Table 13 is a list of default biomagnification factors. Where is the information for Table 13 located?

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

In general, the categories identified in Tables 8-12 are appropriate and the associated scores reflect their relative importance. It must be noted that such relative scores are always open to debate as there are no definitive standards for validation. Some key factors that need to be addressed are identified below.

Table 8: It appears that a study that did not report results of controls, but met all other criteria, would lose 7.5 points and have a final score of 92.5, which would be "relevant and reliable" according to the scoring system (Table7). Although it does not seem likely that an otherwise sound study would not report control data, shouldn't this be a basis for a downgraded reliability rating?

Table 9: It is not clear what the score for measured concentrations (i.e., 3) represents. Is this the sediment and/or porewater concentration? The lack of measured concentrations in a study can greatly reduce reliability of toxicity data as a result of chemical losses due to volatility, sorption to containers, photolysis, etc. The score of 3 does not reflect the significance of this parameter and should be increased to a higher level, perhaps as high as 10.

Table 10: See comments for Table 9 above. Why are measured concentrations given a score of 4 here and 3 in table 8? In both cases this parameter needs to carry more weight.

Table 11: Same issues as for Tables 8 and 9. Here the score is 2 for measured concentrations. It is not clear that a field ecosystem study can have any validity in the absence of measured chemical concentrations. Why is this parameter given such low importance?

Table 12: Here weighting is given to the chemical analysis method (i.e., score of 5), but there is not a parameter (or score) for actual chemical measurements. This appears to be a significant oversight and must be included with an appropriate score (e.g., 10).

6. *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 thus the magnitude of the criteria.

The data prioritization method outlined in Section 2.4 adopts the UCDM approach and includes 15 (i.e., a-o) additional directives. Overall, these additional instructions prescribe approaches that provide clarity to the evaluation process. Item "h" advocates the conversion of toxicity values to OC-normalized sediment toxicity values. While this approach is appropriate, it is not clear how the data should be treated if sediment organic content data is not available. If sediment-specific Kocs are not available, using the mean of acceptable Koc values will only be useful only if the sediment OC value is known.

Section 2.5 is a single paragraph that advocates placing single-species data into separate acute and chronic tables. Further separation into plant and animal categories are also advocated as appropriate. It would be helpful to provide a template for such tables to provide clarity and promote consistency in the user community.

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

Table 14 is a template for a comprehensive summary of data relevant to toxicity studies. In general, this list captures relevant data but some clarification is needed. Overall, it would be worthwhile to include examples of the types of values (and units) that are expected for several of the parameters. Parameters that are followed by question marks imply that a yes/no answer is all that is required. It would be better to eliminate the question marks to make it clear that specific information is what is being requested. Other suggestions for improvement appear below:

- *Results published or in signed, dated format*: should be broken into separate questions.
- *Test method cited*: It is not clear what is being asked for here. Is this a yes/no answer or is the specific method to be listed (e.g., static, flow-through, etc.)?
- *Family relevant for North America?*: The use of the term "relevant" is not clear. This might be better stated as Family present in North America.
- *Data for multiple durations?*: This might be better stated by specifically asking for the lengths of exposure. As stated, it looks like a yes/no answer is all that is required.
- *Exposure type*: Is this intended to be sediment or water? Or is this related to the question above on Test method?
- *Percent moisture*: It is not clear that this parameter is relevant to aquatic toxicity studies.
- Consider adding *Hydrogen sulfide measurement* as a sediment characteristic as this can be a confounding variable in field toxicity studies.
- *Extraction method*: Needs to be clarified as this could be interpreted as porewater isolation or chemical extraction from sediment.
- *Instrumentation:* Needs clarification. Is this analytical instrumentation or other?
- *Control type & response*: It is not clear what is meant by "control type."

8. *Are instructions in sections 3.4-3.7, describing how criteria are derived, clear and easy to follow?*

These sections adopt the UCDM approach and modify it to place a greater emphasis on the inclusion of benthic organisms. This is appropriate for the derivation of sediment criteria. The data analysis and statistical approaches that are presented in these sections have been previously reviewed and are accurately represented and appropriate for the proposed method. As presented, the information is accurate but somewhat hard to follow.

The clarity of the presentation could be improved by providing a flow chart at the beginning of this section that outlines the SSD procedure in a graphical format. The flow chart should identify the purpose of each step (e.g., Ecotox taxa requirements, Burr Type III analyses, etc.) so the user can see the relevance of the analyses up front and understand the purpose for each step in the derivation.

9. *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 (section 3.8.2)? Should only one criterion be derived? Please comment on the thoroughness, validity, and completeness of the review and discussion in section 3.8.2. Are there are any other considerations that should be included for determining criteria averaging periods?*

Section 3.8.2 addresses averaging periods and the issues involved with interpreting toxicity data derived from 10- and 28-day exposure periods. This section provides a sound assessment of relevant environmental factors that influence chemical exposure such as fluctuations in concentrations that result from pesticide applications and chemical degradation processes. The fact that current-use pesticides tend not to be persistent makes the use of both exposure periods more likely to catch pulse exposures. Therefore, the conclusion that both a 10-day averaging period for acute BSQC and a 28-day averaging period for chronic BSQC should be adopted is appropriate. Ultimately, the ability to apply either criteria will depend on the availability of relevant data.

