Responses to Public Comments and Peer Reviews

Phase III: Permethrin Criteria Derivation Report

using the

Phase II: Methodology for Derivation of Pesticide Water Quality Criteria for the Protection of Aquatic Life in the Sacramento and San Joaquin River Basins

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Terms, Abbreviations, Acronyms, and Initialisms Used in this Report

Term	Definition
ACR	Acute to Chronic Ratio- used to estimate concentration that will protect against chronic toxicity
AF	Assessment Factor
CDFG	California Department of Fish and Game
CVRWQCB	Central Valley Regional Water Quality Control Board
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
DPR	California Department of Pesticide Regulation
EC*x*	The chemical concentration that has an effect on *x*% of the test population.
Koc	Organic Carbon Partition Coefficient
LC50	The chemical concentration that is lethal to 50 % of the test population.
LOEC	Lowest Observed Effect Level- lowest concentration tested that has some effect on the test population
MATC	Maximum Allowable Toxicant Concentration -geometric mean of LOEC and NOEC
NOEC	No Observed Effect Level- highest concentration tested that has no effect on the test population
SSD	Species Sensitivity Distribution- Statistical probability distribution of toxicity data
SPME	Solid-phase microextraction
UC Davis	University of California, Davis
US EPA	U.S. Environmental Protection Agency
Water Quality Objective (WQO)	The limits of water quality constituents or characteristics that are established for the reasonable protection of beneficial uses of water or the prevention of nuisance within a specific area.

1.0 Introduction

This document presents the responses to public comments and peer reviews received on a technical report prepared by the University of California at Davis, Environmental Toxicology Department, under contract (#05-100-150-0) to the Regional Water Quality Control Board, Central Valley Region (Regional Board). This report represents one of eight end product reports of the third phase of a three-phase project to evaluate, develop and apply a method to derive pesticide water quality criteria for the protection of aquatic life.

The first phase of the project was to review and evaluate existing water quality criteria derivation methodologies to determine if there was an existing available method that met the Regional Board's stated project goals. The review indicated that there is no single method that meets all of the Regional Boards requirements. Therefore, the second phase of the project was to develop a new method that could meet the project requirements. The Phase II report details this new methodology and its application to chlorpyrifos. The third phase of the project was to apply the criteria derivation method to eight additional pesticides, of which permethrin is one.

The permethrin criteria report was submitted to peer review, conducted by experts from academia and sister agencies, including the Department of Fish and Game and the Department of Pesticide Regulation.

These technical reports may be considered by the Regional Board during the development of the Central Valley Pesticide Basin Plan Amendment or other Board actions. However, the reports do not represent Board Policy and are not regulations. The reports are intended to generate numeric water quality criteria for the protection of aquatic life. However, these should not be construed as water quality objectives. Criteria and guidelines do not have the force and effect of regulation, nor are they themselves water quality objectives.

2.0 Response to Comment to Public Comments

2.1. Comment Letter 1 – Jeffrey M. Giddings, Ph.D. & Jeffrey Wirtz, Compliance Services International (CSI) on behalf of FMC

COMMENT 1-1: 2. Derivation of Acute Criterion
CSI reviewed UCD's acute toxicity study evaluations and data selection, and confirmed all 19 points with the exception of *Daphnia magna*. UCD used the *D. magna* 48-h EC50 of 0.32 µg/L (LeBlanc 1976). Results are also available from one other study (Surprenant 1979) which CSI rated "Relevant and Reliable" (RR), a 48-h LC50 value of 0.92 µg/L. Both LeBlanc (1976) and Surprenant (1979) were 48-h static tests with nominal concentrations. The geomean of the two available endpoints (0.54 µg/L) is the appropriate value to use for this species in deriving an Acute Criterion for permethrin.

Response To Comment (RTC) 1-1: I was not able to find the Surprenant (1979) study listed in either the EPA database or the California Department of Pesticide Regulation database, and the reference given in the CSI comments did not list an identification number for either agency, which I would need to request the data. If this study has not been submitted to a regulatory agency, then we cannot request the study. Because this study is not currently publicly available we cannot use it in the criteria report.

COMMENT 1-2: 2. Derivation of Acute Criterion
The UCD report stated that the BurrliOZ software program (CSIRO 2000) was used to fit the data set to a Burr III distribution. UCD reported a median HC5 of 0.020008 µg/L (20 ng/L). Using the same software and the data shown in UCD's Table 3, CSI obtained a virtually identical median HC5 value. This result corresponds to an Acute Criterion (HC5 divided by 2, reported with one significant digit) of 10 ng/L. With the revised value for *D. magna*, CSI calculated the median HC5 as 0.022213 µg/L (22 ng/L). The revised Acute Criterion is 11 ng/L.

RTC 1-2: Comment acknowledged. Again, we would re-calculate the criterion if the Surprenant (1979) study were available to us, but currently it appears that it is a confidential, unpublished study that we cannot obtain.

COMMENT 1-3: 3. Derivation of Chronic Criterion
UCD's draft permethrin criteria document discussed chronic toxicity data for *Brachycentrus americanus* (caddisfly), *D. magna*, and *Pimephales promelas* (Table 1). CSI agrees with the Maximum Acceptable Toxicant Concentrations (MATCs) presented for *D. magna* and *P. promelas* and does not recommend changes for those species. However, we believe the

data for *B. americanus* should be reconsidered. As the chronic toxicity value for *B. americanus,* UCD used a 48-h EC50 based on behavior from a study by Anderson (1982). While the study is rated RR, this EC50 is not an appropriate chronic endpoint for two reasons: first, it was based on an acute exposure (i.e., an insect test with exposures lasting 24-96 h); second, this behavior endpoint was not linked to survival, growth, or reproduction (TenBrook *et al*. 2009). A 21-d LC50 of 0.17 µg/L is available from this study, but NOEC, LOEC, and MATC values were not reported and raw data were not available to calculate these values using appropriate statistical methods.

RTC 1-3: We agree that the 48-h EC_{50} based on behavior is not an appropriate chronic toxicity value and it has been removed from the RR chronic dataset and replaced with the 21-d LC_{50}. Neither of these data was or is used directly in criterion calculation, so this alteration does not affect the magnitude of the chronic criterion.

COMMENT 1-4: 3. Derivation of Chronic Criterion
Derivation of a chronic criterion using the SSD approach would have required, in addition to the species listed above, data on chronic toxicity to the family Salmonidae, a benthic crustacean, and an aquatic insect. Because chronic toxicity data for these groups were not available, UCD applied an Acute-to-Chronic Ratio (ACR) approach instead (TenBrook *et al*. 2009).

To derive a Chronic Criterion using the ACR approach, ACRs are required for three species, including a fish and an invertebrate. The UCD methodology is unclear about the requirements for ACR calculation. At first, the methodology states that the acute and chronic data used to calculate an ACR must come from the same study in the same dilution water, but then this requirement is relaxed to allow a different study in the same laboratory under identical conditions, or even in a different laboratory – in other words, only the dilution water must be the same. The rationale for this requirement is unclear, since toxicity values are not presumed to be strongly affected by the source of dilution water.

According to UCD's draft criteria report for permethrin, there were no appropriate acute data to pair with any of the available chronic freshwater data. UCD paired one saltwater chronic toxicity value with an appropriate corresponding acute toxicity value to calculate an ACR for *Americamysis bahia*, satisfying one of the three family requirements: an invertebrate. The ACR for *A. bahia* was based on studies by Thompson (1986) and Thompson *et al*. (1989). Both of these studies were rated as "Less Relevant, Reliable" (LR) by UCD, but would have been rated RR had they been freshwater tests. To calculate the ACR, UCD selected a 96-h LC50 for 3- to 5-d shrimp (Thompson 1986) and a 30-d MATC for nauplii survival (Thompson *et al*. 1989). The LC50 selected was the most sensitive acute endpoint available and the MATC selected was the only one that could be calculated from that test. Therefore, the ACR generated by UCD for *A. bahia* is reliable.

RTC 1-4: Comment acknowledged.

COMMENT 1-5: 3. Derivation of Chronic Criterion
However, UCD lacked an ACR value for one fish and one acutely sensitive freshwater species as required to derive a multispecies ACR based on measured data for 3 species. According to the UCD methodology (TenBrook *et al*. 2009), if there are empirical ACRs for fewer than 3 species, a default ACR of 12.4 is used for one or more of three ACR values. The default ACR is the 80th percentile value derived from ACRs for 8 insecticides (chlordane, chlorpyrifos, diazinon, dieldrin, endosulfan, endrin, lindane, and parathion). TenBrook *et al*. (2009) do not explain why these insecticides should be considered representative of pesticides from different chemical groups, or why the 80th percentile should be used as the basis for a default ACR. For permethrin, UCD used the default value for the second and third ACRs along with the calculated ACR for *A. bahia* to derive a multi-species ACR (geomean of the three values) of 8.97.

