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Methodology for Derivation of Pesticide Water Quality Criteria for the Protection of Aquatic Life in the Sacramento and San Joaquin River Watersheds.

Phase II: Methodology Development and Derivation of Chlorpyrifos Criteria Peer Review Addendum

The University of California at Davis, Environmental Toxicology Department, under contract to the Regional Water Quality Control Board, Central Valley Region (Central Valley Water Board), has completed preparation of a report detailing a new method to derive pesticide water quality criteria for the protection of aquatic life (new methodology). The report also includes a derivation of water quality criteria for chlorpyrifos using the new methodology. The new methodology completes the second phase of a three-phase effort to develop water quality criteria for pesticides that pose a potential water column risk in the Sacramento and San Joaquin River Basins. The new methodology has been peer reviewed by a panel of agency and academic experts. This report addendum presents the Peer Review comments and the responses to those comments.

Description of the Peer Review Process:

In accordance with the contractual scope of work, the project director, Ron Tjeerdema and the contract manager, Joe Karkoski convened a peer review panel to review the major deliverables for this project. The peer review panel included the same representatives from academia and partner agencies as were involved in peer reviewing the Phase I report. The members are listed below:

Larry Curtis, Ph.D.
Department Head, Department of
Environmental and Molecular Toxicology
Oregon State University

John Knezovich, Ph.D.
Director, University of California's Toxic
Substances Research and Teaching
Program

Evan Gallagher, Ph.D.
Associate Professor and Consultant in
Toxicology
University of Washington

Marshall Lee,
Senior Environmental Research
Scientist
Environmental Monitoring Branch
California Department of Pesticide
Regulation

Peer reviewers were asked to address the following in their review:

- a. Accuracy and completeness of the information presented: Are any important methodologies, references or other information missing?
- b. Is the approach used to compare and assess methodologies appropriate?
- c. Evaluation and interpretation: Are the key features of the methodologies evaluated thoroughly and correctly? Are strengths and weaknesses identified? Are conclusions supported?
- d. Are there any scientific issues that should have been addressed in the report, but were not included?
- e. Taken as a whole, is the analysis in the report based upon sound scientific knowledge, methods, and practices?

Peer Reviewers were asked to submit their comments directly to the Central Valley Water Board. Once all of the comments were received, Central Valley Water Board submitted the comments to UC Davis for review and response. Responses to comments are included as **Attachment 1**.

To encourage candid comments from the peer reviewers and allow for forthright criticism, comment letters were submitted to UC Davis in a blind fashion. Specifically, minor changes were made to the comment letter text to remove identifying traits. Modifications were largely limited to changes in the header, footer and salutation sections. No modifications were made which could have changed the content of the comments. The compiled comment document is included as **Attachment 2**. Original copies of the comment letters, with identifying information unchanged will be included in the administrative record.

In addition to external peer review, Central Valley Water Board staff members with expertise in the subject matter were asked to review the report. Collected comments were compiled into a separate comment letter, which was withheld from the UC Davis researchers until after the peer review was completed. This was done to assist the researchers in producing as unbiased a report as possible. Staff comments are included in **Attachment 3**. The responses to staff comments are included in **Attachment 1**.

Finally, external peer review and staff comments resulted in several sections of the report being sent to a statistical expert for evaluation. This evaluation is included as **Attachment 4** and was used to respond to individual staff and peer review comments.

Any questions regarding the peer review process may be directed to Paul Hann at (916) 464-4628 or phann@waterboards.ca.gov, or Joe Karkoski at (916) 464-4668 or jkarkoski@waterboards.ca.gov.

ATTACHMENT 1

Response to Comments

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Attachment 1

RESPONSES TO REGIONAL BOARD STAFF COMMENTS

1. The report needs to clarify the language used to discuss dissolved concentrations and sediment load. The calculation of the pesticide concentration in the dissolved phase is discussed in the “bioavailability” section (section 2-3.5.1). Staff recommends that this section be renamed “Calculation of Dissolved Concentration”. An assumption is being made that the dissolved concentration is equivalent to the bioavailable concentration.

Response: Section 2-3.5.1 is still called “bioavailability,” but the discussion has been expanded and clarified to distinguish between phase distribution and bioavailability. The discussion concludes that simple two- or three-phase models are not adequate for prediction of bioavailability.

2. The methodology assumes that the exposure pathway is water-only (section 2-2.1.1.5). Presumably this assumption is based on how most toxicity tests are conducted – in laboratory water that is free of sediment. However, laboratory test animals are also fed during the course of the test. Toxicity test results, therefore, do not generally distinguish whether the effect was caused solely by water exposure or whether there may have been dietary exposure as well (i.e., the contaminant sorbed to the food particles and then de-sorbed upon ingestion).

It is probably more accurate to say that comparing the dissolved concentration to the criteria is consistent with basis for the derivation of the criteria. In other words, the toxicity tests used are based on exposure to dissolved pesticide concentrations, so we should only compare dissolved pesticide concentrations to the criteria. However, this is only a valid rationale if it can be shown that dietary exposure did not occur during the toxicity tests).

Response: Feeding can have various, unpredictable effects on toxicity test results. If food particles are introduced just prior to test solution renewal, and are consumed immediately, then there will be little to no opportunity for the toxicant to interact with the food particles. If too much food is introduced and the uneaten food is not removed as soon as the animals stop feeding, then toxicants can adsorb to food particles and reduce the freely dissolved concentration. If that same food is then later consumed, there is the potential for dietary exposure. Laboratory animals in acute toxicity tests are often not fed. When there is feeding in an acute or chronic test care is usually taken to minimize any potential effects of food on test results. Standard toxicity test methods give careful feeding instructions, which, if followed, minimize any effects of food particles on test results.

As discussed in the Phase I report, dietary uptake is most significant for compounds that have $\log K_{OW}$ values between 5 and 7. Pyrethroids are an example of a class of currently used pesticides that fall into this category. Compounds with $\log K_{OW}$ values in this range will readily partition into any solids (including food particles) or dissolved solids in the water. For such compounds, it is appropriate to specify in the new methodology that toxicity tests used in criteria derivation must follow strict feeding regimes (i.e., either no feeding, or feeding just prior to test solution renewal) such that the test solution concentration is not reduced due to adsorption, and that the dietary uptake route is insignificant. Section

2-2.1.1.5 on multipathway exposure has been revised to reflect this. Section 2-2.5.2 on evaluation of ecotoxicity data has been revised to indicate that tests of compounds with logK_{OW} between 5 and 7 should be eliminated from use in criteria derivation if feeding regimes did not minimize or eliminate the interactions of pesticide with food particles. Section 3-2.3.2 of the methodology has also been revised to reflect this.

To incorporate dietary uptake into water quality criteria would require the use of food web models that are not developed well enough for general application. The discussion in this section applies only to the issue of phase distribution of pesticides in the water column. Whether it is appropriate to determine compliance on the basis of total, dissolved, or some other phase or phases will have to be made on a case-by-case, site-specific, species-specific, pesticide-specific basis.

3. Additional justification for the assumption that toxicity tests represent a water-only exposure pathway should be provided. In the absence of sufficient support for this assumption, the criteria should be based on a whole water sample. Sediment load could be handled on a case-by-case basis as data becomes available consistent with the recommendations of section 2-3.5.3.

Response: See response to 2).

4. If dissolved concentrations are the basis for evaluating the criteria, the author should address a potentially more straightforward way of determining compliance such as simply filtering the sample prior to analysis. Analyzing the sample for percent organic carbon and suspended solids and then calculating the dissolved concentration from the total pesticide concentration could potentially introduce much more error into the evaluation of compliance.

Response: The revised section 2-3.5.1 addresses this concern.

5. In section 2-3.0, the authors indicate that the aim of the criteria calculation is to protect all species in the aquatic ecosystem. This statement is consistent with the Regional Board's narrative toxicity objectives. The authors should refer to this goal in a consistent manner throughout the document. Sometimes the authors refer to protection of "ecosystems" (e.g., 2-3.1.4.1), which could be interpreted as a different goal from protecting "all species" within the ecosystem.

Response: Throughout the document, phrases such as, "protective of ecosystems" have been modified to, "protective to species within ecosystems," or something similar.

6. In a number of places, the authors refer to the 5th percentile as a generally accepted no ecological effect level (see for example sections 2-3.1, 2-3.1.4.1). There should be more discussion of and justification for the choice of the 5th percentile. It is not clear whether the other methodologies chose the 5th percentile based on ecological considerations or statistical considerations (i.e., it is hard to have a high degree of statistical confidence in a number based on a percentile lower than the 5th percentile).

Response: The justification for the 5th percentile was discussed extensively in the Phase I report. To make the Phase II report more self-contained, key elements of that discussion have been added to Chapter 2 of the Phase II report (section 2.3.1.2).

7. The RIVM (2001) method and the ANZECC & ARMCANZ (2000) methods apply the 5th percentile to NOEC data, while the US EPA method applies the 5th percentile to LC50 data. It is unclear how use of the 5th percentile applied to different effects data can provide similar ecological protection.

Response: The use of the 5th percentile with different effects data are not expected to provide the same level of protection. Thus, the 5th percentile values derived from LC₅₀ data are divided by a safety factor to derive the acute criterion (see response to comment #9 for more on the safety factor).

8. The authors should discuss how the use of the 5th percentile applied to MATC data and the 5th percentile divided by 2 applied to LC50 data is expected to meet the aim of the criteria to protect all aquatic species.

Response: See response to #9.

9. Section 2-3.1.4.6 indicates that the final criteria will be derived using the 5th percentile divided by two. The stated purpose of the ½ factor is to compensate for the fact that the Acute Criterion is based on toxicity values that give a 50% value. However, no justification is given for the choice of ½ versus some other factor. The choice of the safety factor should be justified in the report.

Responses: Comments 8 and 9 are similar. The use of the 5th percentile applied to the MATC and the 5th percentile of LC_{50s} divided by 2 have been used in USEPA derivation methodologies (USEPA 1985; 2003), and the 5th percentile applied to the NOEC has been used by others (ANZECC & ARMCANZ 2000; RIVM 2001). Although originally chosen rather arbitrarily, use of these values is widely accepted because they have proven, in most cases, to be protective in ecosystem level studies and in studies with sensitive species. The new methodology includes procedures for checking derived criteria against data from studies of ecosystems, sensitive species, and threatened/endangered species with a recommendation that criteria may require downward adjustment if studies indicate they are under protective.

10. The section defines acute and chronic toxicity and identifies the types of acceptable tests. The authors do not mention in this section acceptable endpoints for acute versus chronic toxicity tests. Are acute tests intended to generally be measurements of lethality or immobility and chronic tests measurements of growth, reproduction, and other non-lethal effects linked to survival?

Response: The following sentence has been added to section 2-2.1.1.1: “Endpoints in acute and chronic tests may be survival, growth, reproduction, measures of population growth, or other endpoints that have been linked to survival, growth or reproduction. See section 2-2.1.1.3 for further discussion of endpoints.” Section 2-2.1.1.3 has been modified to clarify that population growth measures, such as r (intrinsic rate of increase) and λ (factor by which a population increases in a given time) from relevant and reliable studies can be used as long as more sensitive endpoints are not available.

11. In the 3rd paragraph in section 2-2.1.1.2, there is a discussion of equating an EC_x level to a “no-effect” level. Since EC_x represents a concentration at which an effect is observed, it is not clear what is meant by a “no-effect” level.

Response: The discussion has been clarified to distinguish between statistical and biological significance of EC_x values.

12. On page 2-5, there is a discussion of the use of non-traditional endpoints, such as evaluation of AChE inhibition. In this discussion it is not clear in referring to “significant” mortality, whether the authors are referring to statistical significance or ecological significance. The two concepts appear to be used interchangeably. A prediction of mortality (7.5% for Chinook salmon) would seem to be pretty significant from an ecological standpoint, although a standard toxicity test may have trouble identifying statistically significant toxicity (in comparison to controls) unless mortality is greater than 10%.

Response: Section 2-1.1.1.3 has been expanded to clarify that both statistical and biological significance of results from tests measuring acetylcholinesterase inhibition (or other biochemical endpoints) would have to be shown before this endpoint could be used for criteria derivation. A description of what is meant by “biological significance” has also been added.

13. The discussion in section 2-2.4 (page 2-10) critiques the Dutch data tables for not indicating whether the test organisms reside in areas relevant to ecosystems of interest. This statement could suggest that only species resident to the Sacramento and San Joaquin valleys should be used in criteria derivation, although the proposed methodology suggests that North American species should be used. This should be clarified in the methodology. In addition, the “table” referred to in this paragraph should be referenced.

Response: The language in section 2-2.4 has been changed such that it now simply says that the data tables should include information regarding where organisms reside. The data tables are referenced in the first paragraph of the section.

14. In looking for bimodality in the distribution of toxicity data, is it important that the two groups have common features (e.g., vertebrates vs. invertebrates), or is it just important that there is a bimodal distribution? Is the bimodality to be tested, or is it a judgment call based on visual observation of the data distribution?

Response: The reason for the bimodality is not important. The only data in the criteria derivation set will have been thoroughly reviewed for relevance and reliability. It is most likely that multi-modality will be explainable by gross physiological differences, such as vertebrate vs. invertebrate. However, if, say one fish species were to fall into the lower portion of a distribution that included all of the invertebrates, and the fish test was rated reliable and relevant, then there would be no good reason to exclude that particular fish from the lower portion of the distribution.

The first-cut test of bimodality is that no distribution can be properly fit to the data. The reason for that lack of fit may then be investigated visually. Visual inspection is an accepted means of determining multimodality. Sokal and Rolf (1995) simply define distributions with two peaks as bimodal, and those with more than two peaks as multimodal. Regarding multimodal distributions, Quinn and Keough (2002) state:

“The other distribution that will cause major problems is multimodal, where there are two or more distinct peaks. There is not much you can do about this distribution: both parametric and non-parametric tests become unreliable. The best option is to treat each peak of the distribution as representing a different ‘population,’ and to split your analyses in to separate populations.”

No formal statistical test is required. Dr. Jerome Braun of the University of California, Davis Statistics Laboratory agreed that visual inspection is appropriate, but he also suggested a formal test that can be used. The test involves fitting the full data set using a maximum likelihood method, then fitting the split data sets independently to the same model. The difference in the log-likelihoods is distributed as a Chi-square distribution, so a probability can be determined. This approach does not work for the proposed new methodology because a Burr Type III distribution cannot be fit to a full, bimodally distributed data set. Therefore, visual inspection is appropriate.

15. On page 2-17, under item 11, “standard conditions” should be defined.

Response: Standard conditions refer to those defined in standard test methods. This has been clarified in report.

16. In Section 2.3.1.1, the choice of appropriate distribution is discussed. The Burr family of distributions is recommended (pg. 2-34). However, in the report, the authors tested a number of different distributions to determine which distribution generally fit for pesticides. Rather than select a specific distribution (or family of distributions), could the goodness of fit be compared among several distributions, prior to selecting the appropriate distribution to use for a given pesticide?

The goodness-of-fit tests were revisited and Dr. Braun was consulted regarding whether the fit tests were done by a valid method. His response was that the approach used in Chapter 2 to test fits is valid. The atrazine plot in Figure 2.2 was reviewed, as it was the only plot in which the Burr III fit was clearly poorer than the log-normal. The fit parameters for atrazine had been inappropriately rounded leading to erroneous calculations and plots. Fit tests and plots for all pesticides were redone with unrounded Burr III fit parameters. Figures 2.1 and 2.2 and Tables 2.2, 2.3 and 2.4 have been updated with the new results.

Since there are no cases where the log-triangular fit is best, it is not considered further. The USEPA method works reasonably well despite violations of distributional assumptions because the method ultimately focuses on just the four values nearest the 5th percentile, thus often disregarding a large body of available data. There are no cases where the log-normal fit is clearly better than the Burr III, but there are cases where the Burr III fit is far better than the log-normal. This is expected since the Burr III distribution is a family of distributions and the BurrliOZ program finds the best possible fit for the data

within that family. In addition, the Burr III family of distributions approximates log-triangular and log-normal distributions (CSIRO 2001). The data in Table 2.4 indicate that protective criteria can be derived regardless of which distribution is selected. The advantage of the ANZECC & ARMCANZ approach is that it utilizes the Burr III distributions (which are best able to describe data sets and are able to approximate log-triangular and log-normal distributions), utilizes full data sets and derives median, 95th, 99th or other confidence limit estimates of the 5th percentile value. Little to no benefit would be gained by including an additional distributional fitting step in the methodology.

17. The US EPA has generally separated saltwater criteria derivation from freshwater criteria derivation. The authors suggest (section 2-3.1.3) that saltwater and freshwater organisms can be included in the same data set. Is there justification for this?

Rersponse: This issue, which in the end is more of a policy choice than a scientific one, was discussed in the Phase I report. Scientifically, unless a data set is multi-modal, there is no good argument for separating taxa in a species sensitivity distribution. The freshwater vs. saltwater issue is moot for Phase II, since the methodology is only for freshwater species and saltwater data are excluded from criteria derivation. Any references to saltwater vs. freshwater data in discussions of data aggregation are simply given as examples. All such references have been replaced with different examples to avoid confusion. For example, in section 2-3.1.4 “freshwater vs. saltwater” has been replaced with “lentic vs. lotic.”

18. It is not clear from the discussion in Section 2-3.2.3.1 how the application factors were derived. Were they derived from DDT only or calculated as the average of all application factors for the pesticides in table 2.1? Table 2.6 (DDT only) and table 2.8 differ slightly for the sample sizes of 5 and 2 and are the same for samples sizes of 4, 3, and 1.

Response: The factor derivation was re-done to more carefully follow the method of Host *et al.* (1991). Section 2-3.2.3.1 has been revised accordingly. The final factors are based on data for 10 pesticides.

19. The report indicates that ACRs should be calculated for species whose SMAVs are close to the acute criterion. “Close” should be defined.

Response: First, the sentence has been corrected to say, “close to the acute 5th percentile value,” rather than the “acute criterion” so that it properly reflects the language in the USEPA methodologies (USEPA 1985; 2003). This provision only applies to cases in which there is a trend in which the species mean ACRs increase or decrease as the species mean acute values increase. The term “close” in this case is taken straight from USEPA methodologies (USEPA 1985; 2003) where it is not defined, implying that the definition of “close” is left to professional judgment. However, a definition of “close” can be developed based on subsequent ACR derivation procedures included in the USEPA methodologies (and in time 2 of section 2-3.2.3.2.1). According to those methodologies, when there is no trend of increasing or decreasing ACRs with SMAVs, it is acceptable to use the geometric mean of all SMAVs to calculate an interspecies ACR, provided that the ACRs do not differ by more than a factor of 10. Thus, it would make sense to define species with SMAVs “close” to the 5th percentile as those whose species mean ACRs (SMACRs) are within a factor of 10 of the SMACR of the species whose SMAV is nearest the 5th

percentile value. This definition has been added to item 1 in section 2-3.2.3.2.1 and to item 1 in section 3-4.2.1.

