

Proposed Amendments to the Water Quality Control Plan for the Sacramento and San Joaquin River Basins for the Control of Pyrethroid Pesticides Discharges

Peer Review

Jeffrey J Jenkins
Department of Environmental and Molecular Toxicology
Oregon State University

July 13, 2015

As per the statutory mandate for external scientific review (California Health and Safety Code Section 57004) states that it is the reviewer's responsibility to determine whether the scientific portion of the proposed rule (i.e., the Draft Basin Plan Amendment – Appendix A in the Draft Staff Report¹) is based upon sound scientific knowledge, methods, and practices.

Below I provide a review of the scientific portions of the Draft Staff Report that pertain to my expertise in ecotoxicology. In preparing this review I have reviewed the Draft Staff Report, the UC – Davis methodology², and the UC – Davis Water Quality Criteria Reports for the 6 pyrethroids (March 2015). As requested, I will confine my review to the following Draft Staff Report assumptions, findings, and conclusions that support changes to the existing basin plan proposed by the amendment:

1. The proposed water quality objectives are reasonably protective of the beneficial uses that are most sensitive to pyrethroid pesticides.
2. The underlying method for deriving the pyrethroid pesticides water quality criteria, which are proposed as water quality objectives and TMDLs, is scientifically sound.
3. The proposed TMDL loading capacity, allocations, and margin of safety are clearly described and consistent with attaining water quality objectives that are protective of the beneficial use(s) most sensitive to pyrethroid pesticides.
4. For determining compliance with water quality objectives it is scientifically sound and protective of beneficial uses to consider the 6 pyrethroid pesticides additively if more than one is detected in a water sample. Based on current information available, it is not scientifically sound to assume additive toxicity of other constituents with pyrethroid pesticides.

Review comments are organized by the numbered Draft Staff Report assumptions, findings, and conclusions given above.

¹ Proposed Amendments to the Water Quality Control Plan for the Sacramento and San Joaquin River Basins for the Control of Pyrethroid Pesticides Discharges Draft Staff Report May 2015.

² TenBrook, PL, AJ Palumbo, and RS Tjeerdema. Methodology for Derivation of Pesticide Water Quality Criteria for the Protection of Aquatic Life Phase II: Methodology Development and Derivation of Chlorpyrifos Criteria. Report Prepared for the Central Valley Regional Water Quality Control Board. Department of Environmental Toxicology, University of California, Davis. September 2009.

1. The proposed water quality objectives are reasonably protective of the beneficial uses that are most sensitive to pyrethroid pesticides.

Water Quality Objectives for the 6 pyrethroid pesticides are presented in Section 5 of the Draft Staff Report. Water quality is defined in terms of preserving or enhancing aquatic life beneficial uses (aquatic life and their habitat). Protecting against toxicity to aquatic life is considered a primary concern in preserving or enhancing aquatic life beneficial uses. To meet these qualitative objectives numeric water quality objectives (criteria) have been developed for six pyrethroid pesticides for all water bodies designated with aquatic life beneficial uses in the Sacramento River and San Joaquin River basins. Water quality criteria and supporting science for the 6 pyrethroids developed using the UC Davis methodology and contained in the March 2015 reports are scientifically sound. In addition, appropriate use of these numeric criteria can be effective in meeting qualitative water quality objectives that preserve or enhance aquatic life beneficial uses.

2. The underlying method for deriving the pyrethroid pesticides water quality criteria, which are proposed as water quality objectives and TMDLs, is scientifically sound.

The proposed water quality criteria and TMDLs for the 6 pyrethroid pesticides rely on the UC – Davis Methodology reported in TenBrook and Tjeerdema (2006)³, and subsequent derivation and application of the UC-Davis methodology for specific pesticides (TenBrook et al., 2009)⁴. Evaluation of the scientific basis for the assignment of numeric targets will largely rely on the review of methodologies conducted as these reports are considered current, highly relevant, and comprehensive.

The UC-Davis methodology used as the basis for the assignment of acute and chronic numeric targets contains the following elements in a step by step format:

- Guidance for collection, evaluation, and reduction of data;
- Species sensitivity distribution (SSD) methods to derive criteria when data are available for five representative taxa - 1) a warm water fish, 2) a fish in the family Salmonidae, 3) a planktonic crustacean – Ceriodaphnia, Daphnia, or Simocephalus, 4) a benthic crustacean, and 5) an insect (aquatic exposure).
- Data quality and quantity dependent SSD procedures.
- An assessment factor (AF) method to derive acute criteria when fewer than five acute toxicity data are available;
- A default acute-to-chronic ratio (ACR) to derive chronic criteria when fewer than five chronic data are available;
- Methods for assessing bioavailability;

³ TenBrook, TL and RS Tjeerdema. Methodology for Derivation of Pesticide Water Quality Criteria for the Protection of Aquatic Life in the Sacramento and San Joaquin River Basins. Phase I: Review of Existing Methodologies. Report Prepared for the Central Valley Regional Water Quality Control Board. Department of Environmental Toxicology, University of California, Davis. April 2006.