RTC 1-5: The default ACR is based on 8 organochlorines and organophosphates because those were the only pesticides with criteria reports that contained datasets with paired acute and chronic data, and the 80^{th} percentile was chosen based on guidance from the EPA in their Great Lakes criteria derivation methodology (Host et al. 1995, USEPA 2003). The Great Lakes methodology contains a default ACR of 18 that was calculated with data from pesticides and other industrial chemicals, so the data on non-pesticides was removed and the default ACR was re-calculated to be 12.4. Data from criteria reports were used because these data are more carefully reviewed than data in the open literature. The details of the calculation of the default ACR are given in the UCD methodology (section 2-3.2.5.3, TenBrook et al. 2009).

COMMENT 1-6: 3. Derivation of Chronic Criterion
Although valid acute and chronic data were available for *P. promelas*, the methodology's restrictive requirements for ACR calculation prevented UCD from developing an ACR for this species. However, as shown in Table 1, the Species Mean Acute Value (SMAV) for *P. promelas* of 9.38 μg/L is based upon three relevant and reliable studies (Dwyer *et al*. 1995, 2005; Sappington *et al*. 2001). The MATC available for *P. promelas* (0.96 μg/L) from Spehar *et al*. (1983) is also relevant and reliable. Together, these acute and chronic results support an ACR of 9.77 for *P. promelas.* This empirical value, based on valid acute and chronic endpoints for *P.*

promelas and permethrin, is more reliable than the default ACR derived from data for other insecticides.

In the same way, reliable acute and chronic data are also available for *D. magna*. There are two reliable acute values: 0.32 μg/L (LeBlanc 1976) and 0.92 μg/L (Surprenant 1979), with a geometric mean of 0.54 μg/L. There is also a reliable chronic MATC of 0.057 μg/L (Kent *et al*. 1995). These results support an empirical ACR of 9.47 for *D. magna* that is more reliable than the default ACR.

The appropriate ACRs for permethrin are summarized in Table 2. Since no major trend is apparent and the ACRs for all species are within a factor of 10, the multi-species ACR can be calculated as the geometric mean of all of the ACRs (TenBrook *et al*. 2009), which is 7.57.

As discussed in Section 2, the acute toxicity value (HC5) derived based on CSI's revised dataset is 0.022213 μg/L. Applying the multi-species ACR of 7.57 to the acute HC5, the calculated Chronic Criterion is 0.0029 μg/L, or 3 ng/L.

RTC 1-6: We appreciate your comments about the ACR calculation guidance in the UCD methodology. The guidance on ACR calculation was taken directly from the USEPA (1985) methodology, including the requirement that the acute and chronic tests must be performed in the same dilution water (section VI.-I., p. 40-41, USEPA 1985). It is possible that these guidelines will be revised in the future, but at this time the chronic permethrin criterion will be calculated according to the current UCD method, with two default ACRs. As demonstrated, the difference between the draft UCD chronic criterion (2 ng/L) and the chronic criterion proposed by CSI (3 ng/L) is not very big. If we used the UCD final acute value of 0.020009 μg/L with the CSI ACR of 7.57, the chronic criterion would be calculated as 0.00264 μg/L, which would be rounded to 3 ng/L, so the criterion would not actually change. We agree that it is preferable to use ACRs based on measured data over default ACRs, and we agree that dilution water does not likely have a large effect on toxicity, assuming the dilution water is acceptable according to standard methods. If the UCD methodology is revised in the future, this input will be taken into consideration.

COMMENT 1-7: 4. Bioavailability of Permethrin
The draft criteria report summarizes evidence that pyrethroids bound to particulate matter are not biologically available to aquatic organisms and do not contribute to toxicity; only freely dissolved pyrethroids are bioavailable and toxic. Bound pyrethroids become bioavailable only when they desorb from particles or dissociate from dissolved organic matter.

"As a counterpoint" to the evidence relating permethrin toxicity to the freely dissolved fraction, the draft criteria report notes (p. 9) that "equilibrium partitioning would suggest that as organisms take up permethrin, more permethrin will desorb from particles, so the fraction absorbed to solids is likely not completely unavailable." This is not a logical inference. In the equilibrium partitioning model, the flux of permethrin between phases (freely dissolved, associated with dissolved organic matter, and sorbed to particulate organic matter) is such that concentrations in each phase are constant – fluxes into each phase (e.g., desorption from particles as an input to the freely dissolved phase) are balanced by fluxes in the opposite direction (e.g., sorption of freely dissolved permethrin to particles). The fact that permethrin molecules can move from one phase to the other does not "counter" the evidence that permethrin molecules are bioavailable only when freely dissolved.

RTC 1-7: The assumption of the equilibrium partitioning model is that the system is at equilibrium, and at equilibrium, we agree that the fluxes between phases would be constant. The paragraph regarding equilibrium partitioning theory has been revised in the final criteria report to reflect this. Because it is unlikely that environmental ecosystems are at equilibrium, and it has been shown that pyrethroids have a long equilibration time (~30-d, Bondarenko et al. 2006), continued desorption, and the associated toxicity, could persist over long time periods. This concept has been described as the "bioaccessible" fraction (Semple et al. 2004, You et al. 2011), the fraction of a chemical that will rapidly desorb from particles, and has been linked to biological effects.

COMMENT 1-8: 4. Bioavailability of Permethrin
The draft criteria report notes the possibility that pyrethroids can be taken up from ingested particles, citing the findings of Mayer *et al*. (2001) as evidence that hydrophobic compounds can be desorbed by digestive juices. The cited study involved uptake of benzo(a)pyrene and zinc by 18 species of benthic marine invertebrates, including 10 species of worms, 5 species of echinoderms, 2 species of mollusks, and a sea anemone. The relevance of these findings to uptake of pyrethroids by sensitive freshwater taxa (such as insects and crustaceans) is unclear. There is no evidence for uptake of pyrethroids by this route, and the UCD report in fact summarizes the evidence to the contrary.

RTC 1-8: There are very few studies available in the literature regarding dietary exposure of pyrethroids, or any hydrophobic organic compounds, but lack of information does not imply that toxicity due to pyrethroid ingestion does not occur. While the Mayer et al. (2001) study does not use insects or crustaceans, it demonstrates that hydrophobic compounds can be taken up from ingested particles. Pyrethroids are hydrophobic organic compounds with log K_{ow}s ranging from 4-7, similar to benzo(a)pyrene (log K_{ow} = 6.13, Schwarzenbach et al. 2003), which is used in the Mayer et al. (2001) study. The Palmquist et al. (2008) study, also cited in this section of the report, clearly demonstrated toxicity to three aquatic insects due to ingestion of a pyrethroid, including mortality and reduced growth and egg production.

> **COMMENT 1-9:** 4. Bioavailability of Permethrin
> TenBrook *et al*. (2009, Section 3-5.1) state that when a pesticide has only a single bioavailable phase (sorbed to solids, associated with dissolved organic matter, or freely dissolved in water), it is appropriate to evaluate compliance with water quality standards based on concentrations in the bioavailable phase alone. This is the case for permethrin and other pyrethroids, of which only the freely dissolved phase is bioavailable.
>
> Pyrethroid concentrations in the freely dissolved phase can be measured using techniques such as solid-phase microextraction (SPME) or calculated based on partitioning coefficients (Equation 3.6, TenBrook *et al*. 2009, presented as Equation 1 in the draft criteria document for permethrin). UCD notes that Equation 1 should not be used unless site-specific data are available for all the terms in the equation. These terms include SS, the concentration of suspended solids in the water, and foc, the fraction of organic carbon in the suspended sediment. While foc of suspended sediment is not usually measured directly, the term [SS]/foc in Equation 1 is equivalent to the concentration of particulate organic carbon (POC), which can be readily determined as the difference between total organic carbon (TOC) and dissolved organic carbon (DOC). Thus, the site-specific data needed for Equation 1 are the total concentration of permethrin in water, the concentration of DOC, and the concentration of POC. Values for the other terms in Equation 1, KOC and KDOC, are available in the literature. The suggestion by TenBrook *et al.* (2009) that site-specific KOC and KDOC values must be available is unreasonable: it would prevent all use of the model, because such data are virtually non-existent for any chemical.