20. The ACRs as presented in Table 2.9 for chlorpyrifos and diazinon should be based on the California Dept. of Fish and Games criteria. CDFG includes more recent data for chlorpyrifos and more chronic data for diazinon when compared to the respective EPA criteria documents.

Response: Table 2.9 has been modified to include the CDFG ACR for diazinon (3.0) and the new value for chlorpyrifos (2.2) calculated according to the new methodology. With those changes, the default ACR is 12.4 (unchanged from original).

21. Table 3.16 is a reasonable approach to calculating default chronic values when only acute toxicity information is available. However, staff notes that the table is not inclusive of all the common classes of pesticides. The report should specify whether the method could be used to derive ACRs for pesticides classes that are not included in the table. It would seem that this method should only be used if it includes at least one member of the class of pesticides being considered. Also, would it not be more appropriate to determine the ACR based on groupings of similar classes of pesticides (i.e. a separate default ACR when the pesticide of interest is an organophosphate than when it is a carbamate, or a pyrethroid)? Given the small dataset available, calculating the default ACR based on pesticide class might require using the mean or median of the set instead of the 80th percentile.

Response: Tables 2.9 and 3.16 include all available ACRs that were calculated according to USEPA methodologies (USEPA 1985; 2003). No other ACRs are available so it is not feasible to try separating ACRs by class at this time. The default ACR calculation method was originally used by Host *et al.* (1995) with a data set that included pesticides and metals. For the new methodology, the metals data were eliminated, but there are not enough pesticide data to consider groupings by class or mode of action at this time. The 80th percentile of values is used in the Great Lakes methodology (USEPA 2003) and that is why it was selected for the new methodology.

22. The sentence defining the averaging period (section 2-3.3) is unclear. The average concentration during the averaging period cannot exceed the criterion, but must be below the criterion.

Response: The definition has been revised to say, “The averaging period is the period of time over which the receiving water concentration is averaged for comparison with criteria concentrations (USEPA 1994).”

23. There is a good discussion in section 2-3.3.1 regarding pulsed exposures and delayed or sustained impacts. However, it is not clear how the pulsed one-hour exposures relate to the 96-hour LC50 data that are used to derive the criteria.

Response: The pulsed exposure discussion is included to support the selection of the 1-h averaging period for compliance with the acute criterion. Time-concentration-effect models would be needed to be able to fully tie pulse exposures into criteria derivation, but as discussed in Phase I, such models are not developed enough at this time. Thus to ensure comparability among acute toxicity values used to derive

criteria, only values from constant exposure experiments of 24-96-h duration are used. At this time the best way to account for latent effects from very short pulse exposures is by selecting an appropriate averaging period based on available literature.

24. The discussion regarding diazinon and chlorpyrifos in Section 2-3.3.1 was not clear. If mortality occurs throughout the time period of exposure, then the contaminant levels are important right from the beginning of the exposure. This observation would seem to support having a short averaging period for the acute criterion.

Response: The point of this discussion was that diazinon and chlorpyrifos are not particularly fast-acting pesticides, based on the fact that mortality in the cited tests did not occur just within the first 24-h observation period, but was spread out over the entire test.

25. In Section 2-3.4.1, the report assigns several factors to the Sacramento and San Joaquin Rivers to derive a recovery index. The “a” parameter used in this derivation states that unaffected nearby tributaries are expected to be present. This is not likely to be the case in most waters that are surrounded by urban or agricultural areas. In the cases of diazinon and chlorpyrifos, use was fairly ubiquitous, which would limit the number of unaffected tributaries.

Response: The discussion of the recovery index has been modified to reflect that there may be water bodies that do not have unaffected tributaries nearby.

26. Does the literature suggest that there should be a differentiation between organisms with a longer life cycle and those with a shorter life cycle in terms of the allowable frequency of exceedances? If the criterion is driven by organisms with a short life cycle, could the frequency of exceedances be safely made greater (e.g., once every year instead of once every three years)? Of course, care must be taken that the aquatic system is not in a constant state of trying to recover from contaminant pulses.

Response: Yes, the literature discussed in Chapter 2 indicate that, in general, recovery times after toxicant exposure are longer for organisms with longer life cycles (such as salmon) compared to those with shorter life cycles (such as insects and other invertebrates), but there are exceptions (e.g., Hastings *et al.* 1961). Based on the discussion in section 2-3.4.2, particularly the conclusions of Yount & Niemi (1990) and Niemi *et al.* (1990), three years was chosen as the appropriate frequency of exceedance.

27. Did the authors intend for this section to discuss the format of the criteria documents to be produced and not the format of the Phase II report?

Response: This should be a discussion primarily of the methodology format. The Phase II report is described in Chapter 1. This section has been revised.

28. There does not seem to be much discussion of or justification for the division by 2 of the 5th percentile SSD to derive the acute criterion. There should be some discussion as to why division by 2 should provide adequate protection. If multiple stressors are present (e.g., habitat, other contaminants) would a greater safety factor be warranted?

Response: The factor of 2 was chosen because it has been used successfully in criteria derivations by the USEPA methodologies (USEPA 1985; 2003). The rationale for selecting that value is not of concern, as long as it achieves the goal of ensuring that acute criteria are protective. The USEPA methodologies and the new methodology include procedures for checking derived criteria against available data for sensitive species, threatened and endangered species, and ecosystems. If data suggest that the criteria derived using the factor of 2 will not be protective, then criteria may be adjusted downward by applying a larger factor. Whether to apply larger factors due to multiple stressors is a site-specific, policy decision.

29. In the 2nd paragraph, the authors should clarify whether toxicity tests using product formulations are acceptable. Pesticide toxicity tests may be based on product formulations rather than active ingredient. I would suggest that acceptable toxicity tests only be based on tests run with the active ingredient.

Response: Toxicity tests that use formulations are not acceptable for criteria derivation. Such tests will not be rated highly enough on the relevance scale. They can, however, be used as supporting information if they receive an overall rating of LR (less relevant/reliable) or LL (less relevant/less reliable). Some language has been added to the paragraph to clarify that tests with formulations or mixtures are not to be used for criteria derivation.

30. The discussion of how reliable data are determined is unclear (3rd paragraph). The discussion suggests that the toxicity data results for a given pesticide are evaluated relative to each other rather than to some absolute criteria. Reliable data are said to "...fall in the 75th percentile or higher of all scores..." In reviewing tables 3.9-3.11 and section 3-2.3.2, it appears the author is referring to a raw score and not a percentile.

Response: This discussion has been modified to clarify that the percentiles of chlorpyrifos data scores were used only as a means to establish an absolute scale that will be used to rate data for other pesticides.

References

- ANZECC, ARMCANZ. 2000. Australian and New Zealand guidelines for fresh and marine water quality. Report Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand, Canberra, Australia.
- CSIRO. 2001. BurliOZ v. 1.0.13: Commonwealth Scientific and Industrial Research Organization, Australia.
- Hastings E, Kittams WH, Pepper JH. 1961. Repopulation by aquatic insects in streams sprayed with DDT. *Ann Entomol Soc Am* 54:436-437.
- Host GE, Regal RR, Stephan CE. 1991. Analyses of acute and chronic data for aquatic life. Report United States Environmental Protection Agency.
- Host GE, Regal RR, Stephan CE. 1995. Analyses of acute and chronic data for aquatic life. Report United States Environmental Protection Agency, Washington, DC.

- Niemi GJ, Devore P, Detenbeck N, Taylor D, Lima A, Pastor J, Yount JD, Naiman RJ. 1990. Overview of Case-Studies on Recovery of Aquatic Systems from Disturbance. *Environ Manage* 14:571-587.
- Quinn GP, Keough MJ. 2002. *Experimental Design and Data Analysis for Biologists*. Cambridge, UK: University Press.
- RIVM. 2001. Guidance document on deriving environmental risk limits in The Netherlands. Report National Institute of Public Health and the Environment.
- Sokal RR, Rohlf FJ. 1995. *Biometry, the Principles and Practice of Statistics in Biological Research*. New York: W. H. Freeman and Company, New York, NY.
- USEPA. 1985. Guidelines for deriving numerical national water quality criteria for the protection of aquatic organisms and their uses, PB-85-227049. Report United States Environmental Protection Agency, National Technical Information Service, Springfield, VA.
- USEPA. 1994. Water Quality Standards Handbook: Second Edition, EPA 823-B-94-005a. Report United States Environmental Protection Agency, Washington D. C.
- USEPA. 2003. Water quality guidance for the Great Lakes system. *Federal Register* 40.
- USEPA. 2005. Aquatic life ambient water quality criteria, diazinon, final, EPA-822-R-05-006. Report United States Environmental Protection Agency, Washington D. C.
- Yount JD, Niemi GJ. 1990. Recovery of Lotic Communities and Ecosystems from Disturbance - a Narrative Review of Case-Studies. *Environ Manage* 14:547-569.

Attachment 2

RESPONSES TO PEER REVIEW COMMENTS

From the cover letter: Comments about the methodology (Chapters 1-3)

1. The reviewer suggests that passive sampling devices would be a better approach to assessing bioavailability than the suggested partitioning approach.

Response: The sections on bioavailability in Chapters 2 and 3 have been revised extensively. Important conclusions of the new discussion include: “freely dissolved” does not mean bioavailable; the two-phase model originally presented is too simplistic, and; bioavailability can only be assessed on a site-specific, pesticide-specific, species-specific basis. The pros and cons of passive sampling devices are discussed in Chapter 2, and this approach to estimating bioavailable concentrations of contaminants in water is presented as an option in Chapter 3, but with the caveat that there are still a number of technical limitations and that it is not applicable to determination of compliance with acute criteria.

2. The reviewer notes that the Department of Pesticide Regulation (DPR) appreciates how difficult this project is and that water quality criteria and objectives derived from an improved methodology could potentially be a cornerstone of efforts addressing pesticide use and water quality for years. DPR relies on current criteria and objectives to justify its actions related to protecting water quality, and it anticipates that it will respond similarly when new or revised criteria and objectives are exceeded. Thus, DPR has an understandable interest in assuring that a new methodology and water quality criteria and objectives based on it are as defensible as possible.

Response: This is an observational comment with no suggestions for changes to the report.

3. The reviewer suggests further examination of the effects of temperature on chlorpyrifos toxicity.

Response: A discussion of the low LC₅₀ determined for rainbow trout at 18°C has been added to section 4-10.0 of the criteria document.

Rationale: As pointed out in the draft criteria document, there is not enough data of high enough quality, or for enough species, to allow quantification of this effect for criteria derivation. The rainbow trout and bluegill studies (Mayer & Ellersieck 1986) included in the supplemental data table were rated highly enough to be used as supporting information. Therefore, it is appropriate to consider the effects of temperature in comparing derived criteria to data for sensitive species. For both species, the toxicity of chlorpyrifos increased with increasing temperature, but only for rainbow trout at 18°C did the 96-h LC₅₀ of < 1 ug/L approach the proposed acute criterion of 0.013 ug/L. A definitive LC₅₀ value would be needed to make a reasonable assessment of potential risks to rainbow trout exposed to chlorpyrifos at 18°C. At 13°C the 96-h LC₅₀ was 7.1 ug/L, well above the proposed criterion. Bluegill sensitivity was highest at the highest temperature tested (29°C), but the 96-h LC₅₀ at was 1.7 ug/L, well above the proposed acute criterion. The references cited by the reviewer explore the effects of temperature on uptake of chlorpyrifos in aquatic insects (Buchwalter *et al.* 2002; 2003), the effect of temperature on carcinogenicity of 7,1-dimethylbenz[a]anthracene in rainbow trout (El-Zahr *et al.* 2002), and the effect of temperature on liver

function and formation of DNA adducts in rainbow trout exposed to aflatoxin B1 (Zhang *et al.* 1992). Only two of these studies directly address effects of temperature on chlorpyrifos toxicity (Buchwalter *et al.* 2002; 2003), but neither provides data that would aid in the quantification of these effects on survival, growth, or reproduction.

From Enclosure 1: Comments on the derivation of a methodology for the establishment of water quality criteria for the protection of aquatic life

Comment Letter 1

1) Misspelling of “harmonization” in figure 3.2.

Response: Typographical error has been fixed.

2) The reviewer expressed concern for compatibility of criteria derived by the new methodology with existing water quality monitoring programs.

Response: The new criteria are expressed in a form that is identical to current USEPA criteria. That is, criteria have magnitude, duration and frequency components. While the magnitude of criteria derived by the new methodology may differ from those derived by the USEPA methodology (USEPA 1985b), the duration and frequency components are identical. Thus, monitoring programs currently in place should be adequate for determination of compliance with the new criteria.

Comment Letter 2

1) The lower threshold value for hydrophobicity (i.e., $\log K_{ow} = 3$) is appropriate for evaluating multipathway exposures because chemicals with $\log K_{ow} > 3$ are considered likely to bioaccumulate (OECD 1995).

Response: Whether a chemical is likely to bioaccumulate and by what exposure route that occurs are two different issues. The Phase I report presented evidence that dietary exposure is a significant exposure pathway for chemicals with $\log K_{ow}$ values of 5-7 (Gobas *et al.* 1988; Qiao *et al.* 2000). Outside of that range, 85-98% or more of uptake (in fish) is via the gills (Qiao *et al.* 2000). Thus, it is not necessary to consider multipathway exposure for chemicals with $\log K_{ow}$ s outside of the range of 5-7. However, in assessing the protectiveness of criteria, it is necessary to consider bioaccumulative potential for chemicals with $\log K_{ow}$ s as low as 3.

2) A brief synopsis of pesticides that are suspected to elicit toxicity by narcotic modes of action would be useful.

Response: The reviewer raises a good point because there are very few narcotic pesticides. Fumigants (e.g., methyl bromide, chloropicrin) are really the only class of pesticides known to have a narcotic mode of action (Ware & Whitacre 2004). Since there are at least a few narcotic pesticides, the guidance for using QSARs to assess possible risks to threatened and endangered species will remain in the new methodology.

It is an available tool that may be used when applicable. The following has been added to item 3 in section 3-6.4:

“Note that while many industrial chemicals have a narcotic mode of action, very few pesticides fall into this category. Fumigants, (e.g., methyl bromide, naphthalene, chloropicrin, and others) are a class of pesticides with a narcotic mode of action (USEPA 2006). For a complete list of fumigants used in the United States, see USEPA (2006).”

3) The reviewer discusses some studies that show increased toxicity of chlorpyrifos with increased temperature and notes that it is important to consider temperature-based regulation in deriving water quality criteria.

Response: the issue of temperature effects of chlorpyrifos has been addressed. No further response required.

4) In cases where a LOEC is not explicitly reported, the use of the lowest reported concentration that is different from the control may skew toxic effect levels to higher values.

Response: By definition, the LOEC is the lowest tested concentration that produced a response significantly different from the control, so the proposed approach is sound. In many studies, researchers do not explicitly report NOEC, LOEC or MATC values, but they have presented statistical analysis of the data that can be used to state these values. The LOEC and NOEC are not to be used for criteria derivation in the new methodology. Only MATC values will be used, but to calculate the MATC, the LOEC and NOEC must be determined. Items 4 and 5 in section 2-2.7, and items a and b in section 3-2.1.2 have been modified to clarify that the LOEC and NOEC values derived in this way are to be used to calculate the MATC; they are not to be used in criteria derivation.

5) The authors need to identify the criteria for acceptance of solid-water partition coefficients and K_{oc} values.

Response: Section 2-2.5.1 includes the following:

“...reliable physical-chemical data are those determined by current, standard methods (e.g., American Society for Testing and Materials, ASTM; Organization for Economic Co-operation and Development, OECD; American Public Health Association, APHA) applied and performed correctly for the chemical of interest. Non-standard methods may also be appropriate, but only if valid reasons are given for deviation from standard methods, or if studies were done prior to the existence of standard methods, but generally followed currently acceptable methods. In regard to pesticides, which vary widely in characteristics such as hydrophobicity, water solubility, and ionizability, it is particularly important to verify that reported partition coefficients were determined correctly. Thus it is not acceptable to simply use a value reported in a handbook without verifying the value via the original reference.”

Section 3-2.3.1 includes the following:

“Evaluate physical-chemical data according to whether it was obtained by an appropriate method that was properly used. Table 3.4 indicates acceptable methods for determination of a number of physical-chemical parameters other than K_{ow} . Table 3.5 indicates acceptable methods specifically for determination of K_{ow} values. The methods shown in Table 3.5 are listed in order of preference; computational methods should only be used if no measured data are available. The recommended values in the LOGKOW database (Sangster Research Laboratories 2004) may be used without further review because they have been thoroughly reviewed before inclusion in the database. Physical-chemical parameters reported by manufacturers may also be used without further review as they are widely accepted, and original studies are usually not published. Physical-chemical parameters determined by methods not shown in Tables 3.4 and 3.5 (or equivalent methods) should be used with caution.”

These discussions of reliable, acceptable physical-chemical values apply to K_{oc} values. In addition Table 3.4 includes acceptable methods for determination of K_d and K_{OC} values. No further discussion has been added.

6) Toxicity data derived from studies conducted at levels in excess of the compound’s solubility should not be used.

Response: The USEPA (USEPA 1985a; 2003c) allows use of acute toxicity values which are above the solubility of the test material, “because rejection of such acute values would bias the Final Acute Value by eliminating acute values for resistant species.” This explains why the high values are included in the USEPA pesticide data sets (Erickson & Stephan 1988) that appear in Tables 2.1 and 2.6. However, the USEPA species sensitivity distribution method does not use those high values in determination of the 5th percentile value. The bias the methods are referring to is that which would result from having fewer values in the final data set, thus affecting the rankings and p values.

Since the proposed new methodology uses all of the data in calculation of the 5th percentile value (as long as multimodality is not present), the reviewer raises a valid point. There is not agreement among criteria derivation methodologies on how to handle these kinds of data. The Netherlands guidance (RIVM 2001) allows use of values up to 10x the solubility of the test chemical. Contrarily, the OECD methodology (OECD 1995) rejects the use of LC_{50} values that are higher than the solubility of the compound. The Australia/New Zealand methodology (ANZECC & ARMCANZ 2000) is silent on this issue. The draft of the proposed new methodology includes the following test evaluation criterion: “concentrations do not exceed 10x water solubility.” Four reliability points are associated with this criterion, thus a test could potentially be accepted if it fails this criterion and very few others.