⁴ TenBrook, PL, AJ Palumbo, and RS Tjeerdema. Methodology for Derivation of Pesticide Water Quality Criteria for the Protection of Aquatic Life Phase II: Methodology Development and Derivation of Chlorpyrifos Criteria. Report Prepared for the Central Valley Regional Water Quality Control Board. Department of Environmental Toxicology, University of California, Davis. September 2009.

- Methods for assessing compliance in cases of mixtures of chemicals with similar modes of toxic action and for mixtures that exhibit non-additive toxicity;
- Methods for quantifying relationships between toxicity and water quality parameters, such as pH and temperature;
- Techniques for assessing whether derived criteria might harm particularly sensitive species, lead to bioaccumulation, harm ecosystems, harm threatened and endangered species, or lead to unacceptable levels of pesticides in other environmental compartments;
- A template for describing final criteria in terms of magnitude, duration and frequency.

This methodology defines a pesticide as "1) any substance or mixture of substances that is intended to be used for defoliating plants, regulating plant growth, or for preventing, destroying, repelling, or mitigating any pest, which may infest or be detrimental to vegetation, man, animals, or households, or be present in any agricultural or nonagricultural environment whatsoever, or 2) any spray adjuvant, or 3) any breakdown products of these materials that threaten beneficial uses."

The methodology prescribes appropriate endpoints for criteria derivation as those that measure survival, growth, or reproductive effects. Surrogates (i.e., LC₅₀, EC₅₀, NOEC, LOEC, MATC) may be used if those endpoints have been linked to effects on survival, growth, or reproductive effects.

The UC-Davis methodology employs various statistical methods, dependent on data quality and quantity, in deriving SSDs, and when data limited estimating chronic criterion using acute data. For example, details of the application of the log-logistic SSD procedure for bifenthrin are as follows:

"The log-logistic SSD procedure (section 3-3.2.2) was used for the acute criterion calculation because there were not more than eight acceptable acute toxicity values available in the bifenthrin data set (Table 2). The log-logistic SSD procedure was used to derive 5th percentile values (median and lower 95% confidence limit), as well as 1st percentile values (median and lower 95% confidence limit). The median 5th percentile value is recommended for use in criteria derivation by the methodology because it is the most robust of the distributional estimates (section 3-3). Comparing the median estimate to the lower 95% confidence limit of the 5th percentile values, it can be seen that the first significant figures of the two values are different (0.0016419 vs. 0.0000240 ug/L). Because there is uncertainty in the first significant digit, the final criterion will be reported with one significant digit (section 3-3.2.6).

The ETX 1.3 Software program (Aldenberg 1993) was used to fit the log-logistic distribution to the data set, which is plotted with the acute values in Figure 2. This distribution provided a satisfactory fit (see Appendix A) according to the fit test described in section 3-3.2.4. No significant lack of fit was found ($\chi^2_{2n} = 0.1247$) using the fit test based on cross validation and Fisher's combined test (section 3-3.2.4), indicating that the data set is valid for criteria derivation."

This statistical analysis, as well as all methods employed in UC-Davis methodology, demonstrates statistical rigor in the evaluation of all available toxicity values that meet data quality criteria, and is among the most robust evaluations of this type currently employed for regulatory purposes worldwide; these methods have the potential to greatly reduce uncertainty in estimating no-effect exposure levels by reducing the probability of both Type I error or false negative when there is a null hypothesis of some adverse effect, and Type II error or false positive; failure to reject the potentially false null hypothesis, i.e., no effect).

Derivation of Final Criteria Statements

Bifenthrin

The acute criterion for bifenthrin was derived using the SSD method as at least five acceptable acute toxicity values were available and fulfilled the five taxa requirements of the SSD method. Using the log-logistic SSD procedure the resulting acute criterion, based on the median 5th percentile value, is 0.0008 ug/L. This value is considered acceptable for its intended purpose.

As chronic toxicity values from fewer than five different families were available the ACR procedure was used to calculate the bifenthrin chronic criterion. Because an ACR could not be calculated with the available data, the chronic criterion was calculated with the default ACR value of 11.4 = 0.0001 ug/L. This value is considered acceptable for its intended purpose.