RTC 1-9: It is stated clearly in the UCD methodology that regulators have the conservative option to determine compliance based on whole water pesticide concentration, even if there is evidence that some phases are not bioavailable (Section 2-4.1, TenBrook et al. 2009). While we recommend using the concentration of permethrin in freely dissolved phase for compliance determination, we stand by the statement that regulators can also use whole water concentrations because techniques to measure freely dissolved concentrations (e.g., SPME) are not yet included in standardized testing methods. We recommend using site-specific K_{OC} and K_{DOC} values to estimate the dissolved concentration using partition coefficients because these values can vary by several orders of magnitude (Bondarenko et al. 2007, Hunter et al. 2008, Laskowski 2002, Liu et al. 2004, Muir et al. 1994, Yang et al. 2006, 2007). Depending on which partition coefficients are used, predicted dissolved concentrations can also vary by an order of magnitude.

COMMENT 1-10: 5. Conclusions
The data selected by UCD for derivation of the Acute Criterion for permethrin overlooked one Relevant and Reliable study. Inclusion of this study resulted in a recalculated Acute Criterion of 11 ng/L. (UCD's recommended Acute Criterion was 10 ng/L.).

RTC 1-10: Please see RTC 1-1.

COMMENT 1-11: 5. Conclusions
Due to limited data available on chronic toxicity, an ACR approach was used to derive the Chronic Criterion for permethrin. The multi-species ACR used by UCD was based on two default ACRs along with an empirical ACR for *Americamysis bahia*. Using acceptable acute and chronic toxicity data, CSI calculated ACRs for two additional species, *D. magna* and *P. promelas*. Based on the geometric mean of the three ACRs, the recalculated Chronic Criterion is 3 ng/L. (UCD's proposed Chronic Criterion was 2 ng/L.)

RTC 1-11: Please see RTC 1-6.

COMMENT 1-12: 5. Conclusions
Pyrethroids bound to particulate matter or associated with dissolved organic matter are not biologically available to aquatic organisms and do not contribute to toxicity; only freely dissolved pyrethroids are bioavailable and toxic. In laboratory toxicity tests using water with minimal particulate or dissolved organic matter, nearly all the pyrethroid is bioavailable. In ambient water, only a small fraction – a few percent or less – of the total pyrethroid may be bioavailable. For consistency with the underlying data, compliance with permethrin water quality standards should therefore be based on concentrations of freely dissolved permethrin, not total permethrin. Freely dissolved permethrin can be measured directly using SPME or estimated using an equilibrium partitioning model such as the one presented by TenBrook *et al*. (2009).

RTC 1-12: Please see RTC 1-9.

2.2 Comment Letter 2 – Kelye McKinney, City of Roseville; Michael Bryan, Ph.D., Brant Jorgenson, and Ben Giudice, M.S., Robertson-Bryan, Inc.

COMMENT 2-1: The City does not accept the validity of the permethrin chronic criterion. The draft chronic criterion for permethrin may be overprotective. The ACR used to calculate the criterion was heavily influenced by a default ACR derived solely on classes of pesticides whose structures are different, environmental fate is different, and modes of toxic action are mostly different than permethrin.

RTC 2-1: The acute-to-chronic ratio procedure for calculation of chronic criteria has been thoroughly reviewed by both peer review and public comment processes and is a valid procedure for criteria derivation. A default ACR procedure is also used by the EPA in the Water Quality Guidance for the Great Lakes System (USEPA 2003) method for criteria derivation.

COMMENT 2-2: The City does not accept the assumption of dose additivity. Compliance with criteria should not be based on simplifying assumptions of concentration addition as the principals of concentration addition do not necessarily hold true under all possible environmental mixture scenarios. Assumptions of dose additivity are unsuitable for regulatory purposes in this case and as such, the report should specifically recommend against inclusion of dose-additivity assumptions for compliance determination purposes.

RTC 2-2: As discussed in the mixtures section of the report, all studies of pyrethroid mixtures predicted joint toxicity of the compounds using the concentration addition model within a factor of 2, which shows that this model predicts joint pyrethroid toxicity well.

COMMENT 2-3: The City disagrees that whole water analysis is valid for criteria compliance. Scientific evidence points to freely dissolved pyrethroid as the bioavailable fraction. Compliance should be measured against that portion of a pyrethroid that is known to be toxic. The draft criteria reports should be revised in a manner that retains the scientifically-based recommendation for compliance determinations based on either direct measurement of the bioavailable fraction or allowing for some compensating factor accounting for particulate matter and dissolved organic matter, but should remove statements regarding the validity of whole water measurement for compliance, which are not supported.

RTC 2-3: Please see RTC 1-9.

COMMENT 2-4: The limited capability of commercial laboratories in achieving low enough reporting limits is very troubling to the City. Similar to the standardization of minimum mandatory reporting limits in the State Implementation Plan (SIP), the City requests similar effort of standardization for these pesticides. Without such standardization, monitoring and compliance efforts can produce data of limited to no value, and likely at considerable economic expense to the regulated community.

RTC 2-4: The derivation of water quality criteria do not take into account reporting limits of commercial laboratories or other economic feasibility issues.

These considerations are taken into account when setting water quality objectives, while water quality criteria are derived with only the objective of the protection of aquatic life.

> **COMMENT 2-5:** 3.1.1 Permethrin
> In the case of permethrin, the final ACR is calculated as the geometric mean of one ACR for *Americamysis bahia,* and two default values of 12.4, which are based on no data from pyrethroids, but instead are derived solely on classes of pesticides whose structures are different, environmental fate is different, and modes of toxic action are mostly different. The chronic criterion calculated using this ACR is 2 ng/L. The most sensitive maximum acceptable toxicant concentration (MATC) in the data set was 16 ng/L (Fojut et al., 2011a). In this case, the derived criterion may be over-protective, owing to the use of default ACRs which are not based on pesticides with similar mechanisms of action.

RTC 2-5: The default ACR procedure was adopted in the methodology after extensive review, and a similar procedure is used by the EPA in the Water Quality Guidance for the Great Lakes (USEPA 2003). The fact that the chronic criterion is lower than the lowest MATC in the chronic dataset does not show that the criterion is overprotective. As noted in the report, the chronic dataset is very small (3 data), and does not include *Hyalella azteca*, the standard test species known to be most sensitive to pyrethroids, or other relatively sensitive species (as seen in the acute dataset) such as *Chironomus dilutus*, *Orconectes immunis*, *Procambarus blandingi*, and *Procloeon* sp.

> **COMMENT 2-6:** 3.2 Assumed Dose-Effect Additivity
> Environmental toxicologists recognize the importance of considering toxicant mixtures when evaluating and predicting toxicity to an organism. It is a held theory that toxicants of similar mode of action can act additively on an organism. Through such simplifying models of concentration addition, the effect of dose additivity can be predicted.
>
> In past reports, the authors made definitive statements regarding the use of dose-additivity in compliance determination, i.e., “The additivity of pyrethroid mixture toxicity has not been clearly defined I the literature, and in fact, antagonism has been observed, thus the concentration addition method is not recommended for use when multiple pyrethroids are found in a sample.” (Fojut et al, 2010). In the permethrin and cypermethrin reports, although definitive statements regarding the interaction of PBO with pyrethroids and, more generally, non-additive chemicals, are made, no definitive statement is made regarding dose-additivity of pyrethroids for compliance determination. The authors do state that results of Trimble et al., 2009 indicate “…that in general, pyrethroid mixture toxicity is additive.” (Fojut et al., 2011a; Fojut et al., 2011b). The authors rely on the same set of literature in discussing dose-additivity of pyrethroids in the permethrin

and cypermethrin draft reports as they did in the final reports for bifenthrin, lambda-cyhalothrin, and cyfluthrin, and so it is unclear why no definitive statement is made. In absence of such a recommendation, the indication is that the body of evidence supports use of dose–additivity in compliance determination, which is not the case.

Indeed, in investigations conducted by Trimble et al. (2009) on additivity in binary mixtures of Type I and Type II pyrethroids, although concentration addition models predicted experimental results well, as would be hypothesized, in some cases so did independent action models. Furthermore, actual toxicity often deviated substantially from predicted toxicity at low toxicant concentration, well below expected LC50 values (i.e., in the range of the derived acute criterion). There is enough inherent uncertainty in the use and applicability of concentration addition models, be they toxic unit or relative potency factor approaches, that compliance determination should not be based on assumed additivity. The reports should be revised to clearly state that dose-additivity is not recommended for the purposes of compliance determinations.