The data sets in Table 2.1 were examined in light of a recent study that compiled, evaluated and selected physical-chemical parameters for several organochlorine pesticides (Shen & Wania 2005). After selecting values, the authors determined a geometric mean and then reported thermodynamically adjusted values. Water solubility values are summarized in the following table:

Water solubility (S) of some organochlorine pesticides from (Shen & Wania 2005); final S values have been adjusted to conform to thermodynamic constraints; S ranges are shown prior to adjustment

Compound	S (µg/L)	S range (µg/L)	Max:Min
aldrin	985	69-2,481	40
<i>cis</i> -chlordane	533	344-615	1.8
<i>trans</i> -chlordane	615	328-574	1.8
DDT	149	7.1-815	115
dieldrin	4,952	495-12,950	26
heptachlor	1,307	1,046-1,867	1.8
α-endosulfan	2,563	1,628-1,750	1.1
β-endosulfan	36,210	23,190-44,760	1.9
endrin	1,143	110-1,828	17

Shen & Wania (2005) did not determine a solubility value for lindane, but values ranging from 7,300-46,800 µ/L (max:min = 6.4) have been reported (PAN 2006; PHYSPROP 2006). Solubility values for chlorpyrifos included in the draft criteria document range from 1.12-2.0 mg/L (Drummond 1986; Felsot & Dahm 1979; Hummel & Crummet 1964). The maximum-to-minimum ratios reveal that it is not uncommon for reported solubility values to differ by at least 2-fold, and they can differ by as much as 115-fold. Due to this kind of variability in water solubility values it is not unreasonable to accept toxicity values that exceed a single or averaged solubility value to some extent. The median maximum-to-minimum solubility ratio for the values discussed above is 1.8. Based on this admittedly small data set, it is reasonable to use toxicity values that are 2x the water solubility.

The Phase II report has been modified such that toxicity values > 2x the geometric mean of available water solubility values for the tested pesticide will be excluded from criteria derivation. In regards to the data sets in Table 2.1, the values that fall outside this range, based on the values reported in (Shen & Wania 2005), have been removed. The highest value (1,230 µ/L) was removed from the DDT data set and the two highest values (4,900 and 19,000 µ/L) were removed from the aldrin data set. All of the other data fell with the 2x solubility range. Distributional fits, assessment factor derivations, test evaluation criteria, and all associated tables and figures were revised as needed (this will include Table 2.6, which the reviewer specifically mentioned).

7) The basis for inclusion of the high acute-to-chronic ratio (ACR) for lindane should be addressed.

Response: The lindane value, taken from Host *et al.* (1995), was determined an accepted procedure (i.e., USEPA 1985a). There is no valid reason to exclude it. In an analysis of the distribution of the ACR data set (JMP 2004), the value of 25 for lindane was not identified as an outlier. Likewise, the method described by (Sokal & Rohlf 1995) was used to test whether the lindane value was an outlier. A ratio of 0.500 was calculated and since this is less than the critical ratio of 0.512, the value is not considered an outlier.

8) More rigorous documentation is needed to support the conclusion that Sacramento and San Joaquin River basin ecosystems are expected to fully recover from brief excursions above water quality criteria as long as the excursions do not occur more often than once every three years.

Upon request for clarification, the reviewer indicated that conclusions regarding ecosystem recovery could be made more relevant to this methodology by describing why the data derived from studies of invertebrate and fish species in other ecosystems are good surrogates for invertebrate and fish species in the Sacramento and San Joaquin River basins.

Response: The discussion of ecosystem recovery in section 2-3.4.1 of Chapter 2 includes all relevant data that was found in an extensive literature search. Although there are very few data specifically for recovery from mild exposures to pesticides in California, the weight of the evidence presented indicates that three years is a reasonable recovery time for ecosystems. The scoring system developed by (Cairns 1990) was used to specifically consider the case of the Sacramento and San Joaquin River basins. The original analysis has been modified due to concerns of Regional Board staff that many areas within the Central Valley are surrounded by urban areas and thus do not have nearby recolonization sources. Results of the revised analysis indicate that there could be some ecosystems in the Central Valley that would have a poor chance of recovery within three years. However, there is ample evidence that three years is sufficient for recovery in most cases, so decreasing the allowable frequency of exceedance is presented as a site-specific option.

9) The reviewer states that the approach to mixture toxicity is valid.

Response: No response required.

Typographical errors: Typos have been fixed.

10) The (Sangster Research Laboratories 2004)log K_{ow} database should be mentioned in Chapter 2.

Response: The Sangster database is mentioned twice in section 2-2.5.1 and is included in the reference list.

11) The authors need to qualify the term “good” as it refers to solid-water partition coefficients.

Response: This issue was addressed in time 5) above.

12) Re: sensitive species data. How could data this important have been excluded from the original derivation of the criteria?

Response: It is possible for a study with a sensitive species to fail to meet the very rigorous data quality standards for inclusion in the criteria derivation data set, but to be of acceptable quality for use in evaluating the reasonableness of derived criteria. It is also possible, in a very large data set, for the lowest value to fall below the 5th percentile.

13) The authors rightfully conclude that it may not be possible to assess whether the criteria will be protective of threatened or endangered species.

Response: No response required.

14) In Figure 3.1 it appears that a “No” answer to the question of data availability can lead directly to the same “Evaluate and select data” activity as a “Yes” answer. How is this possible? Shouldn’t the line that directly connects “No” to “Evaluate and select data” be removed?

Response: Figure 3.1 was basically correct, but has been modified to clarify where values estimated by time-to-event methods enter the process.

Typographical errors: Typos have been fixed. The sentence, “However, a few tools...” reads as it should and was not changed.

Comment Letter 3

1) Page 2-4, paragraph 2, the term “extrapolation” is incorrect and should be changed to “interpolation.” There are a number of instances in which the text refers to “extrapolation” between values.

Response: “Extrapolation” has been changed to “interpolation” in the noted paragraph, but no other instances of this kind of error were found in a search of chapters 2 and 3.

2) The maximum allowable toxicant concentration is the chronic value used in the derivation of criteria in the new methodology. The draft does not clearly describe the process for deriving this value.

Response: Section 2-2.7 on data reduction includes instructions for calculation of the MATC in cases where it was not explicitly reported. Likewise, this information is given in section 3-2.1.2. The discussion of appropriate toxicity values to use in criteria derivation (section 2-2.1.1.2) was amended to include a definition of the MATC.

3) How can the new methodology discourage registrants from selecting resistant organisms for toxicity testing? Is it certain that data for a resistant species in this family might not yield under-protective criteria?

Response: Certainty is not possible, but the use of resistant organisms can be discouraged by adding a layer of detail to the data requirements. The Great Lakes methodology for derivation of secondary acute values (USEPA 2003c) requires data from the family Daphniidae, and specifies that the organisms must be from one of the following three genera: *Daphnia*, *Ceriodaphnia*, or *Simocephalus*. This requirement has been added to the data requirements for both the SSD and assessment factor methods in the new methodology. To further address this issue when using assessment factors, section 2-2.6 has been revised to include the following:

“For determination of acute criteria by the assessment factor method (minimum of 1 datum):

a. For non-herbicides: the family Daphniidae in the genus *Ceriodaphnia*, *Daphnia*, or *Simocephalus*; for herbicides: alga or aquatic vascular plant.

b. Additional data must be in different families as per the list of those required for the SSD method. For example, to derive insecticide criteria, if data are available from two acceptable studies, then one must be from the family Daphniidae and the other must be either a member of the family Salmonidae, a warm water fish, a benthic crustacean or an insect. If three data are available, then one must be in the family Daphniidae and the others must be from two other, different families, and so on such that each additional datum contributes toward completing the minimum data set required for the SSD method.

The plant requirement for herbicides is added because herbicides are expected to be more toxic to plants than to animals. Item b. is added to ensure that the magnitude of the assessment factor is only reduced in cases where data are available for multiple families and to encourage generation of data that would complete the set required for the SSD method.”

Section 3-3.2 includes:

“The size of the factor is dependent on the number of data available, and at least one of the available, acceptable data must be from the family Daphniidae in the genus *Daphnia*, *Ceriodaphnia*, or *Simocephalus*. Additional data must be from different families as per the list of those required for the SSD method, such that each additional value is building toward completion of the minimum SSD data set.”

4) A phylogenetic rather than geographic basis seems more reasonable for inclusion of toxicity test results for aquatic species.

Response: The question is not whether or not to use a geographic basis for inclusion, but rather at what taxonomic level to consider geographic distribution (assuming that taxonomy is driven by phylogeny). As the reviewer rightly points out, the USEPA interspecies correlation estimation procedure works well at the family level, so there is support for considering family-level distribution. Thus, studies that were otherwise acceptable, but were excluded from criteria derivation because the tested species do not reside in North America, might be included. The reviewer also notes that since data limitation is a major source of uncertainty in criteria derivation it would be wise to reconsider the approach of limiting the data set to species residing in North America.

The hope is that this change will expand the available, relevant data set, but the effect may be minimal. For example, the chlorpyrifos data collected according to the new methodology includes four studies that were excluded because species did not reside in North America (Table 4.5; (Ferrando *et al.* 1991; Rice *et al.* 1997; Vanwijngaarden *et al.* 1993). Three of these studies would not be acceptable due to low reliability ratings (Ferrando *et al.* 1991; Rice *et al.* 1997; Vanwijngaarden *et al.* 1993). The only study that was of high enough quality in every other respect to be included, if not for the North America requirement, is that of Rice *et al.* (1997) with Japanese medaka, *Oryzas latipes*. This species is in the family Adrianichthyidae, which is not found in North America. So, for the example of chlorpyrifos, the data set would not change based on expanding from the species to the family level.

Although the chlorpyrifos data set did not change, including data from families that reside in North America could expand data sets for other pesticides. Since this approach is supported by studies of interspecies toxicity correlations (USEPA 2003b), it has been incorporated into the new methodology.

5) To address the possibility that an insecticide might exhibit phytotoxicity, the methodology should require examination of data from marine or terrestrial plants as supplemental information that is not part of derivation of criteria.

Response: The methodology is designed such that, if it is available, plant data are to be included in criteria derivation data sets, but if no high quality plant data are available for insecticides, criteria can still be derived. Plant data are not precluded from deriving insecticide criteria. By the proposed data rating scheme, marine tests, that are otherwise acceptable, will be available for use as supporting information. Terrestrial studies are expected to be of limited use because data generated in non-aqueous exposures are not generally translatable into aqueous terms (for example, translation of results expressed as g ai/ha into mg/L in water is not possible). Such data are not particularly useful, even as supporting information for this methodology.

Comment Letter 4

1) General: Additional explanation is needed for a reader to independently understand scoring criteria for acceptability and relevance and how they are applied.

Chapter 2 is intended only to evaluate and select elements for the methodology. Specific guidance is provided in Chapter 3.

a) Section 2-2.5.2 is unclear on how to evaluate acceptability and relevance of data.

Response: Details are not given in Chapter 2 for evaluating either acceptability or relevance. The procedures are described in general. The second paragraph of the section lists specific elements that are included in the evaluation of relevance, but the actual numerical rating system and detailed list of elements are given in Chapter 3.

b) Standard test methods are not referenced or described.

Response: A general reference to OECD, ASTM, APHA and USEPA ecotoxicity test methods has been added to the first paragraph of section 2-2.5.2. More specific references will not be provided to ensure inclusion of the widest possible array of the most recent methods available.

c) The report does not provide guidance on how critical factors are to be weighted for scoring data relevance.

Response: Specific guidance is given in Chapter 3.

d) The authors should more fully explain why they prefer their proposed measure of quality (i.e., relative to other studies) to a more absolute measure of quality. Is there precedence for distinguishing data quality in this way? The report does not provide a compelling defense for using the 75th percentile as a cutoff for data to be used in the final derivation.

Response: A relative data-rating scale based on the 75th percentile is NOT proposed for the new methodology. An absolute data rating scale has to be based on some line of reasoning. In this case, the chlorpyrifos data set was used to explore the consequences of selecting various scores to represent what might be called data quality cut-offs. The reasons for selecting the 75th percentile for reliability and the 90th percentile for relevance are given in section 2-2.5.2. This process was used to establish an absolute data-rating scheme for future data sets. Other pesticide data sets will be rated according to how their scores fall on this established scale; NOT according to their own 75th or 90th percentile values. Language has been added to the report to clarify that the procedure described was used to establish a scale. The method proposed here is not based on any known precedent; it simply provided a reasonable data set in light of previously accepted data sets (Siepmann & Finlayson 2000; USEPA 1985a), and of the more rigorous quality requirements of the new methodology.

e) The citation for ECOTOX (2006) on page 2-12 appears misplaced on page 3-25.

Response: ECOTOX is cited in both Chapters 2 and 3, but was omitted from the Chapter 2 reference list. It has been added.

2) The reviewers found the approach used to compare and assess methodologies appropriate.

Response: No response required.

3) Would it be more appropriate to derive the criteria based on which distribution fits the data best on a case-by-case basis?

Response: The goodness-of-fit tests were revisited and Dr. Jerome Braun (University of California, Davis Statistics Laboratory) was consulted regarding whether the fit tests were done by a valid method. His response was that the approach used in Chapter 2 to test fits is valid. The atrazine plot in Figure 2.2 was reviewed, as it was the only plot in which the Burr III fit was clearly poorer than the log-normal. The fit parameters for atrazine had been inappropriately rounded leading to erroneous calculations and plots. Fit tests and plots for all pesticides were redone with unrounded Burr III fit parameters. Figures 2.1 and 2.2 and Tables 2.2, 2.3 and 2.4 have been updated with the new results.

Since there are no cases where the log-triangular fit is best, it is not considered further. The USEPA method works despite violations of distributional assumptions because the method ultimately focuses on just the four values nearest the 5th percentile, thus often disregarding a large body of available data. There are no cases where the log-normal fit is clearly better than the Burr III, but there are cases where the Burr III fit is far better than the log-normal. This is expected since the Burr III distribution is a family of distributions and the BurrliOZ program finds the best possible fit for the data within that family. In addition, the Burr III family of distributions approximates log-triangular and log-normal distributions (CSIRO 2001). Essentially, the program does as the reviewer suggests; it finds the best fit on a case-by-case basis. The data in Table 2.4 indicate that protective criteria can be derived regardless of which distribution is selected. The advantage of the ANZECC & ARMCANZ approach is that it utilizes the Burr III distributions (which are best able to describe data sets), utilizes full data sets and derives median, 95th, 99th or other confidence limit estimates of the 5th percentile value. Little to no benefit would be gained by including an additional distributional fitting step in the methodology.

4) The report should acknowledge that the proposed methodology is sensitive to the assortment of species that represents each of the five taxonomic categories. For example, channel catfish and bluegill are both warm-water fish, but their sensitivity to chlorpyrifos is quite different (96-h LC_{50s} of 806 and 10µg/L, respectively), and the final criteria might have been quite different if only one of those had been in the final set. It appears that the only way to counter this effect is for agencies to have the flexibility to revise criteria at reasonable intervals to account for new toxicity data and expanded data sets.

Response: Agencies do have the flexibility to recalculate criteria as new data become available. It is a policy decision as to how often criteria should be revisited to include new data.

5) The statistical principles underlying the proposed methodology are full of nuance. I recommend that you help assure that someone with a lot of experience with applied statistics has an opportunity to review the proposed methodology.

Response: The statistical underpinnings for the species sensitivity distribution approach are well researched and well supported. The empirical approach to deriving acute factors follows that of Host *et al.* (1991) and was used for derivation of factors in the Great Lakes methodology (USEPA 2003c). Thus, it has been through all the levels of review required by the regulatory process.

A point of disagreement that remains in using SSD procedures is the question of what statistical distribution should be used. Chapter 2 includes a comparison of fits for 12 data sets to log-triangular, log-normal and Burr Type III distributions using the goodness-of-fit procedure described by Erickson & Stephan (1988). As this question is central to selecting one SSD approach over another, Dr. Braun was consulted and determined that the technique used to compare fits is acceptable.

From Enclosure 2: Comments on the application of the new methodology to chlorpyrifos

Comment Letter 1

1) The authors might further comment on the differences between the ACR of 9.06 used in the new methodology and the ACR of 4.064 used in the USEPA (1985) derivation and whether the USEPA method applied the ACR to the 5th percentile value.

Response: The chlorpyrifos ACR and the calculation of the default ACR have been revised. Further examination of USEPA and other methodologies revealed that it is acceptable to use saltwater data that is otherwise of acceptable quality to determine ACRs if not enough freshwater data are available (Siepmann & Finlayson 2000; USEPA 1980a; b; c; d; 2003a; 2005). Differences between the USEPA ACR of 4.1 (USEPA 1986), the California Department of Fish and Game value of 3.5 (Siepmann & Finlayson 2000), and the value of 2.2 derived by the new methodology, are due to the use of different data sets. This difference has been pointed out in Chapter 4.

A note has been added in Chapter 3, section 3-4.2.4 confirming that the chronic criterion is derived by dividing the Final Acute Value (i.e., the 5th percentile value) by the ACR.

2) Is it reasonable to assume that temperatures will fluctuate and specifically rise during some parts of the year and stress fish? Could this potentially coincide temporally to situations when chlorpyrifos is applied and entering receiving waters? The reviewer could not get a clear sense of the potential magnitude of temperature effects on toxicity. However, the authors approach...appears reasonable. The safety margin applied to the draft criteria will likely be protective given temperature considerations, but again, it needs to be acknowledged that this is a potential area of uncertainty.

Response: The issue of the effects of temperature on chlorpyrifos toxicity have been addressed in the response to comment 3 in the cover letter. It is outside the scope of this project to do a full risk assessment to determine times when sensitive aquatic life, chlorpyrifos and elevated temperatures might co-occur. Fish are relatively insensitive to chlorpyrifos, and, as discussed in response to comment 3 in the cover letter, only results of a toxicity test with rainbow trout at 18°C suggested sensitivity in the range of the proposed acute criterion. These results were inconclusive. The influence of temperature on chlorpyrifos toxicity in particular cases would have to be investigated on a case-by-case, site-specific basis.

3) A brief comment on the sensitivity of equilibrium partitioning during temperature fluctuations would be helpful. For chlorpyrifos this may be a non-issue since there are no federal or state air or sediment quality standards.