10. *Is the assumption of concentration addition reasonable for mixtures of pesticides in the same class (section 4.2)?*

The concentration-addition model generally makes sense for compounds that have similar modes of action. Chemicals that are appropriate for this approach are typically neutral organic compounds and care must be taken to ensure that this method is not applied to ionized compounds. The toxic unit and relative potency approaches are both acceptable in regard to their use for determining additivity.

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

Although many QSAR models have been published (e.g., Gobas et al.[2]), they are typically used to estimate bioaccumulation, not toxicity. To my knowledge, QSARs have not been used to estimate toxicity to threatened or endangered species and are not in a stage of development where they can be used for reliable environmental risk assessments. They can, however, be used to screen chemicals for their potential for bioaccumulation and toxicity.

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

The criteria for bifentrhin (i.e., acute = 27 pg/l, chronic = 5 pg/l) were calculated according to the proposed method for derivation of pesticide sediment quality criteria. Thirteen acute toxicity studies that yielded twenty-seven toxicity values from two taxa were deemed sufficiently reliable for use in these derivations. Because data for only two taxa were available, an assessment factor was used to calculate the acute BSQC. No relevant and reliable chronic sediment toxicity studies were identified. Calculations for both the acute- and chronic-BSQC values were accurately calculated.

An inverse relationship between bifenthrin toxicity and water temperature is well documented. This relationship is important as laboratory toxicity tests are often conducted at temperatures that are higher than those in natural ecosystems. Although sufficient data does not exist to enable accurate predictions of temperature-related toxicity in aquatic ecosystems, this relationship should be considered in the derivation of safety factors as it is likely that criteria derived from laboratory studies conducted at relatively high temperatures will under-predict toxicity in many natural environments. With this in mind, the potential for bifenthrin impacts on sensitive species should be reconsidered. Specifically, the authors discount the inclusion of a 25 pg/l LC_{50} value for *H. azteca* in the acute criterion derivation because the test was performed at a temperature (i.e., 19.8^{o}C) that was lower than the standard test temperature (i.e., 23^{o}C). Although the test temperature was not standard, it is relevant to natural environments, including the Sacramento and San Joaquin River basins. Accordingly, the acute criterion is close to a concentration that may be underprotective in some natural environments.

Because bifenthrin often occurs in the presence of other pyrethroid insecticides that have a similar mode of action, the toxic unit or relative potency factor approaches are appropriate to use. However, compounds that have dissimilar modes of action may exhibit additive, synergistic, or antagonistic effects in the presence of bifenthrin. The conclusion that non-additive effects cannot be used for criteria compliance is appropriate due to the lack of a robust predictive model.

The authors reviewed five mesocosm, microcosm and ecosystem studies that had acceptable ratings. These studies provide a realistic approximation of bifenthrin bioavailability as they

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[2] F. Gobas et al. (2003). Quantitative Structure Activity Relationships for Predicting the Bioaccumulation of POPs in Terrestrial Food-Webs. *QSAR Comb Sci* **22** (2003).

included sediments as the principal source of contaminant. In each of these studies, toxicity was only reported for water concentrations that were higher than the proposed acute and chronic criteria. Sensitive taxa included in these studies were only impacted by water column concentrations of bifenthrin that were significantly higher than the proposed acute and chronic criteria. However, these studies were based on bifenthrin concentrations in the water column and sediment, and not in porewater. Therefore, it is not appropriate to use these studies as a basis for concluding that the derived criteria for porewater will be protective of aquatic ecosystems. To be clear, these studies do not contradict the derived criteria, they just do not provide data for a direct comparison to the BSQC values. (Also, see Section 8.11.2, page 87, where the chronic porewater BSQC is listed as 3 pg/L. This should be 5 pg/L).

Data on bifenthrin toxicity is only available for one threatened or endangered species (steelhead trout). Because this species has an LC_{50} of 0.15 µg/L, the authors conclude that the proposed criteria will protect this species. Data for other threatened or endangered species, including plants, were not in the data set and appropriate surrogates were not available. Accordingly, specific conclusions could not be offered for these species. Overall, the proposed criteria appear to be protective of threatened and endangered species.

Bifenthrin has a relatively high K_{ow} and therefore a high potential to bioaccumulate in aquatic organisms. Reported bioconcentration factors are consistent with this K_{ow} and a bioaccumulation factor (BAF) approach was used to estimate the water concentration of bifenthrin that would result in a lethal concentration in wildlife that would consume contaminated fish. Using this approach, the acute and chronic BSQC values are well below the estimated NOECs for mallard duck (267 ng/L) and humans (23 ng/L). However, a rationale for comparing the BSQC values to the water column values that were used to calculate BAFs is lacking. Although it is likely that the BSQCs will be protective of wildlife and human heath, the authors need to provide a rationale for their comparison to WQCs.

The authors correctly point out that the major source of uncertainty in this evaluation stems from the lack of viable bifentrhrin toxicity data for three of the five required taxa. The approaches used (i.e., ACR and Assessment Factor) were appropriate given this limitation. However, the lack of chronic data for *H. azeteca* is cause for concern as this is the most sensitive species for acute effects. Coupled with the potential heightened sensitivity of this species at low water temperatures, it is possible that the proposed chronic criterion would not be protective under some environmental conditions.