RTC 2-6: The recommendations regarding mixture toxicity of pyrethroids have changed in the permethrin and cypermethrin reports compared to the previous pyrethroid criteria reports because when we look at the whole body of evidence for all of the pyrethroids, it appears that the concentration addition model is able to predict observed toxicity of mixtures within a factor of 2. As we gathered more information on this topic it became clear that using the concentration addition model is reasonable for pyrethroids.

COMMENT 2-7: 3.3 Bioavailability
The UCD criteria derivation methodology should be praised for including considerations of bioavailability. In Section 9 of the draft permethrin and cypermethrin criteria reports, the propensity of pyrethroid insecticides to sorb to particulate matter, sediments, and laboratory equipment is discussed. In this discussion several studies are mentioned providing evidence that pyrethroid toxicity in the water column is associated with the dissolved fraction, and that the freely dissolved fraction is the better predictor of toxicity. The reports state:

> "[Studies] suggest that the freely dissolved fraction of permethrin/cypermethrin is the primary bioavailable phase, and that this concentration is the best indicator of toxicity, thus, it is recommended that the freely dissolved fraction of permethrin/cypermethrin be directly measured or calculated based on site specific information for compliance assessment. Whole water concentrations are also valid for criteria compliance assessment, and may be used at the discretion of environmental

managers, although the bioavailable fraction may be overestimated with this method" (Fojut et al., 2011a; Fojut et al., 2011b).

The statement that "whole water concentrations are also valid for criteria compliance" is troubling. After extensive discussion of the scientific reasoning behind the author's recommendation of using the freely dissolved fraction for compliance, there is no support or discussion for the assertion that whole water concentrations are valid for this purpose. The recommendation that compliance determinations be based on the freely dissolved fraction reflects scientific understanding of pyrethroid bioavailability in the environment, and there is no clear basis, scientific or otherwise, for the authors' assertion that whole-water concentrations are valid for compliance determination. In light of the current scientific understanding of pyrethroid bioavailability, any total recoverable measurement unadjusted to account for the fraction that is not bioavailable represents a knowingly biased measurement and should not be used for compliance determination.

RTC 2-7: It is stated clearly in the UCD methodology that regulators have the conservative option to determine compliance based on whole water pesticide concentration, even if there is evidence that some phases are not bioavailable (Section 2-4.1, TenBrook et al. 2009). While we recommend using the concentration of permethrin in freely dissolved phase for compliance determination, we stand by the statement that regulators can also use whole water concentrations because using techniques to measure freely dissolved concentrations (e.g., SPME) are not yet included in standardized testing methods.

COMMENT 2-8: 3.4 Analytical Concerns
For compliance testing purposes through National Pollutant Discharge Elimination System (NPDES) permits, EPA approved methodologies must be used. Existing analytical methods for the measurement of semi-volatile organic pollutants such as pyrethroid insecticides are limited in the capability of achieving the draft criteria values derived for permethrin and cypermethrin. Only the most diligent commercial laboratories can achieve reporting limits near the draft chronic permethrin and acute cypermethrin criteria using these analytical methods and employing good laboratory practices and standard quality assurance. No methods exist for the detection and quantification of cypermethrin near the draft chronic cypermethrin criterion, and indeed, such capabilities will likely not be seen for many years to come. There is limited commercial analytical capacity in California, and at present most laboratories could only assure reporting limits several times greater than the draft acute and chronic criteria. This limits the utility of criteria altogether, and potentially returns the regulated community to a position of providing the Regional Water Board with analytical results containing varied reporting limits. When using such

criteria, maximum matrix-specific reporting limits should be considered so as to avoid the potential of reporting false positives and errant detections.

RTC 2-8: Please see RTC 2-4.

COMMENT 2-9: 4 Summary of Review Findings
1. The draft acute criteria for permethrin and cypermethrin are based on a species distribution approach and result in supportable criteria.

RTC 2-9: Comment acknowledged.

COMMENT 2-10: 4 Summary of Review Findings
2. Available data indicate that the draft chronic criterion for permethrin may be overprotective. The ACR used to calculate the criterion was heavily influenced by a default ACR derived solely on classes of pesticides whose structures are different, environmental fate is different, and modes of toxic action are mostly different than permethrin.

RTC 2-10: Please see RTC 2-5.

COMMENT 2-11: 4 Summary of Review Findings
4**.** For all draft criteria, it is not clear whether the assumption of dose additivity between pyrethroids of similar mode of toxicity is assumed for compliance determination. Caution is advised in applying concentration addition principals to compliance measurements. Dose additivity is not settled science, and its accuracy as a model predictor is sensitive to many variable factors and thus not always good. Where science is not settled, compliance should not be based on simplifying assumptions.

RTC 2-11: Please see RTC 2-6.

COMMENT 2-12: 4 Summary of Review Findings
5. The current scientific understanding regarding pesticide bioavailability should be applied to criteria compliance determinations. The freely dissolved fraction of pyrethroid insecticides, including permethrin and cypermethrin, is a far better predictor of the bioavailable fraction than is total recoverable measurements. Therefore, compliance determinations should be based on measurements that most accurately predict toxicity. Either compliance should be determined using analytical procedures measuring the dissolved fraction, or compliance should be determined using total recoverable methods but adjusted for pyrethroid sorption to particulate matter and dissolved organic matter. There is no scientific support for using whole-water concentrations for compliance determinations.

RTC 2-12: Please see RTC 2-7.

COMMENT 2-13: 4 Summary of Review Findings
6. Achieving commercially available analytical reporting limits below the draft criteria utilizing EPA approved methods is currently lacking or limited. Maximum matrix-specific reporting limits should be considered so as to avoid the potential of reporting false positives and errant detections.

RTC 2-13: Please see RTC 2-4.

2.3. Comment Letter 3 –Debbie Webster, Central Valley Clean Water Association

COMMENT 3-1: CVCWA continues to be concerned with the Regional Water Board's proposed use of *draft criteria* to interpret narrative water quality objectives and potential use of the criteria to set water quality based effluent limitations in NPDES permits, thereby creating liability for Central Valley POTWs. Considering the liability associated with such effluent limitations, the Regional Water Board should take care to use only criteria that are well-developed and well-founded.

RTC 3-1: Policy issues on the how the criteria are applied are outside of the scope of the derivation of criteria by UCD contractors. The criteria document does not address policy issues such as how the criteria could be used by the Regional Board or others.

COMMENT 3-2: The chronic criterion is problematic for a number of reasons, including the lack of available data and the use of the default acute to chronic ratio (ACR) for its calculation. Within the *draft criteria*, the authors note that the chronic toxicity data set was a major limitation, with three of the five taxa requirements not met. Without a complete chronic toxicity data set, the authors relied on an ACR to derive the chronic criterion. The authors noted a number of concerns with the approach, including lack of data on sensitive species such as *Hyalella azteca* or another benthic organism. Due to the use of an ACR to derive the criterion, uncertainty could not be quantified for the chronic criterion.

RTC 3-2: While we would prefer to use more measured data for the chronic criterion calculation, the default ACR is available when there is a lack of chronic data, such as for permethrin. The use of an ACR does not allow for uncertainty quantification, but this does not preclude the use of this procedure for chronic criterion calculation. A similar default ACR procedure is used by the EPA in the Water Quality Guidance for the Great Lakes System (USEPA 2003).

COMMENT 3-3: An additional concern noted in the data sets was the inability to account quantitatively for variable effects of temperature on permethrin toxicity.

RTC 3-3: Comment acknowledged.

COMMENT 3-4: The authors made at least one significant technical error where they incorrectly calculated the example USEPA acute criterion (page 19) and concluded it was identical to the draft acute criterion of 10 ng/L. Assuming that the example USEPA final acute value was correctly calculated by the authors, the example USEPA acute criterion should be 20 ng/L (39.001 ng/L÷2 = 19.5 ng/L, rounded to 20 ng/L) instead of 10 ng/L. This incorrect conclusion that the draft acute criterion is identical to the example USEPA acute criterion is repeated on page 20 of the *draft criteria*. Although this does not affect the draft acute criterion, the correctly calculated comparison instead suggests that the draft criterion may be more stringent than necessary to protect aquatic life.

RTC 3-4: The acute value was incorrectly reported in the draft version of the report in the line before the calculation, but the acute value actually used in the calculation was correct. This error has been corrected in the final report. I have attached the calculation page of the acute criterion according to the EPA (1985) method (Table 1), which results in an example USEPA acute criterion of 10 ng/L.