Response: The effect of temperature on pesticide solid-water partitioning is dependent on the effects of temperature on the activity of the pesticide in water, which drives the enthalpy of sorption of the pesticide (Schwarzenbach *et al.* 1993). The enthalpy of sorption can be positive or negative and changes with temperature, such that it is not possible to make general predictions regarding the effects of temperature on sorption processes; experimental data are required. A brief literature search revealed no studies of the effects of temperature on either the enthalpy of sorption or the aqueous activity of chlorpyrifos. Available chlorpyrifos solubility data over a very small range of temperatures show no apparent patterns, and are not adequate to quantify effects of temperature on chlorpyrifos solubility (Drummond 1986; Felsot & Dahm 1979; Hummel & Crummet 1964). This discussion has not been incorporated into the methodology.

4) There are a few spelling errors in Chapter 4.

Response: The specified errors have been fixed.

Comment Letter 2

General comment: It is imperative that site-specific factors be evaluated in derivation of criteria by this methodology because it is supposed apply uniquely to the Sacramento and San Joaquin River basins. The report falls short in this respect.

Response: See responses to the following specific comments.

1) Freshwater plant data were excluded from the criteria derivation because all available studies were done with chlorpyrifos formulations. The authors conclude, "setting criteria without plant values will not lead to underprotective criteria." Although this is a reasonable conclusion based on data from saltwater species, it

would be useful to estimate toxicity to freshwater species based on the knowledge of the applied formulations.

Response: Data from studies of formulations can potentially be rated acceptable as supporting data according to the data evaluation scheme in the new methodology. However, in this case, all of the freshwater plant studies were rated LN (less reliable, not relevant), NL (not reliable, less relevant), or NN (neither reliable nor relevant) and thus, are not usable even as supporting data.

2) The discussion of chlorpyrifos toxicity in ecosystem studies does not address potential differences in bioavailability between this ecosystem and standard laboratory derived toxicity values. Although data appear to be sparse, this step in the criteria development needs to be specifically addressed.

Response: Criteria are derived from laboratory studies conducted in water with no suspended solids. It is generally accepted that solids plays a role in determination of bioavailability, but as discussed in the revised section 2-3.5.1, it is not possible to make general predictions regarding what kind or magnitude of effect solids may have on bioavailability. Section 4-8.0 has also been revised to indicate that it is not possible to make any predictions about chlorpyrifos bioavailability with the available data. Among the studies cited in section 4-13.0, several only reported nominal concentrations (Brock *et al.* 1992a; Brock *et al.* 1992b; Brock *et al.* 1993; Cuppen *et al.* 1995; Eaton *et al.* 1985; Kersting & Van Den Brink 1997; Van Breukelen & Brock 1993; vandenBrink *et al.* 1996; Vandonk *et al.* 1995; Ward *et al.* 1995), and others reported measured concentrations on unfiltered samples (Eaton *et al.* 1985; Giddings *et al.* 1997; Kersting & Van Wijngaarden 1992; Macek *et al.* 1972; Pusey *et al.* 1994; Rawn *et al.* 1978; Van Wijngaarden 1993; Van Wijngaarden *et al.* 2005; Van Wijngaarden & Leeuwangh 1989; Vandenbrink *et al.* 1995; vanWijngaarden *et al.* 1996). The proposed acute and chronic criteria are below the dissolved concentrations reported in Werner *et al.* (2000). The discussion in section 4-13.0 has been modified to indicate that results of the analysis of ecosystem data are not entirely conclusive because of the unpredictability of the effects of solids in natural waters on chlorpyrifos toxicity given currently available data, but that the results reported by Werner *et al.* (2000) indicate that the criteria will be protective.

3) Section 3-15.0 should be tailored to encompass known conditions in the Sacramento and San Joaquin River basins.

Response: The equilibrium partitioning model is presented as a tool that regulators may choose to use to estimate the potential for levels of pesticides in the water compartment to adversely affect levels in other environmental compartments. For initial criteria-setting (i.e., without site-specific information) it is of value to run the model over a range of values for factors that affect the final equilibrium concentrations. The following has been added to section 2-3.6.5:

“Note that steady state environmental models determine equilibrium concentrations in various compartments. The equilibrium that exists between any two compartments may be described by the following equation (based on a simple first-order kinetic model):

$$C_1k_{12} = C_2k_{21} \quad (2.35)$$

where:

C_1 = concentration of pesticide in compartment 1

C_2 = concentration of pesticide in compartment 2

k_{12} = rate constant for transfer of pesticide from compartment 1 to compartment 2

k_{21} = rate constant for transfer of pesticide from compartment 2 to compartment 1

Equation 2.35 can be rearranged:

$$C_1/C_2 = k_{21}/k_{12} = K \quad (2.36)$$

where:

K = the equilibrium constant between the two compartments

In the simulations that will be run to assess harmonization in the new methodology, the concentration of pesticide in water will be set at the chronic criterion level by adjusting the total mass of pesticide in the system. According to equation 2.36, as long as C_1 is constant, C_2 will also be constant for a given equilibrium constant. Thus, the only kinds of model input changes that will affect final concentrations in non-water compartments are those that affect the equilibrium constant. For example, changing lipid levels in fish, or organic carbon content in suspended sediments will cause changes in equilibria, but changing concentrations of solids, or volumes of air or water will not. Model simulations can be run over a range of values to provide information applicable to a variety of site-specific situations.”

The following sentence has been added to section 3-6.5:

“The model should be run over a range of values for parameters that may affect equilibria (e.g., organic carbon levels or fish lipid levels). If no harmonization problems are apparent from a series of Level I analyses (i.e. steady-state concentrations in all compartments are below their respective levels of concern), then no further analysis is necessary. However, if any problems are identified, then site-specific data should be obtained to allow more refined modeling.”

The modeling in Chapter 4 has been expanded to consider ranges of lipid content, and percent organic carbon in suspended and bed sediments.

4) The reviewer notes typographical errors.

Response: Typographical errors have been fixed.

Comment Letter 3

1) The new methodology should either require data from freshwater plants or formally incorporate conditions for substitution of data for plants from other environments.

Response: The approach taken in the new methodology is consistent with Great Lakes methodology (USEPA 2003c) in that it includes plant data when they are available, but also allows derivation of non-

herbicide criteria without plant data when none are available of adequate quality. As discussed in response number 5 from this reviewer's comment on the methodology, studies from terrestrial plants will be of little use in setting water quality criteria, or in assessing their protectiveness. Nothing in the new methodology precludes the use of studies with pesticide formulations, or with saltwater species, as supporting data, provided such studies are otherwise of acceptable quality.

2) The new methodology selects data for pesticide accumulation that are lipid-based. The rationale for this is unclear. One argument is that lipid-based concentrations may correct for condition (fat content) of individual animals. At very high tissue concentrations of legacy persistent organic contaminants body lipid content may be an important determinant of bioaccumulation. At concentrations of current environmental relevance with current use pesticides this is not consistently the case.

Response: The issue of whether or not to use lipid-normalized bioconcentration factors was investigated further. The Phase I report, and Chapter 2 of the current report misquoted the (OECD 1995) methodology; it requires the use of whole-body, wet-weight bioconcentration factors and provides a method for converting lipid-based values to whole-body values. This is in agreement with the USEPA methodologies (USEPA 1985a; 2003c) that both utilize whole-body BCF and BAF values for determination of final residue values and wildlife/human health criteria, respectively. Lipid-based BCF values are used to allow calculation of residue values or wildlife/human health criteria when maximum permissible tissue concentrations are available for a species, but BCF values are not (USEPA 1985a; 2003c). In these cases, values are converted to a lipid basis, and then converted back to whole-body basis for derivation of final residue values or criteria.

In setting or evaluating water quality criteria, the interest in bioaccumulation is to ensure that derived criteria will not lead to excessive bioaccumulation that could cause harm either to the organism that bioaccumulates, or to predators that may consume that organism. In this case, whole-body, wet-weight contaminant concentrations are important because that is what predators are exposed to. Using lipid-based or dry weight BCFs for evaluating water quality criteria leads to a worst-case scenario, as those values are inevitably higher than whole body values. From the standpoint of evaluating potential risks to predators, the use of whole-body, wet-weight BCFs will give the most reasonable assessment. The methodology has been modified to indicate that BCF values should be determined on a whole-body, wet-weight basis. However, consistent with the ECB (2003) methodology, biomagnification factors should be lipid-based if such values are available.

3) There is no reference to requirements for monitoring frequency in the Phase II documents. The methodology for derivation describes estimation of dissolved pesticide concentrations from measurements of total concentrations. Using this approach for gathering the data necessary for calculating four day average concentrations on a river basin scale is a major logistical issue. Passive sampling devices may greatly increase capacity for a monitoring program.

Response: Since the criteria are stated in terms identical to those currently used with USEPA criteria (USEPA 1985a), thus current monitoring programs should be sufficient for the new criteria, with the addition of measurements of total organic carbon, or dissolved plus particulate organic carbon, in water samples collected concurrently with pesticide samples. Passive sampling devices have been addressed (Cover letter comment 1).

Comment Letter 4

1) Summary sheets of studies not included in the final analysis would be helpful.

Response: To make the final document less unwieldy the studies rated acceptable to use as supporting data are summarized in Table 4.5, which includes ratings and reasons for not accepting the data for criteria derivation. This format provides all relevant information for these studies.

2) All summary sheets should include rating scores.

Response: Ratings for data used in criteria derivations are on the summary sheets. If this comment refers to the actual scores, this could be done, but the value in exchange for the effort is questionable. Readers can refer to Table 3.11 for ranges of scores that apply to R, L and N ratings. Ratings for data rated as acceptable for supporting information are included in Table 4.6 as are notes regarding why these studies were not acceptable for criteria derivation.

3) Would it be more appropriate to use the chlorpyrifos ACR of 4.1 (USEPA 1985a), which was used to derive the default ACR of 12.4, instead of the generic, multi-pesticide value?

Response: See previous comments here, and responses to Regional Board staff comments, regarding the chlorpyrifos ACR.

References

- ANZECC, ARMCANZ. 2000. Australian and New Zealand guidelines for fresh and marine water quality. Report Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand, Canberra, Australia.
- Brock TCM, Crum SJH, Van Wijngaarden R, Budde BJ, Tijink J, Zuppelli A, Leeuwangh P. 1992a. Fate and Effects of the Insecticide Dursban(R) 4e in Indoor Elodea-Dominated and Macrophyte-Free Fresh-Water Model-Ecosystems .1. Fate and Primary Effects of the Active Ingredient Chlorpyrifos. *Arch Environ Contam Toxicol* 23:69-84.
- Brock TCM, Van Den Bogaert M, Bos AR, Van Breukelen SWF, Reiche R, Terwoert J, Suykerbuyk REM, Roijackers RMM. 1992b. Fate and Effects of the Insecticide Dursban(R) 4e in Indoor Elodea-Dominated and Macrophyte-Free Fresh-Water Model-Ecosystems .2. Secondary Effects on Community Structure. *Arch Environ Contam Toxicol* 23:391-409.
- Brock TCM, Vet J, Kerkhofs MJJ, Lijzen J, Van Zuilekom WJ, Gijlstra R. 1993. Fate and Effects of the Insecticide Dursban(R) 4e in Indoor Elodea-Dominated and Macrophyte-Free Fresh-Water Model-Ecosystems .3. Aspects of Ecosystem Functioning. *Arch Environ Contam Toxicol* 25:160-169.
- Buchwalter DB, Jenkins JJ, Curtis LR. 2002. Respiratory strategy is a major determinant of [H-3]water and [C-14]chlorpyrifos uptake in aquatic insects. *Can J Fish Aquat Sci* 59:1315-1322.
- Buchwalter DB, Jenkins JJ, Curtis LR. 2003. Temperature influences on water permeability and chlorpyrifos uptake in aquatic insects with differing respiratory strategies. *Environ Toxicol Chem* 22:2806-2812.

- Cairns J. 1990. Lack of Theoretical Basis for Predicting Rate and Pathways of Recovery. *Environ Manage* 14:517-526.
- CSIRO. 2001. BurrliOZ v. 1.0.13: Commonwealth Scientific and Industrial Research Organization, Australia.
- Cuppen JGM, Gylstra R, Vanbeusekom S, Budde BJ, Brock TCM. 1995. Effects of Nutrient Loading and Insecticide Application on the Ecology of Elodea-Dominated Fresh-Water Microcosms .3. Responses of Macroinvertebrate Detritivores, Breakdown of Plant Litter, and Final Conclusions. *Archiv Fur Hydrobiologie* 134:157-177.
- Drummond JN. 1986. Solubility of chlorpyrifos in various solvents. Report DowElanco, Indianapolis, IN.
- Eaton J, Arthur J, Hermanutz RO, Kiefer R, Mueller L, Anderson R, Erickson RJ, Nordling B, Rogers J, Pritchard H. 1985. Biological effects of continuous and intermittent dosing of outdoor experimental streams with chlorpyrifos. *Aquatic Toxicology and Hazard Assessment: Eighth Symposium*: American Society for Testing and Materials.
- ECB. 2003. Technical guidance document on risk assessment in support of commission directive 93/67/EEC on risk assessment of new notified substances, commission regulation (EC) no. 1488/94 on risk assessment for existing substances, directive 98/8/EC of the European Parliament and of the Council concerning the placing of biocidal products on the market. Part II. Environmental risk assessment. In: European Chemicals Bureau ECJRC, editor. Report European Communities.
- El-Zahr CR, Zhang Q, Hendricks JD, Curtis LR. 2002. Temperature-modulated carcinogenicity of 7,12-dimethylbenz[a]anthracene in rainbow trout. *Journal of Toxicology and Environmental Health-Part A* 65:787-802.
- Erickson RJ, Stephan CE. 1988. Calculation of the final acute value for water quality criteria for aquatic organisms. Report Environmental Research Laboratory-Duluth, United States Environmental Protection Agency, Duluth, MN.
- Felsot A, Dahm PA. 1979. Sorption of Organophosphorus and Carbamate Insecticides by Soil. *J Agric Food Chem* 27:557-563.
- Ferrando MD, Sancho E, Andreumoliner E. 1991. Comparative Acute Toxicities of Selected Pesticides to *Anguilla-Anguilla*. *Journal of Environmental Science and Health Part B-Pesticides Food Contaminants and Agricultural Wastes* 26:491-498.
- Giddings JM, Biever RC, Racke KD. 1997. Fate of chlorpyrifos in outdoor pond microcosms and effects on growth and survival of bluegill sunfish. *Environ Toxicol Chem* 16:2353-2362.
- Gobas F, Muir DCG, Mackay D. 1988. Dynamics of Dietary Bioaccumulation and Fecal Elimination of Hydrophobic Organic-Chemicals in Fish. *Chemosphere* 17:943-962.
- Host GE, Regal RR, Stephan CE. 1991. Analyses of acute and chronic data for aquatic life. Report United States Environmental Protection Agency.
- Host GE, Regal RR, Stephan CE. 1995. Analyses of acute and chronic data for aquatic life. Report United States Environmental Protection Agency, Washington, DC.
- Hummel RA, Crummett WB. 1964. Solubility of ethyl O,O-diethyl O-(3,5,6-trichloro-2-pyridyl)phosphorothioate in various solvents. Report DowElanco, Indianapolis, IN.
- JMP. 2004. Statistical discovery software. Version 5.1.2: SAS Institute, Inc., Cary NC.
- Kersting K, Van Den Brink PJ. 1997. Effects of the insecticide Dursban(R)4E (active ingredient chlorpyrifos) in outdoor experimental ditches: Responses of ecosystem metabolism. *Environ Toxicol Chem* 16:251-259.

- Kersting K, Van Wijngaarden R. 1992. Effects of Chlorpyrifos on a Microecosystem. *Environ Toxicol Chem* 11:365-372.
- Macek KJ, Hogan JW, Holz DD, Walsh DF. 1972. Toxicity of Insecticide Dursban to Fish and Aquatic Invertebrates in Ponds. *Trans Am Fish Soc* 101:420-&.
- Mayer FL, Ellersieck MR. 1986. Manual of acute toxicity: interpretation and data base for 410 chemicals and 66 species of freshwater animals. Report United States Department of the Interior.
- OECD. 1995. OECD environment monographs No. 92, OECD environmental health and safety publications, series on testing and assessment, No. 3, guidance document for aquatic effects assessment. Report Organization for Economic Co-operation and Development, Paris.
- PAN. 2006. Pesticide Action Network Pesticide Database; <http://www.pesticideinfo.org/Index.html>. Report.
- PHYSPROP. 2006. Physical Properties Database; www.syrres.com/esc/physprop.htm. Report.
- Pusey BJ, Arthington AH, McLean J. 1994. Effects of a Pulsed Application of Chlorpyrifos on Macroinvertebrate Communities in an Outdoor Artificial Stream System. *Ecotoxicol Environ Saf* 27:221-250.
- Qiao P, Gobas F, Farrell AP. 2000. Relative contributions of aqueous and dietary uptake of hydrophobic chemicals to the body burden in juvenile rainbow trout. *Arch Environ Contam Toxicol* 39:369-377.
- Rawn GP, Webster GRB, Findlay GM. 1978. Effect of Pool Bottom Substrate on Residues and Bioactivity of Chlorpyrifos, against Larvae of *Culex-Tarsalis* (Diptera-Culicidae). *Can Entomol* 110:1269-1276.
- Rice PJ, Drewes CD, Klubertanz TM, Bradbury SP, Coats JR. 1997. Acute toxicity and behavioral effects of chlorpyrifos, permethrin, phenol, strychnine, and 2,4-dinitrophenol to 30-day-old Japanese medaka (*Oryzias latipes*). *Environ Toxicol Chem* 16:696-704.
- RIVM. 2001. Guidance document on deriving environmental risk limits in The Netherlands. Report National Institute of Public Health and the Environment.
- Sangster Research Laboratories. 2004. LOGKOW. A databank of evaluated octanol-water partition coefficients (Log P); <http://logkow.cisti.nrc.ca/logkow/index.jsp>. Report Canadian National Committee for CODATA.
- Schwarzenbach RP, Gschwend PM, Imboden DM. 1993. *Environmental Organic Chemistry*. New York, NY: John Wiley & Sons, Inc.
- Shen L, Wania F. 2005. Compilation, evaluation, and selection of physical-chemical property data for organochlorine pesticides. *Journal of Chemical and Engineering Data* 50:742-768.
- Siepmann S, Finlayson B. 2000. Water quality criteria for diazinon and chlorpyrifos. Report California Department of Fish and Game.
- Sokal RR, Rohlf FJ. 1995. *Biometry, the Principles and Practice of Statistics in Biological Research*. New York: W. H. Freeman and Company, New York, NY.
- USEPA. 1980a. Ambient water quality criteria for aldrin/dieldrin. Report United States Environmental Protection Agency, Washington D. C.
- USEPA. 1980b. Ambient water quality criteria for chlordane, EPA 440/5-80-027. Report United States Environmental Protection Agency, Washington D. C.
- USEPA. 1980c. Ambient water quality criteria for endosulfan, EPA 440/5-80-046. Report United States Environmental Protection Agency, Washington D. C.
- USEPA. 1980d. Ambient water quality criteria for endrin, EPA 440/5-80-047. Report United States Environmental Protection Agency, Washington D. C.

- USEPA. 1985a. Guidelines for deriving numerical national water quality criteria for the protection of aquatic organisms and their uses. Report United States Environmental Protection Agency, National Technical Information Service, Springfield, VA.
- USEPA. 1985b. Guidelines for deriving numerical national water quality criteria for the protection of aquatic organisms and their uses, PB-85-227049. Report United States Environmental Protection Agency, National Technical Information Service, Springfield, VA.
- USEPA. 1986. Ambient water quality criteria for chlorpyrifos, EPA 440/5-86-005. Report United States Environmental Protection Agency, Washington, D. C.
- USEPA. 2003a. 2003 Draft update of ambient water quality criteria for copper, EPA 822-R-03-026. Report United States Environmental Protection Agency, Washington D. C.
- USEPA. 2003b. Interspecies correlation estimation (ICE) for acute toxicity to aquatic organisms and wildlife, II. User manual and software, EPA/600/R-03/106. Report United States Environmental Protection Agency, Washington D. C.
- USEPA. 2003c. Water quality guidance for the Great Lakes system. *Federal Register* 40.
- USEPA. 2005. Aquatic life ambient water quality criteria, diazinon, final, EPA-822-R-05-006. Report United States Environmental Protection Agency, Washington D. C.
- USEPA. 2006. Recognition and management of pesticide poisonings, 5th edition, Section IV, Chapter 16 Fumigants. Report United States Environmental Protection Agency, Washington D. C.
- USGS. 2005a. Water resources data, California water year 2004, Volume 3, Southern Central Valley basins and the Great Basin from Walker River to Truckee River. Report United States Geological Survey, Sacramento, CA.
- USGS. 2005b. Water resources data, California water year 2004, Volume 4, Northern Central Valley basins and the Great Basin from Honey Lake basin to Oregon state line. Report United States Geological Survey, Sacramento, CA.
- Van Breukelen SWF, Brock TCM. 1993. Response of a macro-invertebrate community to insecticide application in replicated freshwater microcosms with emphasis on the use of principal component analysis. *Sci Total Environ* Supplement:1047-1058.
- Van Wijngaarden RPA. 1993. Comparison of response of the mayfly *Cloen dipterum* to chlorpyrifos in a single species toxicity test, laboratory microcosms, outdoor ponds and experimental ditches. *Sci Total Environ* Supplement:1037-1046.
- Van Wijngaarden RPA, Brock TCM, Douglas MT. 2005. Effects of chlorpyrifos in freshwater model ecosystems: the influence of experimental conditions on ecotoxicological thresholds. *Pest Manage Sci* 61:923-935.
- Van Wijngaarden RPA, Leeuwangh V. 1989. Relation between toxicity in laboratory and pond: an ecotoxicological study with chlorpyrifos. *International Symposium on Crop Protection*:1061-1069.
- Vandenbrink PJ, Vandonk E, Gylstra R, Crum SJH, Brock TCM. 1995. Effects of Chronic Low Concentrations of the Pesticides Chlorpyrifos and Atrazine in Indoor Fresh-Water Microcosms. *Chemosphere* 31:3181-3200.
- vandenBrink PJ, vanWijngaarden RPA, Lucassen WGH, Brock TCM, Leeuwangh P. 1996. Effects of the insecticide Dursban(R) 4E (active ingredient chlorpyrifos) in outdoor experimental ditches .2. Invertebrate community responses and recovery. *Environ Toxicol Chem* 15:1143-1153.
- Vandonk E, Prins H, Voogd HM, Crum SJH, Brock TCM. 1995. Effects of Nutrient Loading and Insecticide Application on the Ecology of Elodea-Dominated Fresh-Water Microcosms .1. Responses of Plankton and Zooplanktivorous Insects. *Archiv Fur Hydrobiologie* 133:417-439.

- Vanwijngaarden R, Leeuwangh P, Lucassen WGH, Romijn K, Ronday R, Vandervelde R, Willigenburg W. 1993. Acute Toxicity of Chlorpyrifos to Fish, a Newt, and Aquatic Invertebrates. *Bull Environ Contam Toxicol* 51:716-723.
- vanWijngaarden RPA, vandenBrink PJ, Crum SJH, Voshaar JHO, Brock TCM, Leeuwangh P. 1996. Effects of the insecticide Dursban(R) 4E (active ingredient chlorpyrifos) in outdoor experimental ditches .1. Comparison of short-term toxicity between the laboratory and the field. *Environ Toxicol Chem* 15:1133-1142.
- Ward S, Arthington AH, Pusey BJ. 1995. The Effects of a Chronic Application of Chlorpyrifos on the Macroinvertebrate Fauna in an Outdoor Artificial Stream System - Species Responses. *Ecotoxicol Environ Saf* 30:2-23.
- Ware GW, Whitacre DM. 2004. An introduction to insecticides, 4th edition. *IPM World Textbook*: University of Minnesota.
- Werner I, Deanovic LA, Connor V, de Vlaming V, Bailey HC, Hinton DE. 2000. Insecticide-caused toxicity to *Ceriodaphnia dubia* (Cladocera) in the Sacramento-San Joaquin River Delta, California, USA. *Environ Toxicol Chem* 19:215-227.
- Zhang Q, Suorsasuper K, Curtis LR. 1992. Temperature-Modulated Aflatoxin-B1 Hepatic Disposition and Formation and Persistence of DNA Adducts in Rainbow-Trout. *Toxicol Appl Pharmacol* 113:253-259.

ATTACHMENT 2

Transmitted Comment Letter

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METHODOLOGY FOR DERIVATION OF PESTICIDE WATER QUALITY CRITERIA, PHASE II REPORT – COMPILED PEER REVIEW COMMENTS

Enclosed are the compiled comments received from 4 peer reviewers on the Methodology for Derivation of Pesticide Water Quality Criteria, Phase II Report. A fifth peer reviewer has not yet submitted comments. Any additional comments will be forwarded at such time as they are received. Staff also has additional comments on the Phase II report. These will be sent under a separate cover.

The response to the Phase II report has been very positive and your efforts are to be commended. The Comments have been divided into two sections. Enclosure 1 compiles the peer reviewer comments on the Method. Enclosure 2 compiles the comments on the application of the method.

As with the peer review of the Phase I report, the comments letters have been compiled and stripped of identifying information to provide anonymity for, and facilitate greater candor by the peer reviewer. Where necessary, minor changes may have been made to the comment letters to remove identifying traits. The following Changes have been made to the comment letters

- All identifying information in the comment headers, footers, and any salutation information has been removed.
- In some instances, peer reviewers bulleted some comments. The bullets have been converted to sequential comment numbers to facilitate future communications and preparation of responses to comments. If the comment letter did not include bulleted comments, no attempt was made to insert comment numbers. Parsing non-bulleted comments into discretely numbered comments would have required interpretation of the comments on our part, which could have modified the meaning of the comment.
- Because some reviewers referenced their review of the methodology in their review of the application of the methodology, the comment letters are listed in the same order in both

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enclosures (i.e. enclosure 1, comment letter 1 and enclosure 2, comment letter 1 were both written by the same reviewer.)

- Minor typographical errors of the kind found by common spell-check utilities (i.e. “fro” instead of “for”) have been corrected. If there was any question about whether a word was misspelled, it was not corrected.
- Some comments included references or other information that would have identified the commenter. To maintain the anonymity of the remainder of the comment letter, the comment was extracted and is reproduced below:

Comments About the Methodology (Chapters 1 – 3)

1. *The method the draft report advocates for determination of the dissolved phase concentration of pesticides in water samples is acceptable but perhaps not optimal. There are significant advantages to passive sampling devices for assessing bioavailable pesticide concentrations in water. Advantages include: it is practical to deploy these devices for weeks of continuous sampling; the cost of analysis is much reduced since it only deals with one matrix; sensitivity can be greatly increased because the effective volume of water sampled is large. Villeneuve et al. (2005) presents one good example for application of this method but many more exist in the literature.*

Reference

Villeneuve, D. L., L. R. Curtis, J. J. Jenkins, et al. 2005. Environmental stresses and skeletal deformities in fish from the Willamette River, Oregon. *Environ. Sci. Technol.* 39: 495 – 3506.

2. *“As an additional comment, the Department of Pesticide Regulation (DPR) appreciates how difficult this project is and that water quality criteria and objectives derived from an improved methodology could potentially be a cornerstone of efforts addressing pesticide use and water quality for years. DPR relies on current criteria and objectives to justify its actions related to protecting water quality, and it anticipates that it will respond similarly when new or revised criteria and objectives are exceeded. Thus, DPR has an understandable interest in assuring that a new methodology and water quality criteria and objectives based on it are as defensible as possible.”*

Comment About the Application to Chlorpyrifos (Chapter 4)

3. *Chlorpyrifos toxicity increases at higher temperatures (page 4-8). Accumulation of waterborne lipophilic organic contaminants (including chlorpyrifos) by aquatic animals increases with exposure temperature (Buchwalter et al., 2003; El-Zhar et al., 2002; Zhang et al. 1992). This is particularly evident for acute exposures. Higher ventilation and blood (for fish) flow rates at warmer temperatures increase*

accumulation minutes to hours after initiation of a waterborne exposure. The report cites work that demonstrates rather remarkable increases in chlorpyrifos toxicity at higher temperatures (15-fold decrease in LC50 for rainbow trout from 7 to 18 degrees Celsius). Water is highly regulated in Sacramento and San Joaquin Rivers and their tributaries and temperature elevation is a major issue for salmonids. For these, reasons temperature-based regulation is worthy of serious consideration.

References

Buchwalter, D. B., J. J. Jenkins, and L. R. Curtis. 2003. Temperature and respiratory strategy effects [3H]water and [14C]chlorpyrifos accumulation in aquatic insects. Environ. Toxicol. Chem. 22: 2806 – 2812.

El-Zhar, C. R., Q. Zhang, J. D. Hendricks, and L. R. Curtis. 2002. Temperature-modulated carcinogenicity of 7, 12-dimethylbenz[a]anthracene in rainbow trout. J. Toxicol. Environ. Hlth. 65: 787-802.

Zhang, Q., K. Surorsa-Super, and L. R. Curtis. 1992. Temperature modulated aflatoxin B1 hepatic disposition, and formation and persistence of DNA adducts in rainbow trout. Toxicol. Appl. Pharmacol. 113: 253-259.

Prior to making changes to the Phase II report, I would like to arrange a meeting with the project team to discuss these comments. I want to make sure that the comments and proposed document changes are mutually understood and agreed upon; and that any potential impacts to the existing scope of work are addressed. If you have any questions about this information, please call me. Thanks again for your hard work.

Paul Hann
Environmental Scientist
Pesticide TMDL Unit

Enclosure(s) – 3

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Comments on the Derivation of a Methodology for the Establishment of Water Quality Criteria for the Protection of Aquatic Life

COMMENT LETTER 1

Summary

The goal of this project is to develop a methodology for derivation of pesticide water quality criteria for the protection of aquatic life in the Sacramento River and San Joaquin River basins. The current report is organized into four chapters, and entails development of a new methodology that was based on the phase 1 review of existing methodologies. Because the phase 1 review did not reveal a single methodology that could be used to derive robust protective criteria, a new methodology was developed consisting of a combination of features from existing methodologies with refinements based on research in aquatic ecotoxicology. The current document will provide a framework for deriving criteria for a number of pesticides in the Sacramento River and San Joaquin River basins.

The report is organized into four chapters. The first chapter provides a background and justification of the approaches taken to develop the new methodology, and sets the stage for the second chapter which covers an in-depth evaluation and rationale for selection of methods for inclusion in the new methodology. This chapter includes a discussion of the step-by-step process used to derive criteria. The number of data sets (12) used to evaluate the various techniques is reasonable. In the third chapter is presented a detailed analysis of approaches for data collection, evaluation, and reduction, and also methods of incorporation of water quality parameters, as well as considerations of sensitive species and challenges of chemical mixtures. The authors clearly addressed a criticism raised in one of the reviews of the phase I document associated with providing guidance for data evaluation and filtering. In this regard, a number of flow charts, data summary sheets, web addresses and tables are provided that will help provide guidance for determination of physical chemical parameters, default acute-to-chronic ratio and BMF values, assessment factors, and other statistically-based support values. Also provided are acceptability criteria for aquatic toxicology data and water quality parameters. As discussed, the fourth chapter covers the use of the new methodology in the derivation of acute and chronic criteria for chlorpyrifos, and is evaluated separately.

There is a thoughtful and detailed discussion justifying procedures in the new methodology for assessing applicability of toxicity test results, dealing with issues associated with uncertainty, limited data sets and data set variability. Methods from prior existing methodologies that do not substantially contribute to the development of the new methodology are thoughtfully excluded, and the rationale for exclusion appears reasonable and based on science and practicality. The authors have conducted an extensive and reasonable review and evaluation of applicable

toxicity literature in context of deriving water quality data for the CVRWQCB. The authors provide guidelines for the rejection of toxicity test information, and include at the end of each chapter a list of appropriate references. While there is not a detailed methodology associated with protection of wildlife or human health, these issues do not appear to be relevant to the requirements and guidelines associated with the new methodology, which are primarily addressed towards protection of aquatic life in the Sacramento and San Joaquin River basins. As with the phase 1 document, this document is clearly written with only a few typographical errors. The references appear current. I could not identify any major scientific issues of relevance that were not addressed in the current report.

II. *[sic.]* Critique of specific elements of the document.

A. *Accuracy and completeness of the information presented.*

It is this reviewer's opinion that the reviewed methodology meets the requirements set forth by the CVRWQCB for water quality criteria derivation. For example, included is a detailed procedure for assessing the quality and applicability of toxicity test results. The new methodology also describes a process for the derivation of pesticide criteria from literature toxicity studies that range from limited data sets to more robust data sets. There is the flexibility to incorporate safety factors into setting criteria that addresses issues of uncertainty, and the use of the species sensitivity distribution (SSD) model is exploited as a means of comparing cumulative exposure concentration distributions to cumulative species-sensitivity distributions. Guidance for the use of the SSD model (*i.e.* considerations of numbers of sensitive species observations, relative values of all species in an ecosystem, etc.) in the context of species protection is provided. There is also a reasonable framework for consideration of sublethal chemical effects and impacts to endangered species. The authors address in detail procedures for deriving criteria that are based on the short-term and long-term exposures as well as considerations for dealing with toxic effects to different classes of aquatic organisms, and also water quality parameters. The number of data sets (12) used to evaluate the various techniques is reasonable.

There is a detailed analysis of approaches for data collection and evaluation, data reduction, and also methods of incorporation of water quality parameters and considerations associated with issues associated with sensitive species, and challenges of assessing the effects of chemical mixtures. There is appropriate guidance provided for the reduction of multiple data for a given chemical-species combination to single species acute and chronic values, and also how to manage statistical issues regarding bimodal distributions and data outliers. Based on the information and references provided, the scientific information presented appears to be technically accurate. References included at the end of each chapter arise from a diversity of sources including ASTM documents, state federal and international water quality and derivation guidelines, and aquatic toxicology studies from mainstream journals. It is evident

that a comprehensive review of the literature was undertaken by the authors in the preparation this document. There are a few typos that do not detract from the scientific quality (i.e. misspelling of the word “harmonization” in figure 3.2).

B. Appropriateness of the approach used to compare and assess and select methodology elements

The fact that the phase 1 report did not reveal a single methodology that contained all the features deemed important for the derivation of robust protective criteria led the authors to develop a new methodology consisting of features from existing methodologies with refinements. Elements from the existing methodologies that were selected for inclusion in the new method are based upon strong scientific basis and also given in light of considerations of practicality. The authors approach to compare and select methodology elements appears to be appropriate and fair, and under those circumstances where elements of other methodologies are omitted, the authors present reasonable justification for exclusion.

C. Evaluation and interpretation. Key components, identification of strengths and weaknesses support of conclusions.

Evaluation and interpretation of ecological risk assessment techniques and other methodologies are fairly evaluated and in light of practicality and current aquatic toxicology literature. The authors point out the limitations on hypothesis testing and regression analysis and the lack of agreement among scientists among no effect levels. The authors propose that acute toxicity data should be in the form of LC50 or EC50 values derived from regression analysis, and propose that chronic data expressed as EC values from regression analysis should be acceptable only if species-specific studies are available for determination of true no-effect levels. The fact that the MATC is an accepted method of estimating “no effect” levels justifies this index as a chronic value in the new methodology.

The authors provide a thoughtful evaluation of the controversial issues surrounding the incorporation of nontraditional endpoints. Chemical effects on reproduction, tissue pathology, mutagenesis, and behaviors critical to survival certainly have the potential to threaten survival to the organism and potentially affect populations. However, the fact is that there are few currently clear-cut and established links among the manifestation of these effects in the individual to those at the population, community, or ecosystem levels. Again, the current state of the scientific knowledge is more to use these indicators as markers of toxic exposure or effects. It is anticipated that these data gaps will be lessened in the future.

Because there is more scientific data regarding the linkages among acetylcholinesterase inhibition and survival, this is discussed in detail and is of relevance to the pesticides under analysis. However, this is also a complex issue and would involve, at minimum, derivation of

inhibition concentration values in which enzyme inhibition is linked to mortality for a given chemical and species. Accordingly, the authors propose to use individual sublethal level endpoints only if linked to survival, growth reproduction, and population-level effects. Such a conclusion is reasonable considering the state of the science.

The rationale for omitting population level endpoints in the new methodology was based on existing evidence that such endpoints may not be any more protective of ecosystems than traditional endpoints. While this is an area some debate, the authors provide a strong rationale for exclusion in the new methodology.