COMMENT 3-5: The authors also neglected to include their own recommendation to implement the criteria based on dissolved concentrations of permethrin in the final criteria statement (from page 11 of the *draft criteria*: "*The freely dissolved permethrin concentration is recommended for determination of criteria compliance because the literature suggests that the freely dissolved concentrations are the most accurate predictor of toxicity*.") Including this in the final criterion statement recommendation is vital for permethrin (and other pyrethroid pesticides) for which the total concentrations will be many times the dissolved concentration under typical ambient conditions and will greatly overestimate the bioavailable concentration and risk of toxicity.

RTC 3-5: The recommendation to measure the freely dissolved concentration of permethrin to determine criteria compliance will not be included in the final criteria statement, because it is up to environmental managers to decide what methods they will employ to measure permethrin for criteria compliance. The recommendation to measure the freely dissolved concentration of permethrin is now reiterated in the section 19 of the final report.

COMMENT 3-6: Because there are not adequate data to set a chronic criterion, CVCWA recommends that the *draft criteria* refrain from setting a chronic criterion until additional studies are completed. The USEPA 1985 guidance[1] for deriving numeric water quality criteria states that "It is not enough that a national criterion be the best estimate that can be obtained using available data; it is equally important that a criterion be derived only if adequate appropriate data are available to provide reasonable confidence that it is a good estimate," and that "If all required data are not available, usually a criterion should not be derived."

RTC 3-6: The criteria calculation procedures were thoroughly reviewed by the peer review and public comment processes during the review of the UCD methodology. One of the main goals of the UCD methodology was to create a methodology that allowed for the derivation of criteria with data sets with varying quantities of toxicity values and diversity. Thus, a chronic criterion is calculated for permethrin according to the UCD methodology, even though there is limited chronic data.

COMMENT 3-7: In addition, CVCWA is generally concerned with the Regional Water Board bypassing the USEPA process of deriving water quality criteria to create independent criteria that may be used to interpret narrative water quality objectives. The *draft criteria* should be thoroughly vetted through the public and regulatory process before they are made available for potential use by the Regional Water Board in NPDES permits. Considering the uncertainties associated with the draft criteria, it is ill-advised to utilize them at this stage. Thus, CVCWA respectfully requests that the Central Valley Water Board refrain from using the *draft criteria* for permethrin until the criteria are properly adopted as water quality objectives pursuant to all requirements in Porter-Cologne.

RTC 3-7: Policy issues on the how the criteria are applied are outside of the scope of the derivation of criteria by UCD contractors. The criteria document does not address policy issues such as how the criteria could be used by the Regional Board or others.

Table 1. Derivation of FAV and acute criterion according to the EPA (1985) method using the UCD dataset.

Species	Common identifier	Family	GMAV	Rank	p=R/(N+1)	ln GMAV	(ln GMAV)^2	√p
Pimephales promelas	Fathead minnow	Cyprinidae	9.38	16				
Xyrauchen texanus	Razorback sucker	Catostornidae	5.95	15				
Ictalurus punctatus	Catfish	Ictaluridae	5.4	14				
Notropis mekistocholas	Cape Fear shiner	Cyprinidae	4.16	13				
Etheostoma spp.	Darters	Percidae	3.0086	12				
Oncorhynchus spp.	Trout	Salmonidae	2.6643	11				
Danio rerio	Zebra fish	Cyprinidae	2.5	10				
*Erimonax monachus (*formerly *Hybopsis monacha)*	Spotfin chub	Cyprinidae	1.7	9				
Salmo salar	Atlantic Salmon	Salmonidae	1.5	8				
Ceriodaphnia dubia	Daphnid	Daphniidae	0.664	7				
Daphnia magna	Daphnid	Daphniidae	0.32	6				
Procambarus blandingi	Crayfish	Cambaridae	0.21	5				
Orconectes immunis	Crayfish	Astacidae	0.21	4	0.2353	-1.5606	2.4356	0.4851
Chironomus dilutus	Midge	Chironomidae	0.189	3	0.1765	-1.6660	2.7756	0.4201
Procloeon sp.	Mayfly	Baetidae	0.0896	2	0.1176	-2.4124	5.8197	0.3430
Hyalella azteca	Amphipod	Hyalellidae	0.0211	1	0.0588	-3.8585	14.8879	0.2425
Sum of lowest 4 values					0.5882	-9.4975	25.9188	1.4907

s^2=	103.0033
s=	10.1491
L=	-6.1567
A=	-3.8873
FAV	0.02050
Acute criterion	0.01025 (5th percentile)

2.4. Comment Letter 4 – Linda Dorn, Sacramento Regional County Sanitation District

COMMENT 4-1: SRCSD has technical and regulatory comments with the draft acute/chronic criteria. Our primary concern with the derivation of draft criteria and its possible use directly relates to our ability to maintain our excellent compliance record should the Central Valley Regional Water Quality Control Board (CVRWQCB) staff use this draft criteria to interpret narrative objectives in the Sacramento-San Joaquin Basin Plan. Additionally, SRCSD has technical concerns with how the draft acute/chronic criteria were derived. Following are SRCSD's concerns regarding use of draft criteria to interpret narrative water quality objectives based on technical issues with the derivation of the draft criteria.

SRCSD is concerned with the CVRWQCB's proposed use of the draft criteria to interpret narrative water quality objectives. The specific concern is the Regional Board's potential use of the criteria to set water quality based effluent limitations in NPDES permits, as it will create liability for SRCSD. Considering the liability associated with complying with such effluent limitations, the CVRWQCB should take care in using only criteria that are well-developed and well-founded. As indicated above, the draft criteria for permethrin are likely overly-protective, thereby creating unnecessary liability for wastewater dischargers. Effluent limitation violations may subject dischargers to the CVRWQCB's discretionary administrative civil liability authority, mandatory minimum penalties, or to third party lawsuits brought under the CWA's citizen suit enforcement provisions. (See 33 U.S.C. SS 505.)

SRCSD is concerned with the use of the draft criteria to interpret narrative objectives as it creates de facto water quality objectives that have not been adopted in accordance with the law. Under the Porter-Cologne Water Quality Control Act (Porter-Cologne), the CVRWQCB is required to regulate water quality in a manner that attains the highest level of water quality which is reasonable, considering all demands being made and to be made on those waters. (See Wat. Code, SS 13000.)

RTC 4-1: Policy issues on the how the criteria are applied are outside of the scope of the derivation of criteria by UCD contractors. The criteria document does not address policy issues such as how the criteria could be used by the Regional Board or others.

COMMENT 4-2: Further, water quality objectives are supposed to be established to ensure reasonable protection of beneficial uses, considering a number of different factors. The factors that must be considered include: past, present and probable future beneficial uses;

environmental characteristics of the hydrographic unit under consideration, including the quality of water; water quality conditions that could reasonably be achieved though the coordinated control of all factors which affect water quality in the area; economic consideration; the need for developing housing; and the need to develop and use recycled water. (Wat. Code, SS 13241.)

The CVRWQCB is required to adopt a program of implementation for achieving water quality objectives at the time of adoption (Wat. Code, SS 13242). In other words, when adopting water quality objectives, the CVRWQCB must determine if the objective is necessary to provide for reasonable protection of the beneficial uses, and must balance all of the competing demands on the water and consider the economic implications associated with adoption of water quality objectives. SRCSD respectfully requests that the CVRWQCB refrain from using the draft criteria for permethrin until the criteria are properly adopted as water quality objectives pursuant to all requirements in Porter-Cologne.

RTC 4-2: Water quality criteria were derived only with regard to the protection of aquatic life and the UCD criteria report does not address how the criteria could be used or implemented.

COMMENT 4-3: As confirmed by UCD, the main problems with permethrin criteria development are the lack of good toxicity data. Because the necessary toxicity studies are insufficient to use standard EPA methodology to develop the criteria, the draft criteria were developed based on unique criteria derivation techniques. As noted, these criteria are within the range of criteria developed by other jurisdictions. The example acute criterion calculated by the USEPA 1985 method is identical to the criterion derived using this methodology.

RTC 4-3: Comment acknowledged.

COMMENT 4-4: SRCSD support the authors' recommendation that "The freely dissolved permethrin concentration is recommended for determination of criteria compliance because the literature suggests that the freely dissolved concentrations are the most accurate predictor of toxicity." This conclusion is based on multiple study findings that "toxicity is believed to occur primarily from the fraction of the compound that is dissolved in the water, not from the compound that is associated with the particulate phase." SRCSD does not find it scientifically defensible and does not agree with the recommendation to use whole water concentrations for criteria compliance assessment at the discretion of the environmental managers; however, total concentrations could be an indicator of where additional information is needed to determine if there is a potential risk to the aquatic community from permethrin.