The authors provide guidance in the form of summary tables to help deal with the issue of comparing data from diverse studies and systematically rating the quality of a given study, as well as acceptability ratings for laboratory and field aquatic data. These tools should be of great use to water quality managers. When dealing with the range of taxonomic diversity that could be potentially represented in ecotoxicity data in the context of data reduction, the authors draw heavily upon the US EPA methodologies. The modification to reduce required number of species from eight to five to reflect species of importance to the Central Valley of California appears reasonable given the attributes of this ecosystem, and should help streamline the process. Species sensitivity distribution (SSD) techniques are discussed in detail the context of extrapolating available toxicity data for toxicity values from a limited number of species that will be protective of all species in an ecosystem.

In dealing with the issues of chemical mixtures, the new methodology includes guidelines for the use of concentration addition approaches, and non-additive toxicity models. The inclusion of a template for how water quality criteria can be presented in terms of magnitude, duration, and frequency, should help provide guidance for water quality managers. The inclusion of several appendices (flowcharts for data collection and criteria derivation processes, blank data summary sheets, and numerous tables of data sources, assessment factors, and sample quantitative structure activity relationships) should also help regulators in the development of new water quality criteria in the region.

D. Scientific issues of relevance that were not addressed in the current report

This is a well researched and comprehensive report. While there is some reference to considerations of criteria regarding human and wildlife health (p. 2-65), the current report does not include detailed methodology associated with protection of wildlife or human health. However, such level of detail would likely confound the process and is likely not relevant to the requirements of the new methodology, which is to protect aquatic life in the Sacramento and San Joaquin River basins.

The reviewer could not get a strong sense of how criteria produced by the new methodology would be more-or-less compatible with typical monitoring programs required to assess compliance relative to those established by other programs (*i.e.* most monitoring programs collect a single daily grab sample for a site or a composite sample that represents a single day). This reviewer could find no other major scientific issues of relevance that were not addressed in the current report.

E. Scientific soundness of the analysis of the report

The technical basis for the executive summary and first three chapters of this report appears to be solid. The report provides an excellent context for development of draft water quality criteria for chlorpyrifos. It is the reviewer's opinion that this report is scientifically and technically sound and that this document will be applicable to other regional water quality control Boards or State regulatory agencies involved in setting and enforcing water quality criteria.

COMMENT LETTER 2

Review of methodology development (Chapters 1-3)

Chapters 1-3 provide a comprehensive evaluation of existing methods for toxicity tests that are appropriate for assessing the potential harm that pesticides may impart on freshwater aquatic ecosystems. The proposed methodology adequately addresses all of the specified requirements (e.g., short- and long-term exposures, lethal and sublethal effects) in a manner that is compatible with existing methods and monitoring programs. The report contains a complete list of references and is scientifically defensible.

Overall, the report positively addresses the review criteria of accuracy, completeness, appropriateness, and interpretation. Taken as a whole, the report is based on commonly accepted knowledge, methods and practices. The overall approach is conservative (e.g., use of most sensitive species and/or life stage), which is an appropriate and accepted approach for the protection of aquatic life.

Specific comments and observations that appear below address a handful of scientific issues that require some clarification and/or expanded discussion.

Chapter 1: Introduction and Approach

The introduction provides a brief and appropriate presentation of relevant existing methods and literature references.

Chapter 2: Evaluation and Selection of Methods

1. The authors state that water-only provide the best approach for criteria derivation until models are further developed to incorporate multipathway exposures (p 2-6). Further studies of dietary exposures are recommended for chemicals with log Kow values between 5 and 7. However, in the later section on bioaccumulation (p 2-66), the authors cite OECD (1995) guidance that states chemicals with log Kows greater than 3 are likely to bioaccumulate. Although there is a greater tendency of chemicals with higher log Kows to bioaccumulate, the lower threshold for hydrophobicity (i.e., log Kow = 3) is appropriate for evaluating multipathway exposures.
2. The new methodology does not include a provision for use of quantitative structure activity relationships (QSARS) in the derivation of criteria as they are generally of limited utility for pesticides (p 2-7). However, QSARs are recommended as an option for assessing the hazards to threatened and endangered species (p 2-69). As stated, this option only makes sense if the pesticide of interest is known to have a narcotic mode of action. A brief synopsis of pesticides that are suspected to elicit toxicity by narcotic modes of action would be useful.
3. Criteria for the non-acceptance of single-species ecotoxicity data include inadequate documentation of controls, tests with species that do not reside in North America, tests with endpoints that are not linked to survival, growth or reproductive effects, tests that do not produce numerical toxicity values, tests with saltwater species, tests conducted with less than technical grade chemicals, or tests performed with chemical mixtures. The proposed method for assigning reliability and relevance scores provides a legitimate degree of rigor for accepting or rejecting data.
4. If an LOEC is not explicitly reported in chronic toxicity tests, the authors recommend using the lowest reported concentration that is statistically different from the control (p 2-16). Although this will produce a value that represents a relatively low effect level for the study in question, it may be far from a threshold effect level depending on the exposure regime for the study. This may skew the interpretation of toxic effect levels to higher values.
5. The authors state that “a good solid-water partition coefficient” should be used to convert the total concentration of a toxicant to a dissolved concentration (p 2-17). Although this is an important derivation, it is not clear what constitutes the criteria for “goodness.” Later in the document (p 2-58), the statement is made that “A reliable Koc value must also be available.” In both cases, the authors need to identify the criteria for acceptance.

6. Acceptability of data should consider solubility exceedances for the toxicant in question. Table 2.1 (and Table 2.6) includes data for acute toxicity data sets that are far in excess of compound solubility in water (e.g., DDT sol. < 5µg/L). Toxicity data derived from studies conducted at levels in excess of the compound's solubility should not be used.
7. The derivation of a default acute-to-chronic ratio (ACR) was performed by re-examination of data from the Great Lakes guidance (Host *et al.*, 1995) and from USEPA criteria for diazinon (USEPA, 2000). The default value of 12.4 represents the 80th percentile of this data set. Because the ACR for lindane is substantially higher than values for the other chemicals, the authors should address the basis for its inclusion in this assessment.
8. The review of ecosystem recovery following an episode of toxicity gives reasonable evidence that lotic ecosystems generally recover over a period of weeks to years (p 2-54 - 2-57). The ability of an ecosystem to recover depends on several site-specific factors such as the re-colonization potential of the affected ecosystem. A statement is made that "It is reasonable to assume that rapid recovery is likely in the Sacramento and San Joaquin River basins following brief, mild, limited-scope excursions above criteria levels" (p 2-55). Furthermore, the authors conclude that "...three years between exposure events should allow full recovery from effects of an excursion above either acute or chronic water quality criteria in the Sacramento and San Joaquin River basins" (p 2-57). Unfortunately, this conclusion is not supported by a specific assessment of species endemic to the Sacramento and San Joaquin River basins, nor to the physical and chemical characteristics of these waters. Accordingly, the recommendation that "exceedances should not occur more than once every three years" (p 2-58) requires more rigorous documentation for the ecosystems in question.
9. The review and discussion of the potential for the influence of mixtures on toxicity is good. The conclusion that only the concentration-addition models are useful for determination of compliance is valid.

Chapter 2 Typographical errors:

- Global: Throughout the chapter, µ/L is often appears where µg/L is intended.
- p 2-17, line 2: RIMV should be RIVM.
- p 2-40, line 1: casue should be cause.
- p 2-49, 2nd to last line: delete extra period after zooplankton.

Chapter 3: Methodology

10. A log Kow database (Sangster Research laboratories, 2004) is recommended for use. This database is appropriate and should be mentioned in Chapter 2 as a source of this information.
11. The recommended use of "... a good solid-water partition coefficient..." to convert total concentrations to dissolved (p 3-7) is appropriate. However, as in Chapter 2, the authors need to qualify the term "good."
12. The section on sensitive species (p 3-19) states that a calculated criterion that exceeds toxicity values for a "particularly sensitive species" may require downward adjustment. How could data this important have been excluded from the original derivation of the criteria?
13. As in Chapter 2, the new methodology does not include a provision for use of quantitative structure activity relationships (QSARS) except for application to threatened and endangered species (p 3-22). In addition to the questions about the chemical's mode of action, toxicity estimates derived from QSARS for a surrogate species may not reflect the sensitivity of the species in question. For these reasons, the authors rightfully conclude that it may not be possible to assess whether the criteria will be protective of threatened and endangered species.
14. Figure 3.1 presents a flow chart that shows a decision point for ecotoxicity data. It appears that a "No" answer to the question of data availability can lead directly to the same "Evaluate and select data" activity as a "Yes" answer. How is this possible? Shouldn't the line that directly connects "No" to "Evaluate and select data" be removed?

Chapter 2 Typographical errors:

- Global: Throughout the chapter, μ/L is often appears where $\mu g/L$ is intended.
- p 3-13, line 14: characteristic should be characteristics.
- p 3-21, 2nd line in 3-6.4: sentence should read "However, few tools..." instead of "However, a few tools..."
- Figure 3.2, 2nd line from bottom: "harmonizaiont" should be "harmonization."

COMMENT LETTER 3

This document provides an excellent description of modifications of existing approaches and procedures for development of new methodology for derivation of pesticide water quality criteria for protection of aquatic life. There is particular attention to critical evaluation of extant data for inclusion in the derivation process, exposure duration/concentration/response relationships, and selection of the appropriate frequency distribution to avoid violation of assumptions necessary for statistical analyses. There are several technical points worthy of additional consideration prior to adoption of the methodology. These are given in the context of evaluation of the strengths and weakness of the methodology below.

Accuracy and Completeness

Development of the new methodology largely derives from procedures drawn from six existing methodologies: two from the United States Environmental Protection Agency (USEPA); one each for Canada, Australia/New Zealand, The Netherlands, and the European Union. All of these use results of toxicity tests with aquatic animals as the fundamental basis for derivation of numerical criteria. Applicable responses include mortality, and reductions in growth and/or reproduction. Responses such as enzyme inhibition or increases in proteins that contribute to adaptation to contaminants (e.g., cytochrome P450s) do not directly apply to criteria derivation. They are “non-traditional endpoints” that only can provide supporting information. There are significant barriers to application of biochemical or molecular measures of exposure or response (biomarkers) to population level responses. However, results of traditional toxicity tests do not consider some very significant ecological risks. Two examples are: increase in disease susceptibility, and disruption of ion regulatory changes during smoltification for anadromous salmonids. The data necessary to consider such toxicities in ecological risk assessment and water quality criteria are usually not available. This reflects failure to invest in the science not limitations in technology. Fully addressing this issue is outside the scope of this document but it is an important limitation in derivation of water quality criteria for protection of aquatic life.

The draft report accurately identifies exposure duration is an important factor in addition to exposure concentration (page 2-51). The physical and chemical properties of a particular chemical, and physiological and biochemical processes that jointly determine the disposition of that chemical, underlie time/concentration relationships that contribute to response in a particular organism. Within the context of this complexity and narrowing the chemical universe to current use pesticides, the averaging techniques the draft report advocates are reasonable. The issue of recovery time after toxicity insult to an ecosystem is equally or even more complex. The empirical approach through review of the literature provides a rational approach to placing limitations on exceedances. The case study involving DDT exposure of Atlantic

salmon (page 2-56) illustrates that allowable frequency of exceedance may protect in the majority of instances but for animals with long, complex life history problems may arise.

The twelve practices for data reduction in the new methodology are reasonable and complete.

Appropriateness of Approach

As stated above, the new methodology refined existing approaches. The process for derivation of water quality criteria for pesticides follows two different general approaches: One is for pesticides for which results from a good number of reliable and relevant toxicity studies are available (species sensitivity distribution). Another is for pesticides for which results for a minimal number of toxicity tests are available (assessment factor). These approaches are consistent with current regulatory practice and are likely to provide acceptable criteria. The empirical work to identify the appropriate frequency distribution for the species sensitivity distribution is robust.

There are a number of instances in which the text refers to "extrapolation" between values (e.g., page 2-4, paragraph 2). First, interpolation is the correct term if one is estimating the position of a point on a line between two other points. Second, the maximum allowable toxicant concentration is the chronic value used in derivation of criteria in the new methodology. The draft does not clearly describe process for deriving this value.

One of the major barriers to protection of aquatic life with this or any methodology is data scarcity. The draft clearly describes and evaluates derivation of assessment factors in an effort to set protective criteria with few data. A concern lingers: how can the new methodology discourage registrants from selecting resistant organisms for toxicity testing? The species sensitivity distribution requires data for a salmonid, typically sensitive species. The new methodology for the assessment factor procedure requires data for the family Daphniidae. Is it certain that a data for a resistant species in this family might not yield under-protective criteria?

Evaluation and Interpretation

Interpretation of the literature and regulatory guideline documents in the draft report is consistent with the current conceptual framework for ecotoxicology. The data summary sheet in Appendix 3a (Figure 3.3) is very useful for assuring consistent and rigorous evaluation of toxicity test results by those applying the new methodology. The guidance for data collection, evaluation, and reduction is very good. Consideration of mixtures is more than adequate. The information available allows reasonable quantification of additive toxicity for some classes of pesticides. Dealing with non-additive interactions such as antagonism or synergism is extremely difficult and I believe the draft addresses what is feasible. Interactions with water

quality parameters are potentially problematic. A specific concern about temperature receives attention in the review of the draft Chlorpyrifos Criteria Derivation.

Additional Scientific Issues

The draft points out that interspecies correlation estimation software developed by USEPA works well within taxonomic families (page 2-8). There is also a recommendation to eliminate toxicity test results for species that do not reside in North America (page 3-1). Since data limitation is a major source of uncertainty in criteria derivation it seems wise to reconsider this recommendation. A number of genera of aquatic life occur in California and Asia (especially Japan and South Korea). Multiple but distinct species of the genus *Oncorhynchus* (Pacific salmon) occur in California and Japan. If toxicity test results for these species from Japan were available it seems wasteful of resources not to consider them for use in the new methodology. This seems especially important since there are threatened or endangered species of salmon in the Sacramento River basin. The situation for aquatic insects is similar. A number of genera are common to California, Asia, and Europe. The caddis fly genera of the Pacific Northwest derive from Asia. A phylogenetic rather geographic basis seems more reasonable for inclusion of toxicity test results for aquatic species.

There is no requirement to include toxicity test results for a freshwater aquatic plant in the new methodology unless the pesticide is an herbicide. It is unlikely but possible that an insecticide might exhibit unpredictable phytotoxicity. One compromise is to require examination of data for tests with marine or terrestrial plants as supplemental information that is not part of derivation of numerical criteria (this was done in the draft Chlorpyrifos Criteria Derivation).

Scientific Basis of Report

The report addresses assumptions common to all modeling efforts for derivation of water quality criteria for protection of aquatic life. It also considers an extensive body of the literature in methodology development. It employs direct and rational approaches to data reduction and analysis. These are significant strengths of the draft report. Most of the limitations the text above addresses stem from data scarcity and gaps in the theoretical basis for ecological risk assessment. To the extent possible, environmental regulators must foster generation of quality data in the pesticide registration process. If registrants accept that more rather than less data provides more rational criteria it may encourage conduct of the work necessary for more rigorous methodology such as the species sensitivity distribution approach.

COMMENT LETTER 4

Thank you for the opportunity to review the draft report, *Methodology for Derivation of Pesticide Water Quality Criteria for the Protection of Aquatic Life in the Sacramento and San Joaquin River Basins, Phase I: Methodology Development and Derivation of Chlorpyrifos Criteria*. When Dr. Patti TenBrook, University of California, Davis, requested my review, she asked me to respond to specific questions related to the draft report and to submit separate comments for the Executive Summary and Chapters 1 through 3 and for Chapter 4. My comments on the Executive Summary and Chapters 1 through 3 are presented below.

1. Accuracy and completeness of the information presented: Are any important methodologies, references or other information missing?

General Comment: The information is complete and appropriately referenced, particularly when the Phase I and Phase II reports are considered together. Specific Comments on Section 2-2.5.2: This section describes how ecotoxicity data are evaluated for inclusion in subsequent criteria setting procedures. The section references ECOTOX (2006), which provides directions for quantitatively scoring the completeness of the data's accompanying documentation. (Table 1 [Documentation Code Scoring for Aquatic and Terrestrial Laboratory/Field Data] in ECOTOX [2006] provides a scoring scheme for documentation). The section also notes that the data's acceptability and relevance need to be evaluated as well, but is unclear how to do so. "Weighting of scores for acceptability is based upon test acceptability criteria as stated in standard methods," but such methods are not references or further described. Similarly, the section notes that ". . . elements for judging relevance . . . can be weighed and rated in a similar fashion," but the reference is unclear. Also, the system for scoring relevance needs to weigh "critical factors," but the report does not provide guidance on how this should be done. Additional explanation is needed for a reader to independently understand scoring criteria for acceptability and relevance and how they are applied.

The third paragraph in the section describes how reliability scores (the average of the documentation scores and acceptability scores) and relevance scores are used to select ecotoxicity data that will be used to calculate water quality criteria. As proposed, the selection process depends on how a data score compares to other scores (i.e., in the 75th or higher percentile of all scores), not whether a score meets a predetermined measure of quality. This may inappropriately exclude high quality data that may not qualify—compared to other data—as top quality data. A study's reliability and appropriateness for criteria setting should be judged on its own merits, not how it compares to other toxicity studies. The authors should more fully explain why they prefer their proposed measure of quality to a more absolute measure of quality. Is there precedence for distinguishing data quality in this way? If so, references would be helpful. In addition, the report does not provide a compelling defense for using the 75th percentile as a cutoff for data to be used in the final derivation.

Lastly, note that the citation for ECOTOX (2006) on page 2-12 appears misplaced on page 3-25.

2. Appropriateness of the approach used to compare and assess methodologies.

The authors gave a logical, well-researched, and well-referenced approach for comparing, assessing, and recommending methodologies for criteria development. The Phase I report offers an excellent complement to the Phase II report in this regard and provides essential information for understanding how the methodology was selected.

3. Evaluation and interpretation: Are the key features of the methodologies evaluated thoroughly and correctly? Are strengths and weaknesses identified? Are conclusions supported?

Except where noted in this review, the authors thoroughly and correctly evaluated and presented the key features of the methodology, particularly when the Phase 2 report is read with the Phase 1 report as a resource.

One of the key features of the methodology is the selection of the distribution used to characterize the toxicity data set. As the report—and the Phase 1 report—makes clear, several distributions have been used worldwide and all of them (log-normal, log-logistic, log-triangular, and the Burr Type III distributions) typically show a good fit for the data and provide for the derivation of protective criteria. The authors' preference for the Burr Type III distribution is based on its performance when a "goodness of fit" comparison was made among the log-normal, log-triangular, and Burr Type III distributions, and on its capability to deal with data sets that violate assumptions of log-normality. Because the fits of the log-normal and Burr Type III distributions were apparently very close and because the toxicity data sets that provide the basis for these comparisons can change through time, it would not be surprising if—with the addition of additional toxicity values—the outcomes of fitness comparisons were different. Given these apparent conditions, would it be more appropriate to derive the criteria based on which distribution fits the data best on a case-by-case basis? This approach is apparently similar to that used by the Dutch and the Danish, as stated in Section 7.2.2.1. of the Phase I report.