RTC 4-4: It is stated clearly in the UCD methodology that regulators have the conservative option to determine compliance based on whole water pesticide concentration, even if there is evidence that some phases are not bioavailable (Section 2-4.1, TenBrook et al. 2009). While we recommend using the concentration of permethrin in freely dissolved phase for compliance determination, we stand by the statement that regulators can also use whole water concentrations because using techniques to measure freely dissolved concentrations (e.g., SPME) are not yet included in standardized testing methods.

> **COMMENT 4-5:** Because of the uncertainty in these draft WQC (e.g., base on whole water concentrations when the dissolved phase determines toxicity, fewer species data than recommended by both the EPA (1985) and TenBrook et al. (2009) methods) SRCSD does not support their use by the CVRWQCB as water quality objectives (WQOs) until there is a better understanding of fate and transport, chronic toxicity, and affects of dissolved solids and suspended particles that can be accounted for in an empirical model. The suggested WQC may be useful as risk screening values and concentrations above them could be evaluated further for possible environmental relevance, but the proposed water quality criteria are insufficiently supported to support the regulatory weight associated with WQO.

RTC 4-5: While there is uncertainty in the draft WQC, it does not preclude the use of WQC, but rather should inform regulators. The fate and transport of pyrethroids are relatively well-understood in that they are predominately determined by the fate and transport of particulate and dissolved solids. The effects of dissolved solids and suspended particles can be accounted for in an empirical model, which is recommended for use in the Bioavailability section of the final criteria report. We agree that more chronic toxicity data would reduce the uncertainty in the chronic criterion.

> **COMMENT 4-6:** The proposed draft criteria (10 and 2 ng/L acute and chronic, respectively) create a number of problematic analytical issues. The chronic criterion is below reporting limits and detection limits for most, if not all, labs (in clean matrices such as deionized water). Although not recognized in the draft criteria document, analytical quantitation limits have an impact on the ability of dischargers to achieve compliance with effluent limitations and receiving water limits. Moreover, the ability to detect concentrations below one ppt (less than one ng/L) in a complex matrix such as effluent is even more challenging than detecting these low concentrations in a clean matrix. In fact, because of the challenges, detections below one ppt have yet to be demonstrated in the complex effluent matrix. Currently, one ppt detection limits are the goal of California

organizations evaluating pyrethroids (i.e., DPR, TriTAC, and the pyrethroid Working Group [PWG]).

The lack of a standard EPA methodology for analyzing pyrethroids may also pose a problem for pyrethroid analyses. For example, the academic lab of Dr. Mike Lydy (University of Southern Illinois) claims one of the lowest reporting limits (3 ng/L) for pyrethroids, yet it is higher than the suggested chronic criterion in the draft criteria. Questions have been raised about the possibility of interferences or false positive identification without confirmation by other methods. To achieve such low reporting limits, Dr. Lydy must perform multiple clean-up steps that are not available or commonly performed by commercial labs, and samples are concentrated 20,000 times (1,000x is normal). These extreme steps in non-standard methods can have an unknown effect on analytical precision and accuracy.

RTC 4-6: Analytical issues are not considered in the derivation of water quality criteria; criteria are derived solely to be protective of aquatic life. Analytical and other economic issues are considered when setting water quality objectives.

COMMENT 4-7: Authors' note that the dietary pathway for chronic exposure from permethrin may be an important exposure route, but inclusion of this exposure route into criteria compliance assessment is not possible due to lack of information. SRCSD agrees that future criteria updates should consider this pathway and be done as soon as additional information becomes available.

RTC 4-7: Comment acknowledged.

COMMENT 4-8: Because of the lack of information and understanding of the impacts to the aquatic life from permethrin, and analytical limitations associated with detections of permethrin to the levels of concern, SRCSD cannot support their use by the Regional Board until there is a better understanding of fate and transport, chronic toxicity, and affects of dissolved solids and suspended particles that can be accounted for in an empirical model. Therefore, SRCSD requests that the CVRWQCB Board refrain from using the draft criteria for permethrin until more research is completed and the criteria are properly adopted as water quality objectives.

RTC 4-8: Please see RTC 4-5 for our response to the fate and transport, chronic toxicity, and effects of dissolved and suspended solids.

3.0 Response to Comment to Peer Reviews

3.1. Peer Review 1 – John P. Knezovich, Ph.D., UC-Davis, Lawrence Livermore National Laboratory

REVIEW 1-1: *Overview*
The freshwater criteria for permethrin (3-phenoxyphenyl) methyl 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate) defined in this draft report was derived using methodology recently developed by Tenbrook *et al*. (2009)[1]. The methodology considers relevance of the endpoints and quality of the data in derivation of the criteria. This methodology was motivated by the California Regional Water Quality Control Board's desire to employ rigorous methods to develop criteria for protection of the Sacramento and San Joaquin River Watershed.

Response to review (RTR) 1-1: Comment acknowledged.

Review 1-2: *Basic information and physical-chemical data*
The report provides a comprehensive summary of the physical-chemical data for permethrin. This data set is straightforward and indicates that this pesticide has low solubility, high density, low volatility, high ability to bioaccumulate, and is moderately persistent in aqueous environments (i.e., slow rates of hydrolysis, moderate rates of photolysis and biodegradation). This pesticide's physical-chemical characteristics make its exposure to aquatic organisms a relevant concern.

RTR 1-2: Comment acknowledged.

Review 1-3: *Human and wildlife dietary values*
The FDA has not set action levels for permethrin in fish tissue.

Avian mortality does not appear to be a concern for permethrin as the NOEC for mallard ducks is 125 mg/kg and the LOEC is 500 mg/kg based on concentrations in feed. (Concentrations should be consistently reported in metric units and not ppm).

RTR 1-3: The concentration units have all been changed to metric (mg/kg) instead of ppm.

Review 1-4: *Ecotoxicity data and data reduction*
The authors evaluated 155 published studies of permethrin toxicity to develop the proposed criteria. Relevance was determined using the aforementioned criteria[1] and data for studies that were deemed acceptable were evaluated. Adequate and reliable data is available for

[1] P. Tenbrook *et al*. (2009). *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 chloropyriphos criteria.* Report prepared for the Central Valley Regional Water Quality Control Board, Rancho Cordova, CA.

determining acute toxicity using animal studies and exclusion criteria appear to have been applied properly. Fourteen acute, 3 chronic, and 6 mesocosm studies were found to contain relevant and reliable data.

The final acute data set contains 19 species mean acute toxicity values (SMAV) and the final chronic data set contains 3 species mean chronic values (SMCV). The criteria used for data reduction (e.g., preference for flow-through tests, sensitive species) are appropriate and appear to have been correctly applied.

RTR 1-4: Comment acknowledged.

Review 1-5: *Acute criterion calculation*
The acute criterion for permethrin was calculated using methods defined by Tenbrook *et al*. (2009). The five taxa required for the species sensitivity distribution (SSD) were available and the species sensitivity distribution (SSD) method was used. The Burr Type III SSD method was used to derive the median 5th and 1st percentile values. The median 5th percentile value was used in accordance with the Tenbrook et al. (2009) methodology to derive an acute criterion of 10 ng/L. These calculations appear to have been correctly performed.

Figure 2 appears to have an incorrect label on the *y* axis. This axis appears to represent the frequency of studies, not probability.

RTR 1-5: Comment acknowledged. The *y* axis has been re-labeled as frequency.

Review 1-6: *Chronic criterion calculation*
The acute-to-chronic ratio (ACR) method was used to derive the chronic criterion. Only two data sets were rated as reliable, which only satisfied two of the five taxa requirements. A saltwater species (*Americamysis bahia*) was used in accordance with the methodology to calculate an ACR, but data for two additional acutely sensitive species was not available. A species mean acute to chronic ratio (SMACR) for measured data was calculated by dividing the acute LC50 value by the chronic MATC value.
This section needs to include more information on the derivation of the criterion. Specifically, the authors need to:

1) Define the source of the default values were used for the second and third ACRs;
2) Be consistent: the ACR for *A. bahia* is referred to as the “species mean ACR (SMACR)” on page 8, but is identified as the ACR in Table 8;
3) Reference the source of the default values used in Table 8. These values have a profound effect on the final multi-species ACRs and their use needs to be justified; and
4) Use the same number of significant figures for the ACR as for the acute 5th percentile value.