4. Are there any scientific issues that should have been addressed in the report, but were not included?

The report should acknowledge that the proposed methodology is sensitive to the assortment of species that represents each of the five taxonomic categories. For example, the final acute toxicity data set for chlorpyrifos presented in Table 4.1 includes 96 hour LC/EC50s for channel catfish (*Ictalurus punctatus*; 806 µg/L) and bluegill (*Lepomis macrochirus*; 10 µg/L). Each could

represent the “warm water fish” requirement; each has very different sensitivity to chlorpyrifos. If, hypothetically, the warm water fish requirement were satisfied only by bluegill or only by channel catfish, the resulting criteria could be quite different, particularly if the rest of the data set representing the other four categories were small. It appears that the only way to counter this effect is for agencies to have the flexibility to revise criteria at reasonable intervals to account for new toxicity data and expanded data sets.

5. Taken as a whole, is the analysis in the report based upon sound scientific knowledge, methods, and practices?

Yes. The report was well researched, and the references were objectively reviewed.

Most of the proposed methodology has underlying statistical principles that are undoubtedly full of nuance. I do not know the expertise of your academic peer reviewers, but I trust that you sought out experienced applied statisticians who could effectively comment on the method's statistical underpinnings. I recommend that you help assure that someone with a lot of experience with applied statistics has an opportunity to review the proposed methodology. Thank you for your consideration of these comments—I hope they are helpful. Please feel free to contact me if you have any questions.

Comments on the Application of the New Methodology to Chlorpyrifos

COMMENT LETTER 1

Overview

In Chapter 4 is presented a draft of proposed acute and chronic chlorpyrifos criteria based on the new methodology. Approximately 340 studies of the effects of chlorpyrifos on aquatic life were identified and evaluated. Ultimately, 22 acute studies yielding 58 toxicity values were judged relevant for criteria derivation (presented in tables 4.1 and 4.2, appendix 4A). Of the 22 studies, 4 chronic studies yielding 19 toxicity values were deemed relevant and reliable based on the new methodology. The authors obviously undertook a thorough examination and compilation of existing studies.

The authors provide a rationale for exclusion of non-qualifying studies. Because formulations of chlorpyrifos (as opposed to pure compound) were used in studies of the effects of chlorpyrifos on freshwater plants, these studies were excluded in criteria derivation. Similarly, several microcosm and field studies used chlorpyrifos formulations and thus were excluded. Some acute and chronic data that were deemed acceptable for evaluation were reduced in accordance with the data reduction strategies established in the new methodology (tables 4.1-4.4). For some of these studies, no NOEC, LOEC or MATC had been determined or there were other studies available that were conducted under similar conditions but exhibited less variation in responses, used more sensitive endpoints, or employed flow-through dosing procedures. The reviewer could find no evidence to suggest bias in exclusion of studies.

The information is summarized in several appendices and a comprehensive set of citations is provided. A few references pertaining to physicochemical characteristics of chlorpyrifos are from unpublished reports from the manufacturer, whereas the bulk of the references arise from the ecotoxicology literature and from state and federal regulatory documents. The references appear appropriate.

Information in the summaries was used to evaluate each study for reliability based on the rating system established in the new methodology. Final acute and chronic data sets used to establish the criteria are presented in two tables (4.1 and 4.3). Five acceptable acute toxicity values were ultimately available to derive acute criteria, and the SSD procedure was used to derive fifth percentile values as well as first percentile values. An acute value of 0.026 ug/L was recommended that represented the median fifth percentile value derived from the SSD procedure, and an acute criteria of 0.013 ug/L (incorporating a safety factor of two) was ultimately established.

Further incorporation of assessment factors was applied to the chlorpyrifos datasets to determine the range of acute criteria that would establish chronic criteria, and dependent upon whether the data set contained 1, 2, 3, or 4 values. Because fewer than 5 chronic toxicity values from five different families were available, the ACR (acute-to-chronic ratio) method was used to establish a final chronic criteria of 0.003 ug/L. The draft final criteria was concise and was stated as follows; "Aquatic life in the Sacramento River in San Joaquin River basin should not be affected unacceptably if the four-day average concentration of chlorpyrifos does not exceed 0.003 ug/L more than once every three years on average, and if the one-hour average concentration does not exceed 0.013 ug/L more than once every three years on average".

Comment on discrepancies among the proposed and existing criteria

The criteria proposed are lower than the USEPA chlorpyrifos acute and chronic freshwater criteria of 0.083 and 0.041 ug/L established in 1986. The proposed criteria were also lower than the current water quality objectives for the lower San Joaquin and Sacramento Rivers, which, for acute and chronic exposures, are 0.025 ug/L and 0.015 ug/L, respectively. The older values were established by CVRWQCB in 2005-2006 based upon criteria derived by California Department of Fish and Game using the 1985 USEPA methodology. The new methodology provides criteria with a larger margin of safety.

Because the authors derived a new methodology which was a hybrid of other methods, it is not surprising that the new draft criteria would differ from that previously established. The authors report that the median 95th percentile acute value determined by the new methodology (0.026 ug/L) is relatively similar to that determined by the US EPA (0.032 ug/L). The discrepancies in the final two criteria values appear to be largely based upon the selection of different data sets. In this regard, the current data set includes 22 studies published after the EPA established chlorpyrifos criteria in the 1986 document and is thus more relevant given the availability of new data over the past 20 years.

Fewer than five chronic toxicity values from five different data sets were available to help establish chronic criteria. Three chronic values had corresponding acute values, including two for Ceriodaphnia and one for fathead minnow. There were not three chronic data for which corresponding acute values existed from at least three different families. Accordingly, an acute-to-chronic ratio (ACR) was applied to the 5th percentile. The chronic criteria of 0.003 ug/L reflected an acute 5th percentile value of 0.026 ug/L divided by 9.06.

Similarly, the prior chronic values derived in the US EPA methodology used the ACR approach, but the ACR in the new methodology was 9.06, which differed relative from that from the USEPA which was 4.064. The authors might further comment on these differences, and specifically if the ACR in the original US EPA method was also applied to the 5th percentile.

Critique of other considerations in the development of the new criteria

Several threatened or endangered species inhabit the San Joaquin's Sacramento ecosystems, including chinook salmon, Lahontan cutthroat trout and Colorado squawfish. For two of these species, (steelhead and chinook salmon), there are acute values that indicate the acute criterion of 0.013 ug/L should be protective. However, none of the other listed animals or plants were represented in acute or chronic toxicity data sets. Some listed species were represented in the acute data set by members of the same family or genus. In those situations, interspecies correlation estimations were applied to estimate toxicity values. This is an area of some uncertainty for fish, as closely related species may differ with regards to chemicals susceptibility. None of the chlorpyrifos studies involved plants on the state or federal endangered, threatened or rare species list. However, based on the available scientific data and the safety margins supplied, there is not evidence that the calculated acute and chronic criteria would be underprotective of threatened or endangered species. The estimated chronic value of 0.001 ug/L for *Neomysis mercedis*, a sensitive species, was below the proposed chronic criterion, but it was recommended that the chronic criteria and not be adjusted until the estimated value for *Neomysis* is validated. This is reasonable. Accordingly, the acute chronic criteria as calculated seem to be justified in regards to the protective of sensitive species based on single species toxicity tests.

Although there's evidence in the literature to suggest that temperature can affect chlorpyrifos toxicity, there does not appear to be enough published data to adequately quantify this relationship, and therefore only tests conducted at standard temperatures were included in the data set. This is another area of uncertainty of relevance to the San Joaquin and Sacramento River systems. Specifically, is it reasonable assume that temperatures will fluctuate and specifically rise during some parts of the year and stress of fish? If so, could this potentially coincide temporally to situations when chlorpyrifos is applied and enter receiving waters? The reviewer could not get a clear sense of the potential magnitude of temperature effects on toxicity. However, the authors approach to this issue given the lack of scientific data and a limited state of knowledge appears reasonable. The safety margin applied to the draft criteria will likely be protective given temperature considerations, but again, it needs to be acknowledged that this is a potential area of uncertainty.

The safety margin applied to the chronic criteria is also probably appropriate given that there are studies available that report the occurrence of sublethal effects of chlorpyrifos, including those on skeletal deformities and neurobehavioral indices. It was decided (justifiably) not to quantitatively consider sublethal effects in the new methodology because of the poor linkages to population effects.

The mean log Koc value of 4.064 for chlorpyrifos was used to relate total concentrations of chlorpyrifos in water to dissolved concentrations and thus compliance with bioavailability

considerations. Based on its physicochemical properties, chlorpyrifos has the potential to bioaccumulate in fish and plants. Several studies have demonstrated the potential for chlorpyrifos to bioconcentrate in fish. Unfortunately, there are no tolerance or FDA action levels for fish tissues, and only a few reported NOEC values (46 mg/kg, 30 mg/kg, 25 mg/kg) available for Mallard ducks. Based upon a dietary NOEC of 25 mg/kg in mallards from one study (Fink and Beavers, 1978), the calculated acute and chronic criteria are at least 50-fold below the estimated NOEC values, and should thus provide a reasonable safety factor for adverse effects due to bioaccumulation.

A fugacity-based environmental equilibrium partitioning model was used to estimate equilibrium concentrations of chlorpyrifos expected in sediment, biota and air based upon the chronic criteria of 0.003 ug/L. The values for model parameters appear appropriate, but it is unclear how changes deviations in water temperature (25°C was used in the model) may potentially affect partitioning. A brief comment on the sensitivity of equilibrium partitioning during temperature fluctuations would be helpful. However, the reviewer admits that this may be a “non-issue”, as there are no federal or state air or sediment quality standards for chlorpyrifos. Again, the margin of safety built into the chronic criterion suggests that the final value should not cause problems in other environmental compartments.

Minor comments:

There are a few spelling errors in Chapter 4, including the spellings that of:

1. chlorpyrifos on the bottom of pages 4 – 3, as well as on pages 4-4, 4-6
2. “lowest” is misspelled on page 4-13, third full paragraph.
3. “sensitive species” are both misspelled- third full paragraph page 4-13

Overall Evaluation:

Consistent with the earlier documents which formed the basis for the development of the new methodology, it is my opinion that the draft criteria presented in this document are based upon a thorough and reasonable evaluation of prior studies. I could find no major scientific inaccuracies or omissions in this chapter.

COMMENT LETTER 2

Review of draft chlorpyrifos criteria (Chapter 4)

Chapter 4 provides the derivation of acute and chronic water quality criteria for chlorpyrifos in the Sacramento and San Joaquin River basins. These criteria were derived using methods defined in Chapters 1-3 of this report. The recommended criteria of 0.013 µg/L for acute and

0.003 µg/L for chronic protection of aquatic life would provide more realistic standards for protection than existing USEPA (1986) criteria. The recommended criteria are lower than existing USEPA criteria, which is not unexpected given that the recommended criteria were derived from more recent data that has been subjected to rigorous acceptance criteria. Given that the USEPA chronic criterion of 0.041 µg/L is higher than the lowest reported acute value of 0.035 µg/L for *Daphnia ambigua*, a downward revision of the criteria is clearly in order to provide adequate protection of aquatic life.

Overall, the report positively addresses the review criteria of accuracy, appropriateness, and interpretation. Taken as a whole, the criteria derived from the developed methodology are based on commonly accepted knowledge, methods and practices. The overall approach is conservative (e.g., use of most sensitive species and/or life stage), which is an appropriate and accepted approach for the protection of aquatic life. The literature reviewed is appropriate as is the rationale for the acceptance or rejection of toxicity test data.

Because the new criteria were being derived specifically for the Sacramento and San Joaquin River basins, it is imperative that site-specific factors be evaluated. In this respect the report falls short. As written, it provides a generic derivation of freshwater criteria for chlorpyrifos. Although a more thorough evaluation of site-specific factors may not alter the derived criteria, it would meet the intended objective of this effort.

Because comments specific to the criteria derivation methodology have been previously presented, only comments specific to Chapter 4 are listed below.

1. Because all of the data for freshwater plant studies were derived from studies that used formulations of chlorpyrifos, the data was not acceptable for use in the derivation of criteria. The authors conclude, "setting criteria without plant values will not lead to underprotective criteria." Although this is a reasonable conclusion based on data from saltwater species, it would be useful to estimate toxicity to freshwater species based on the knowledge of the applied formulations. This would strengthen the basis for this conclusion.
2. The discussion of chlorpyrifos toxicity in ecosystem studies, including those from the Sacramento-San Joaquin River Delta (Werner *et al.*, 2000), does not address potential differences in bioavailability between this ecosystem and standard laboratory derived toxicity tests. Although data appear to be sparse, this step in the criteria development needs to be specifically addressed.
3. Section 4-15.0 (Harmonization/coherence across media) should be tailored to encompass known conditions in the Sacramento and San Joaquin River basins. The default values (i.e., 0.2 g/g for organic carbon and 7.5 mg/L for suspended sediment) appear to be generic and need to be put in the context of these ecosystems.

Typographical errors:

- Global: Throughout the chapter, µ/L is often appears where µg/L is intended.
- p 4-9, 3rd paragraph, line 11: provide should be provided.

- p 4-11, 2nd paragraph, line 6: “with not other pesticides” should be “with no other pesticides.”
- p 4-13, 2nd paragraph, line 4: “acuate” should be “accurate.”
- p 4-13, 3rd paragraph, line 1: “lowes” should be “lowest.”
- p 4-13, 3rd paragraph, line 3: “sensitivie apspecies” should be “sensitive species.”
- p 4-13, 3rd paragraph, line 5: “marging” should be “margin.”
- Tables 4.5, legend: “derivtion” should be “derivation.”

COMMENT LETTER 3

Applying the new methodology that is a Phase II product of this project to derive draft water quality criteria for chlorpyrifos is worthwhile and prudent. It provides context for interpreting the potential regulatory issues resulting from proposing new standards for pesticides for protection of aquatic life in the Sacramento and San Joaquin River Basins.

Accuracy and Completeness

Derivation of the draft chlorpyrifos criteria follows the methodology described in the Phase II: Methodology Development document and is accurate and complete in that sense. After application of rigorous data quality standards a good number of results for acute toxicity studies with aquatic life (22) are available. This allows application of the species sensitivity distribution approach for derivation of the acute criterion. There is a much smaller data base for chronic studies (4). This results in application acute-to-chronic ratio methodology for derivation of the chronic criterion. Working through the new methodology with a specific example is an essential test of strengths and weaknesses of it. Derivation of the new acute criterion yields a concentration about two-fold lower than existing objectives for the lower San Joaquin River. This is almost certainly protective and a rich data set supports acceptance. Derivation of the new chronic criterion yields a concentration about five-fold lower than existing guidance. The small amount of data that qualifies for inclusion in derivation is problematic in this case. The relatively large acute-to-chronic ratio the new methodology applies drives the criterion. This is likely to draw scrutiny and criticism from those subject to regulation since no new empirical evidence underlies the change. One potential remedy is new studies with cladocerans and insects that might permit application of the species sensitivity distribution approach to a chronic criterion.

Appropriateness of Approach

The approach to derivation of the chlorpyrifos criteria is quite appropriate since it applies new methodology to a specific data set to yield numerical results suitable for comparison to results of other methodologies.

No data for freshwater plants were acceptable for the new methodology (page 4-4). Data for saltwater plants indicated insensitivity to chlorpyrifos in terms of growth inhibition. It seems the new methodology should either require data for freshwater plants or formally incorporate conditions for substitution of data for plants from other environments.

The new methodology selects data for pesticide accumulation that are lipid-based. The rationale for this is unclear. One argument is that lipid-based concentrations may correct for condition (fat content) of individual animals. At very high tissue concentrations of legacy persistent organic contaminants body lipid content may be an important determinant of bioaccumulation. At concentrations of current environmental relevance with current use pesticides this is not consistently the case.

Evaluation and Interpretation

Evaluation of the results in the draft includes comparisons the chlorpyrifos criteria that the new methodology yields to those older methodologies provide. They are consistently lower (page 4-13). The authors identify the factors that underlie the result.

Chlorpyrifos toxicity is primarily due to inhibition of acetyl cholinesterase activity. This mode of action is common to organophosphate and carbamate insecticides. An additive model for interaction of these insecticides might be of substantial value to protection of aquatic life. Examination of monitoring data for the Sacramento and San Joaquin River basins can provide insight into potential importance of this approach.

Additional Scientific Issues

The ability to monitor chlorpyrifos concentrations in aquatic ecosystems to assess compliance with the criteria is another issue. There is no reference to requirements for monitoring frequency in the Phase II documents. The methodology for derivation describes estimation of dissolved pesticide concentrations from measurements of total concentration. Using this approach for gathering the data necessary for calculating four day average concentrations on a river basin scale is a major logistical issue. Passive sampling devices may greatly increase capacity for a monitoring program.

Scientific Basis of Report

This report follows the process the "Methodology for derivation of pesticide water quality criteria for the protection of aquatic life in the Sacramento and San Joaquin River Basins" describes. The major scientific issue is the adequacy of survival, growth, and reproduction data from toxicity tests with aquatic organisms for derivation of criteria to protect integrity of

aquatic ecosystems. The weight of evidence supports this approach. The major technical issue is availability of adequate high quality data for robust analysis such as the species sensitivity distribution. This report demonstrates that application of the acute-to-chronic ratio approach with the new methodology can yield criteria that differ substantially from existing guidance. Those subject to regulation are likely to contest such new standards. Public policy decisions determine whether new work is available and the mechanism for supporting it.

COMMENT LETTER 4

Thank you for the opportunity to review the draft report, *Methodology for Derivation of Pesticide Water Quality Criteria for the Protection of Aquatic Life in the Sacramento and San Joaquin River Basins, Phase I: Methodology Development and Derivation of Chlorpyrifos Criteria*. When Dr. Patti TenBrook, University of California, Davis, requested my review, she asked me to respond to specific questions related to the draft report and to submit separate comments for the Executive Summary and Chapters 1 through 3 and for Chapter 4. My responses on Chapter 4 are presented below.

1. Accuracy and completeness of the information presented: Are any important methodologies, references or other information missing?

Appendix B presents data summary sheets for data rated as reliable and relevant. These sheets are very clear and their inclusion in the report was very helpful. The summary sheets of studies that were not included in the final analysis would be helpful as well. Additionally, all summary sheets should include rating scores. Without them, readers cannot appreciate the scope of the studies, nor can they understand why some were deemed reliable and relevant and others were not.

2. Appropriateness of the approach used to compare and assess methodologies.

For the most part, the application of the methodology described in the Chapters 1-3 is appropriate. It is unclear, however, why the calculation of the final multi-species acute-to-chronic ratio (ACR) on page 4–6 used a default value of 12.4. The 12.4 value was derived, as explained on page 2–51, as the 80th percentile value of the ACRs of eight pesticides, including chlorpyrifos. Under these circumstances, would it be more appropriate to use that chlorpyrifos ACR instead of a generic, multi-pesticide one? More explanation would be helpful.

3. Evaluation and interpretation: Are the key features of the methodologies evaluated thoroughly and correctly? Are strengths and weaknesses identified? Are conclusions supported?

Yes, unless otherwise noted in this review.

4. Are there any scientific issues that should have been addressed in the report, but were not included?

The report appears complete, unless otherwise noted.

5. Taken as a whole, is the analysis in the report based upon sound scientific knowledge, methods, and practices?

Yes.

ATTACHMENT 3

Central Valley Water Board Staff Comments

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Linda S. Adams
Secretary for
Environmental Protection

California Regional Water Quality Control Board Central Valley Region

Robert Schneider, Chair



**Arnold
Schwarzenegger**
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26 September 2006

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METHODOLOGY FOR DERIVATION OF PESTICIDE WATER QUALITY CRITERIA, PHASE II REPORT – STAFF REVIEW COMMENTS

Please find enclosed staff comments on the peer review draft of the *Methodology for Derivation of Pesticide Water Quality Criteria for the Protection of Aquatic Life in the Sacramento and San Joaquin River Basins, Phase II: Methodology Development (Phase II Report)*. These comments include technical and policy issues that were withheld until after the scientific peer review.

In addition to the enclosed peer review comments, I have also enclosed a redline copy of the Phase II report. This redline copy includes miscellaneous typographical errors and some margin notes that may help to elucidate our comments. The margin notes are included as useful information. Only the formal comments in Enclosure 1 need be addressed.

Prior to making changes to the Phase I report, I would like to arrange a meeting with the project team to discuss these comments. I want to make sure that the comments and proposed document changes are mutually understood and agreed upon; and that any potential impacts to the existing scope of work are addressed. If you have any questions about this information, please call me. Thanks again for your hard work.

Paul Hann
Environmental Scientist
Pesticide TMDL Unit

Enclosure(s): 1

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Staff Comments on the Derivation of a Methodology for the Establishment of Water Quality Criteria for the Protection of Aquatic Life

Overall, the report is very well organized and demonstrates a clear understanding of the factors that must be considered in deriving pesticide water quality criteria. The following comments include both technical comments and formatting or clarification suggestions.

There are several important technical issues that should be addressed in the revision of the document.

Bioavailability

Staff had several concerns about the treatment of bioavailability, especially in regards to sediment load. Staff is concerned that the discussion of bioavailability is not sufficiently supported to allow criteria derived by the method to withstand US EPA review. Specific concerns are enumerated below:

1. The report needs to clarify the language used to discuss dissolved concentrations and sediment load. The calculation of the pesticide concentration in the dissolved phase is discussed in the “bioavailability” section (section 2-3.5.1). Staff recommends that this section be renamed “Calculation of Dissolved Concentration”. An assumption is being made that the dissolved concentration is equivalent to the bioavailable concentration.
2. The methodology assumes that the exposure pathway is water-only (section 2-2.1.1.5). Presumably this assumption is based on how most toxicity tests are conducted – in laboratory water that is free of sediment. However, laboratory test animals are also fed during the course of the test. Toxicity test results, therefore, do not generally distinguish whether the effect was caused solely by water exposure or whether there may have been dietary exposure as well (i.e., the contaminant sorbed to the food particles and then de-sorbed upon ingestion).

It is probably more accurate to say that comparing the dissolved concentration to the criteria is consistent with basis for the derivation of the criteria. In other words, the toxicity tests used are based on exposure to dissolved pesticide concentrations, so we should only compare dissolved pesticide concentrations to the criteria. However, this is only a valid rationale if it can be shown that dietary exposure did not occur during the toxicity tests).

3. Additional justification for the assumption that toxicity tests represent a water-only exposure pathway should be provided. In the absence of sufficient support for this assumption, the criteria should be based on a whole water sample. Sediment load could be handled on a case-by-case basis as data becomes available consistent with the recommendations of section 2-3.5.3.

4. If dissolved concentrations are the basis for evaluating the criteria, the author should address a potentially more straightforward way of determining compliance such as simply filtering the sample prior to analysis. Analyzing the sample for percent organic carbon and suspended solids and then calculating the dissolved concentration from the total pesticide concentration could potentially introduce much more error into the evaluation of compliance.

Level of protection to be provided by criteria

5. In section 2-3.0, the authors indicate that the aim of the criteria calculation is to protect all species in the aquatic ecosystem. This statement is consistent with the Regional Board's narrative toxicity objectives. The authors should refer to this goal in a consistent manner throughout the document. Sometimes the authors refer to protection of "ecosystems" (e.g., 2-3.1.4.1), which could be interpreted as a different goal from protecting "all species" within the ecosystem.

Justification for 5th percentile

6. In a number of places, the authors refer to the 5th percentile as a generally accepted no ecological effect level (see for example sections 2-3.1, 2-3.1.4.1). There should be more discussion of and justification for the choice of the 5th percentile. It is not clear whether the other methodologies chose the 5th percentile based on ecological considerations or statistical considerations (i.e., it is hard to have a high degree of statistical confidence in a number based on a percentile lower than the 5th percentile).
7. The RIVM (2001) method and the ANZECC & ARMCANZ (2000) methods apply the 5th percentile to NOEC data, while the US EPA method applies the 5th percentile to LC50 data. It is unclear how use of the 5th percentile applied to different effects data can provide similar ecological protection.
8. The authors should discuss how the use of the 5th percentile applied to MATC data and the 5th percentile divided by 2 applied to LC50 data is expected to meet the aim of the criteria to protect all aquatic species.
9. Section 2-3.1.4.6 indicates that the final criteria will be derived using the 5th percentile divided by two. The stated purpose of the ½ factor is to compensate for the fact that the Acute Criterion is based on toxicity values that give a 50% value. However, no justification is given for the choice of ½ versus some other factor. The choice of the safety factor should be justified in the report.

Definition of acute vs. chronic toxicity data (section 2-2.1.1.1)

10. The section defines acute and chronic toxicity and identifies the types of acceptable tests. The authors do not mention in this section acceptable endpoints for acute versus chronic toxicity tests. Are acute tests intended to generally be measurements of lethality or immobility and chronic tests measurements of growth, reproduction, and other non-lethal effects linked to survival?

Discussion of “no-effect” level

11. In the 3rd paragraph in section 2-2.1.1.2, there is a discussion of equating an EC_x level to a “no-effect” level. Since EC_x represents a concentration at which an effect is observed, it is not clear what is meant by a “no-effect” level.

Use of Non-traditional endpoints

12. On page 2-5, there is a discussion of the use of non-traditional endpoints, such as evaluation of AChE inhibition. In this discussion it is not clear in referring to “significant” mortality, whether the authors are referring to statistical significance or ecological significance. The two concepts appear to be used interchangeably. A prediction of mortality (7.5% for Chinook salmon) would seem to be pretty significant from an ecological standpoint, although a standard toxicity test may have trouble identifying statistically significant toxicity (in comparison to controls) unless mortality is greater than 10%.

Clarification of the type of species to use

13. The discussion in section 2-2.4 (page 2-10) critiques the Dutch data tables for not indicating whether the test organisms reside in areas relevant to ecosystems of interest. This statement could suggest that only species resident to the Sacramento and San Joaquin valleys should be used in criteria derivation, although the proposed methodology suggests that North American species should be used. This should be clarified in the methodology. In addition, the “table” referred to in this paragraph should be referenced.

Discussion of Bimodality (section 2-2.7, page 2-16)

14. In looking for bimodality in the distribution of toxicity data, is it important that the two groups have common features (e.g., vertebrates vs. invertebrates), or is it just important that there is a bimodal distribution? Is the bimodality to be tested, or is it a judgment call based on visual observation of the data distribution?

Standard conditions

15. On page 2-17, under item 11, “standard conditions” should be defined.

Fitting the Distribution

16. In Section 2.3.1.1, the choice of appropriate distribution is discussed. The Burr family of distributions is recommended (pg. 2-34). However, in the report, the authors tested a number of different distributions to determine which distribution generally fit for pesticides. Rather than select a specific distribution (or family of distributions), could the goodness of fit be compared among several distributions, prior to selecting the appropriate distribution to use for a given pesticide?

Saltwater vs. freshwater

17. The US EPA has generally separated saltwater criteria derivation from freshwater criteria derivation. The authors suggest (section 2-3.1.3) that saltwater and freshwater organisms can be included in the same data set. Is there justification for this?

Derivation of Application Factors

18. It is not clear from the discussion in Section 2-3.2.3.1 how the application factors were derived. Were they derived from DDT only or calculated as the average of all application factors for the pesticides in table 2.1? Table 2.6 (DDT only) and table 2.8 differ slightly for the sample sizes of 5 and 2 and are the same for samples sizes of 4, 3, and 1.

Calculation of ACRs

19. The report indicates that ACRs should be calculated for species whose SMAVs are close to the acute criterion. "Close" should be defined.
20. The ACRs as presented in Table 2.9 for chlorpyrifos and diazinon should be based on the California Dept. of Fish and Games criteria. CDFG includes more recent data for chlorpyrifos and more chronic data for diazinon when compared to the respective EPA criteria documents.
21. Table 3.16 is a reasonable approach to calculating default chronic values when only acute toxicity information is available. However, staff notes that the table is not inclusive of all the common classes of pesticides. The report should specify whether the method could be used to derive ACRs for pesticides classes that are not included in the table. It would seem that this method should only be used if it includes at least one member of the class of pesticides being considered. Also, would it not be more appropriate to determine the ACR based on groupings of similar classes of pesticides (i.e. a separate default ACR when the pesticide of interest is an organophosphate than when it is a carbamate, or a pyrethroid)? Given the small dataset available, calculating the default ACR based on pesticide class might require using the mean or median of the set instead of the 80th percentile.

Averaging periods

22. The sentence defining the averaging period (section 2-3.3) is unclear. The average concentration during the averaging period cannot exceed the criterion, but must be below the criterion.

Acute average period

23. There is a good discussion in section 2-3.3.1 regarding pulsed exposures and delayed or sustained impacts. However, it is not clear how the pulsed one-hour exposures relate to the 96-hour LC50 data that are used to derive the criteria.
24. The discussion regarding diazinon and chlorpyrifos in Section 2-3.3.1 was not clear. If mortality occurs throughout the time period of exposure, then the contaminant levels are important right from the beginning of the exposure. This observation would seem to support having a short averaging period for the acute criterion.

Recovery Index parameters

25. In Section 2-3.4.1, the report assigns several factors to the Sacramento and San Joaquin Rivers to derive a recovery index. The "a" parameter used in this derivation states that unaffected nearby tributaries are expected to be present. This is not likely to be the case in most waters that are surrounded by urban or agricultural areas. In the cases of diazinon and chlorpyrifos, use was fairly ubiquitous, which would limit the number of unaffected tributaries.

Allowable Frequency of Exceedance

26. Does the literature suggest that there should be a differentiation between organisms with a longer life cycle and those with a shorter life cycle in terms of the allowable frequency of exceedances? If the criterion is driven by organisms with a short life cycle, could the frequency of exceedances be safely made greater (e.g., once every year instead of once every three years)? Of course, care must be taken that the aquatic system is not in a constant state of trying to recover from contaminant pulses.

Guideline format (section 2-4.0)

27. Did the authors intend for this section to discuss the format of the criteria documents to be produced and not the format of the Phase II report?

Conclusion

28. There does not seem to be much discussion of or justification for the division by 2 of the 5th percentile SSD to derive the acute criterion. There should be some discussion as to why division by 2 should provide adequate protection. If multiple stressors are present (e.g., habitat, other contaminants) would a greater safety factor be warranted?

Ecotoxicity data evaluation (section 2-2.5.2)

29. In the 2nd paragraph, the authors should clarify whether toxicity tests using product formulations are acceptable. Pesticide toxicity tests may be based on product formulations rather than active ingredient. I would suggest that acceptable toxicity tests only be based on tests run with the active ingredient.

30. The discussion of how reliable data are determined is unclear (3rd paragraph). The discussion suggests that the toxicity data results for a given pesticide are evaluated relative to each other rather than to some absolute criteria. Reliable data are said to "...fall in the 75th percentile or higher of all scores..." In reviewing tables 3.9-3.11 and section 3-2.3.2, it appears the author is referring to a raw score and not a percentile.

ATTACHMENT 4

Statistical Evaluation

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December 4, 2006

Patti L. TenBrook, Ph.D.
Department of Environmental Toxicology
University of California, Davis
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Dear Dr. TenBrook,

I was asked to review and comment on a few statistical aspects of the draft report, "Methodology for Derivation of Pesticide Water Quality Criteria for the Protection of Aquatic Life in the Sacramento and San Joaquin River Basins. Phase II: Methodology Development and Derivation of Chlorpyrifos Criteria." Following is a summary of my findings.

Goodness of fit comparisons

The report uses a pseudo- R^2 approach (described by Erickson & Stephan 1988) to compare goodness of fit for several data sets to log-triangular, log-normal and Burr Type III distributions.

The general area of measuring goodness of fit for nonlinear models is not well organized. In the linear regression case, the R-squared value is 1 minus the ratio of the sum of squares due to residuals (SSR) and the corrected total sum of squares SSTO (sum of the squared residuals after subtracting the overall mean from all observations), i.e., $1 - SSR/SSTO$. A higher R-squared is better; equivalent to a lower SSR/SSTO.

In the linear model case, it is possible to develop statistical theory around the R-squared value, and obtain an overall goodness of fit test for the regression compared to just fitting an overall mean. That's usually denoted as the model p-value in an overall summary analysis of variance (ANOVA) table.

For nonlinear regression, the analogue is usually called a pseudo R-squared. However, there are many different definitions of "pseudo R-squared" floating around. The differences arise due to the use of different sets of assumptions.

There does not seem to be a general statistical theory around these pseudo R-squared values, except perhaps in special cases. But, they are comparable, in the sense that they measure the same thing on the same scale and refer it to the same denominator.

There are other measures available. The first is -2 times the log likelihood ($-2\ln L$). With this measure, smaller is better. The log likelihood is a measure based directly on the probability distribution presupposed by the model. So, it can always be calculated if there is an underlying probability model.

With nested models (i.e., with models where a full model "contains" a reduced model by virtue of having less or restricted parameters), there is statistical theory that allows testing of goodness of fit using the chi-squared distribution with the statistic as the difference of the $-2\ln L$ values and with degrees of freedom equal to the number of parameters that the two models differ by. But, this approach only works with nested models – not with different models.

It is reasonable to compare $-2\ln L$ also. However, models with more parameters generally tend to have higher likelihoods. There are many possibilities to correct this problem. A well-known one is the Akaike information criterion (AIC). This one is $2p - 2\ln L$, where p is the number of parameters. So, it penalizes for more parameters (gets higher). A model with similar $-2\ln L$, but less parameters, will be "better" than another with more parameters. There are also versions of the AIC that account for sample size.

In brief: The fit can be assessed using the pseudo R-squared as defined in the report. Another possibility is to use the $-2\ln L$ or the AIC (or other pseudo R-squareds or other information criteria). The pseudo R-squared is usually thought of in the context of a predictive model.

Although there are alternative approaches, the approach taken in the report is acceptable. It is likely that sometimes the log-normal, or even the log-triangular, distribution might fit the data better than the Burr III, but the concept of indicating that the Burr family fit is best most of the time seems like the best way for moving forward.

Testing for bimodality

The report suggests that bimodality may be determined by simple visual inspection of data sets that cannot be fit to a Burr Type III distribution. In this report, the bimodality question arose in the context of the diazinon data. Plotting the data suggests another possibility, which is that some of the intermediate values (specifically 425.8, 459.6, 602 and 723) are outliers for some reason—otherwise an overall curve fit looks very reasonable.

Notwithstanding that, here are the basic choices:

1) *Visual inspection of the residuals*: Fit the Burr distribution and look at the residuals. They should display a distribution with no systematic biases either in distribution or in relation to the underlying distributional fit. The graphical depiction using the histogram is a minimal check. Of course, this method relies upon fitting the distribution in the first

place. Statistical tests might be applied to the residuals as well, though generally these would be expected to confirm the results of visual inspection.

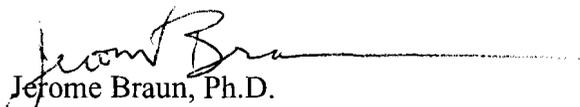
2) *Likelihood ratio test*: A formal method is to fit the model, then fit another model that is a superset of the first model (fitting both sets of parameters separately). Then, asymptotically the difference in the log-likelihoods is distributed as a chi-squared random variable with degrees of freedom equal to the difference in the number of parameters between the full model and the reduced model (full = two curves, reduced = single curve).

There is a broader question at work here. That is whether fitting a single distribution is appropriate at all. Problems involving mixtures of populations are notorious for creating issues with parameter estimation. The correct response in these cases is to assess the aptness of the statistical model in light of scientific knowledge.

In the case of the diazinon data, removing the intermediate values mentioned above did not resolve the problem of the BurliOZ program failing to fit a Burr Type III distribution. This may be a feature of the software, or may be a result of indentifiability of parameter issues in this particular data set. Since no Burr III fit could be accomplished on the full diazinon data set, neither of the formal bimodality tests suggested in 1) and 2) above is an option for the diazinon set.

In such cases it is important to bring scientific knowledge to bear for an assessment of the appropriateness of the model. In the diazinon case, all of the data in the lower set were for invertebrates, while 11 of 14 values in the higher set were for fish. It is possible to fit the two groups of data separately with differing distributions. This suggests on physiological and statistical grounds that a single distributional fit is not appropriate – fitting two separate distributions seems best both statistically and scientifically.

Sincerely,



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References

Erickson RJ, Stephan CE. 1988. Calculation of the final acute value for water quality criteria for aquatic organisms. Report. Environmental Research Laboratory-Duluth, United States Environmental Protection Agency, Duluth, MN.