RTR 1-6:
1) The following sentences have been added to the chronic criterion section in the final report: The default ACR value of 12.4 is equal to the 80th percentile of the multispecies ACRs available in eight pesticide criteria reports (section 2-3.2.5.3, TenBrook et al. 2009). This is the same procedure used by the USEPA to derive a default ACR in the Water Quality Guidance for the Great Lakes System (Host et al. 1995, USEPA 2003).
2) Table 8 has been revised so that the column formerly labeled ACR is now labeled SMACR.
3) The source of the default ACRs has been added to Table 8.
4) The number of significant figures reported for the final ACR is now consistent with the acute 5th percentile value, although this did not change the outcome of the chronic criterion.

Review 1-7: *Bioavailability*
Permethrin has a relatively high log K_{ow} value and therefore has a high tendency to sorb to dissolved and particulate organic materials. The authors correctly point out that although ingestion of contaminated particles and food sources is likely an important route of exposure, it is not possible at this time to incorporate this pathway into criteria due to the lack of sufficient quantitative studies. Using the dissolved phase of permethrin to assess compliance is appropriate and will require site-specific data on water characteristics.

Isolation of the dissolved phase of permethrin by solid-phase micro-extraction presents a practical approach for approximating the bioavailable phase of this compound. Determination of site-specific dissolved concentrations of permethrin may not be practical, however, due to the need for accurate measurements of dissolved organic compounds and suspended solids, which require significant effort to acquire. The fact that these parameters can vary spatially and temporally further complicates such assessments and should be mentioned here.

RTR 1-7: The following sentence has been added to the bioavailability section of the final report to address variation in dissolved and suspended solids:

Such physical-chemical properties can vary both spatially and temporally, further complicating measurement of these properties and subsequent assessment of bioavailability using site-specific partition coefficients.

Review 1-8: *Mixtures*
Additive and synergistic toxicity effects in the presence of other pesticides have been reported for permethrin. Because a variety of potential

interactions are possible, it is not practical to apply a single model to predict toxicity at this time.

RTR 1-8: Comment acknowledged.

Review 1-9: *Temperature, pH effects*
An inverse relationship between pyrethroid toxicity and water temperature is well documented. This relationship is important as laboratory toxicity tests are often conducted at temperatures that are higher than those in natural ecosystems. Although sufficient data does not exist to enable accurate predictions of temperature-related toxicity due to permethrin in aquatic ecosystems, this relationship should be considered in the derivation of safety factors as it is likely that criteria derived from laboratory studies conducted at relatively high temperatures will under-predict toxicity in many natural environments.

Permethrin does not undergo significant hydrolysis and pH does not appear to significantly influence its environmental fate.

RTR 1-9: Additional safety factors are not recommended for the permethrin criteria at this time to adjust for temperature-related toxicity because there is inadequate aqueous exposure data to quantify this effect across species at this time. Environmental managers could choose to add an additional safety factor if it appeared that the criteria were not protective of aquatic life in a colder water body.

Review 1-10: *Sensitive species*
The calculated acute and chronic criteria (10- and 2-ng/L, respectively) are both below the lowest reported acute value of 21.1 ng/L reported for an amphipod. The chronic criterion is also below the lowest reported maximum acceptable toxicant concentration of 16 ng/L reported for a marine mysid shrimp. The conclusion that both the calculated acute and chronic criteria derived in this report should be adequately protective of aquatic environments is appropriate.

RTR 1-10: Comment acknowledged.

Review 1-11: *Ecosystem and other studies*
The authors reviewed several studies that evaluated potential ecosystem impacts of permethrin in mesocosms and ecosystems. Impacts on invertebrates were only noted at concentrations of permethrin that exceeded the proposed acute and chronic criteria. The studies support the use of dissolved permethrin as the principal exposure medium.

RTR 1-11: Comment acknowledged.

Review 1-12: *Threatened and endangered species*
Fish (*Oncorhynchus spp.*) that are listed as endangered in California are represented in the data set that was used to derive the acute criterion. Because fish in general, and these species specifically, are relatively insensitive to permethrin, the proposed acute and chronic criteria are protective of these species. Data for other threatened or endangered species, including plants, were not in the data set and appropriate surrogates were not available. Accordingly, specific conclusions could not be offered for these species. However, the mode of action of permethrin indicates that it should not be highly toxic to plant species.

RTR 1-12: Comment acknowledged.

Review 1-13: *Bioaccumulation*
Permethrin has a high K_{ow} and therefore a high potential to bioaccumulate in aquatic organisms. Reported bioconcentration factors are consistent with this K_{ow} and a bioaccumulation factor (BAF) approach was used to estimate the water concentration of permethrin that would result in a lethal concentration in wildlife that would consume contaminated fish. A NOEC value of 125 mg/kg for mallard ducks was used in this calculation. Because this was the highest dose tested, a higher NOEC is probable. Using this approach, a water concentration of at least 4.46 µg/l would be required to produce a body burden of permethrin in fish that would be below the toxic threshold for mallards. This result clearly indicates that toxicity to mallards via food web transfer is unlikely. The high likelihood that such a water concentration, which is close to the aqueous solubility of permethrin and would be acutely lethal to prey species, including fish, should be mentioned.

RTR 1-13: The bioaccumulation section has been revised to note that food-web transfer would not be likely because the aqueous concentrations required for such transfers to occur are nearing the aqueous solubility of permethrin or would be likely to cause acute toxicity to aquatic organisms.

Review 1-14: *Harmonization with air and sediment criteria*
Sediment and air quality standards for permethrin do not exist. However, because permethrin has a relatively high partition coefficient, dissolved concentrations may serve as a proxy for sediment burdens if Koc values are available for a given site. This is consistent with the previous discussion of bioavailability.

RTR 1-14: Comment acknowledged.

Review 1-15: *Limitations, assumptions and uncertainties*
The authors correctly point out that the major sources of uncertainty in this evaluation stem from three of the five taxa requirements not being met for

the chronic toxicity data set. The approach used (i.e., ACR) is appropriate given this limitation. The potential effect of lower temperatures on permethrin toxicity is potentially significant and should be considered in criterion development as more data becomes available.

RTR 1-15: Comment acknowledged.

Review 1-16: *Comparison to national standard methods*
EPA (1985) methods were also used to derive acute and chronic criteria for permethrin. The EPA method faces the same limitation encountered in this report, that is, lack of data for all required taxa. The acute criterion proposed in this study is identical to the EPA-derived value for invertebrates (10 ng/L). A chronic criterion could not be calculated by the EPA method due to the lack of sufficient ACR data.

RTR 1-16: Comment acknowledged.

Review 1-17: *Final criteria statement*
The recommended acute criterion is equivalent to the standard derived using EPA criteria. As proposed, the acute criterion of 10 ng/L and the chronic criterion of 2 ng/L should be protective of aquatic species in the Sacramento and San Joaquin River basins. The statement that the criteria were derived to be protective of aquatic life in the Sacramento and San Joaquin Rivers is a bit misleading, however, as the criteria were not derived exclusively using endemic species. The criteria were in fact derived for a generic freshwater North American ecosystem. The authors appropriately point out that the robustness of the derived criteria is limited by available data and should be updated as new information becomes available.

RTR 1-17: The statement regarding use of the criteria for freshwater ecosystems has been revised to the following:

While the aim of this criteria report was to derive criteria protective of aquatic life in the Sacramento and San Joaquin Rivers, these criteria would be appropriate for any freshwater ecosystem in North America, unless species more sensitive than are represented by the species examined in the development of these criteria are likely to occur in those ecosystems.

Review 1-18: *Typographical corrections*
Table 4: For the column header “Chemical grade,” “Chemical” needs to be on the same line.

Table 9: For the column header “Chemical grade,” “Chemical” needs to be on the same line.

RTR 1-18: The typographical errors mentioned above have been corrected in the final permethrin report.

3.2. Peer Review 2 – Stella McMillan, California Department of Fish and Game

REVIEW 2-1: The proposed acute and chronic criteria for diazinon are 10 ng/L and 2 ng/L, respectively. It appears that sufficient data were available to derive these criteria and they appear appropriate to protect aquatic organisms.

RTR 2-1: Comment acknowledged.

3.3. Peer Review 3 – Xin Deng, California Department of Pesticide Regulation

REVIEW 3-1: The permethrin water quality criteria were derived by applying a new methodology developed by the University of California, Davis (TenBrook *et al*. 2009). Explicitly following the data evaluation criteria of the methodology, the author(s) identified 14 acute and 3 chronic toxicity studies that were reliable and relevant for permethrin criteria derivation from approximately 155 original studies. As acute toxicity data were acceptable from five taxa (i.e., a warm water fish, a cold water fish, a planktonic crustacean, a benthic crustacean, and an insect), a species sensitivity distribution procedure was applied to derive the acute water quality criterion and yielded a recommended criterion of 10 ng/L. The acute criterion is identical to the value calculated by the US EPA method. The chronic criterion was calculated by using the acute-to-chronic ratio (ACR) method that yielded a chronic value of 2 ng/L. Analyses on the existing toxicity data from sensitive species, threatened and endangered species, and ecosystem studies suggested that the derived acute and chronic criteria be protective of aquatic organisms under the current knowledge of permethrin toxicity.

RTR 3-1: Comment acknowledged.

REVIEW 3-2: The authors appropriately addressed the limitations and uncertainties involved in the criteria derivation. Because of the high hydrophobicity of pyrethroids that could lead to significant chemical loss in dissolved phase during toxicity tests, it is more appropriate to derive the criteria with toxicity data that are calculated by using measured concentrations from flow-through tests. However, only two flow-through tests and two measured toxicity tests in the data sets are available for the acute criterion derivation. This limitation could lead to an underestimated criterion. For the chronic criterion, the limitations and uncertainties are primarily attributed to the limited number of data sets (only three reliable and relevant data available), lack of paired data to calculate a multi-species ACR (only one pair available thus two default ACR values were used), and absence of the chronic toxicity data on the most sensitive species, *Hyalella azteca*. Other uncertainties are related to toxicity increases with lower temperatures and addition of PBO in pyrethroid formulations. Nevertheless, those limitations and uncertainties could not be corrected or quantified unless additional data are available in the future.

RTR 3-2: Comment acknowledged.

4.0 References

Anderson RL. 1982. Toxicity of fenvalerate and permethrin to several nontarget aquatic invertebrates. Environ Entomol 11:1251-1257.

Bondarenko S, Putt A, Kavanaugh S, Poletika N, Gan JY. 2006. Time dependence of phase distribution of pyrethroid insecticides in sediment. Environ Toxicol Chem 25:3148-3154.

Bondarenko S, Spurlock F, Gan J. 2007. Analysis of pyrethroids in sediment pore water by solid-phase microextraction. Environ Toxicol Chem 26:2587-2593.

CSIRO. 2000. BurrliOZ v. 1.0.13: Commonwealth Scientific and Industrial Research Organization, Australia.

Dwyer FJ, Sappington LC, Buckler DR, Jones SB. 1995. Use of a surrogate species in assessing contaminant risk to endangered and threatened fishes. Final report – September, 1995. EPA/600/R-96/029.

Dwyer FJ, Mayer FL, Sappington LC, Buckler DR, Bridges CM, Greer IE, Hardesty DK, Henke CE, Ingersoll CG, Kunz JL, Whites DW, Augsprger T, Mount DR, Hattala K, Neuderfer GN. 2005. Assessing contaminant sensitivity of endangered and threatened aquatic species: Part I. Acute toxicity of five chemicals. Arch Environ Contam Toxicol 48:143-154.

Fojut TL, Tjeerdema RS. 2010. Water quality criteria report for lambda-cyhalothrin. Draft. Phase III: application of the pesticide water quality criteria methodology. Department of Environmental Toxicology, University of Davis. Report prepared for Central Valley Regional Water Quality Control Board.

Fojut TL, Rering C, Tjeerdema RS. 2011a. Water quality criteria report for permethrin. Draft. Phase III: application of the pesticide water quality criteria methodology. Department of Environmental Toxicology, University of Davis. Report prepared for Central Valley Regional Water Quality Control Board.

Fojut TL, Mulligan R, Tjeerdema RS. 2011b. Water quality criteria report for cypermethrin. Draft. . Phase III: application of the pesticide water quality criteria methodology. Department of Environmental Toxicology, University of Davis. Report prepared for Central Valley Regional Water Quality Control Board.

Host GE, Regal RR, Stephan CE. 1995. Analyses of acute and chronic data for aquatic life. Report. United States Environmental Protection Agency, Washington, DC.

Hunter W, Xu Y, Spurlock F, Gan J. 2008. Using disposable polydimethylsiloxane fibers to assess the bioavailability of permethrin in sediment. Environ Toxicol Chem 27:568-575.

Kent SJ, Williams NJ, Gillings E, Morris DS. 1995. Permethrin: chronic toxicity to *Daphnia magna.* Zeneca Brixham Environmental Laboratory: Brixham, UK. Laboratory project ID BL5443/B. EPA MRID 43745701.

Laskowski DA. 2002. Physical and chemical properties of pyrethroids. Rev Environ Contam Toxicol 174:49-170.

LeBlanc GA. 1976. Acute toxicity of FMC-33297 technical to *Daphnia magna.* EG&G, Bionomics: Wareham, MA. CDPR ID: study number 15100.

Liu WP, Gan JJ, Lee S, Kabashima JN. 2004. Phase distribution of synthetic pyrethroids in runoff and stream water. Environ Toxicol Chem 23:7-11.

Mayer LM, Weston DP, Bock MJ. 2001. Benzo[a]pyrene and zinc solubilization by digestive fluids of benthic invertebrates – A cross-phyletic study. Environ Toxicol Chem 20:1890-1900.

Muir DCG, Hobden BR, Servos MR. 1994. Bioconcentration of pyrethroid insecticides and DDT by rainbow trout: uptake depuration, and effect of dissolved organic carbon. Aquatic Toxicol 29:223-240.

Palmquist KR, Jenkins JJ, Jepson PC. 2008. Effects of dietary esfenvalerate exposures on three aquatic insect species representing different functional feeding groups. Environ Toxicol Chem 27:1721-1727.

Sappington LC, Mayer FL, Dwyer FJ, Buckler DR, Jones JR, Ellersieck MR. 2001. Contaminant sensitivity of threatened and endangered fishes compared to standard surrogate species. Environ Toxicol Chem 20:2869-2876.

Schwarzenbach RP, Gschwend PM, Imboden DM. 2003. Environmental Organic Chemistry. New York, NY: John Wiley & Sons, Inc.

Semple KT, Doick KJ, Jones KC, Burauel P, Craven A, Harms H. 2004. Defining bioavailability and bioaccessibility of contaminated soil and sediment is complicated. Environ Sci Technol 38:228A-231A.

Spehar RL, Tanner DK, Nordling BR. 1983. Toxicity of the synthetic pyrethroids, permethrin and AC 222,705 and their accumulation in early life stages of fathead minnows and snails. Aquat Toxicol 3:171-182.

Surprenant DC. 1979. Acute toxicity of FMC 33297 to the water flea (*Daphnia magna)*. EG&G Bionomics Report BW-79-12-547.

TenBrook PL, Palumbo AJ, Fojut TL, Tjeerdema RS, Hann P, Karkoski J. 2009. 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. Report prepared for the Central Valley Regional Water Quality Control Board, Rancho Cordova, CA.

Thompson RS. 1986. Supplemental data in support of MRID 42584001. Permethrin: Determination of acute toxicity to mysid shrimps (*Mysidopsis bahia).* Laboratory project ID BL/B/2921. Brixham study no P131/B. Study performed by Brixham Environmental Laboratory: Devon, UK. EPA MRID 43492902.

Thompson RS, Williams TD, Tapp JF. 1989. Permethrin: Determination of chronic toxicity to mysid shrimps (*Mysidopsis bahia)* (Run 2). Laboratory project ID: BL/B/3574. Study performed by Imperial Chemical Industries PLC Brixham Laboratory Freshwater Quarry: Brixham, Devon, UK. EPA MRID 41315701.

Trimble AJ, Weston DP, Belden JB, Lydy MJ. 2009. Identification and evaluation of pyrethroid insecticide mixtures in urban sediments. Environ Toxicol Chem 28:1687-1695.

USEPA. 1985. Guidelines for deriving numerical national water quality criteria for the protection of aquatic organisms and their uses, PB-85-227049. United States Environmental Protection Agency, National Technical Information Service, Springfield, VA.

USEPA. 2003. Water quality guidance for the Great Lakes system. Federal Register, 40 CFR Part 132. US Environmental Protection Agency, Washington DC.

Yang W, Gan J, Hunter W, Spurlock F. 2006. Effect of suspended solids on bioavailability of pyrethroid insecticides. Environ Toxicol Chem 25:1585-1591.

Yang WC, Hunter W, Spurlock F, Gan J. 2007. Bioavailability of permethrin and cyfluthrin in surface waters with low levels of dissolved organic matter. *J Environ Qual* 36:1678-1685.

You J, Harwood AD, Li H, Lydy MJ. 2011. Chemical techniques for assessing bioavailability of sediment-associated contaminants: SPME versus Tenax extraction. J Environ Monit 13:792-800.