However, further “sensitivity analysis” determined that this acute criterion is not protective of the sensitive species *H. azteca*. This determination was based on comparing the result of the SSD analysis – the median 5th percentile acute value – to the lowest acute value for *H. azteca*. Consequently the median 1st percentile estimate was used to derive the acute and chronic criteria, resulting in final bifenthrin criteria of acute = 0.00006 ug/L and chronic = 0.00001 ug/L. While these criteria are sufficiently conservative and deemed acceptable for the intended purpose, use of the median 1st percentile estimate of acute criterion, a less reliable estimate, is inconsistent with the derivation of other acute and chronic criteria for which there is sufficient data to use the SSD approach. Given the premise for use of the SSD approach in the UC-Davis Methodology – a robust statistical analysis using all of the available toxicity values that meet data quality criteria – it seems arbitrary to use the median 1st percentile estimate for the sole purpose of deriving a toxicity value that is less than the *H. azteca* lowest acute value, a single value of unknown significance. If a goal of the SSD approach is to reduce the probability of both Type I and Type II error in estimating the acute value, use of the median 5th percentile acute value is consistent with other assessments and appropriate for its intended purpose, regardless of whether the result is greater than an independent acute value of unknown significance.

Alternatively, if *H. azteca* is significantly more sensitive than taxa required for use of the SSD approach in the UC-Davis methodology, and is ultimately the driver in determining criteria, then it should be included as a required species for SSD analysis. Otherwise, the statistical power that is derived from the SSD approach for determination of water quality criteria needs careful consideration.

λ-cyhalothrin

For λ-cyhalothrin The Burr Type III SSD procedure was used for the acute criterion calculation because more than eight acceptable acute toxicity values were available in the λ-cyhalothrin data set. This procedure, roughly equivalent to the Clean Water Act (CWA) National Standard methodology, the acute criteria=0.0007 ug/L is based on the median 5th percentile acute value. This value is considered acceptable for its intended purpose.

As chronic data for only 3 of the 5 representative taxa (including a saltwater species) were available for λ-cyhalothrin, the ACR method was used to calculate the chronic criterion by pairing chronic toxicity values (MATC) with an appropriate corresponding acute toxicity value (LC₅₀) in order to calculate an ACR; the species mean ACR (SMACR) for each of the three species was calculated by dividing the acute LC50 value by the chronic MATC value. The final multi-species ACR was obtained by calculating the

geometric mean of the three SMACR resulting in the ACR-derived chronic criterion = 0.0003 ug/L. This value is considered acceptable for its intended purpose.

However, further “sensitivity analysis” determined that this acute criterion is not protective of the sensitive species *H. azteca*. This determination was based on comparing the result of the SSD analysis – the median 5th percentile acute value – to the lowest acute value for *H. azteca*. Consequently the median 1st percentile estimate was used to derive the acute and chronic criteria, resulting in final λ-cyhalothrin criteria of acute = 0.00003 ug/L and chronic = 0.00001 ug/L. While this value is considered acceptable for its intended purpose, see discussion above regarding use of the median 1st percentile to estimate of bifenthrin acute criterion.

Cyfluthrin

The acute criteria for cyfluthrin was derived using the log-logistic SSD method as at least five acceptable acute toxicity values were available and fulfilled the five taxa requirements of the SSD. The resulting acute criterion = 0.0008 ug/L, based on the median 5th percentile acute value.

As chronic toxicity values from fewer than five different families were available the ACR procedure was used to calculate the cyfluthrin chronic criterion. The ACRs were calculated for each of the three species by dividing the acute LC50 value by the chronic MATC value. The final multi-species ACR of 10.27 was obtained by calculating the geometric mean of the three ACR values; resulting in a chronic criterion = 0.0002 ug/L. This value is considered acceptable for its intended purpose.

However, further “sensitivity analysis” determined that this acute criterion is not protective of the sensitive species *H. azteca*. This determination was based on comparing the result of the SSD analysis – the median 5th percentile acute value – to the lowest acute value for *H. azteca*. Consequently the median 1st percentile estimate was used to derive the acute and chronic criteria, resulting in final cyfluthrin criteria of acute = 0.00007 ug/L and chronic = 0.00001 ug/L. While this value is considered acceptable for its intended purpose, see discussion above regarding use of the median 1st percentile to estimate of bifenthrin acute criterion.

Cypermethrin

As at least five acceptable acute toxicity values were available and fulfilled the five taxa requirements and more than eight acceptable acute toxicity values were available the Burr Type III SSD procedure was used to determine the median 5th percentile acute value, resulting in cypermethrin acute criterion = 0.001 ug/L. This value is considered acceptable for its intended purpose.

As chronic toxicity values from fewer than 5 different families were available the acute-to-chronic ratio (ACR) method was used to calculate the chronic criterion. While chronic toxicity data was available for one freshwater species and one saltwater, however only the saltwater species data met data quality requirements and could be paired with acute data to determine the ACR. Surrogate (default) data for cyfluthrin and λ-cyhalothrin were used to meet data requirements of the ACR method. The final multi-species ACR was obtained by calculating the geometric mean of the saltwater species with two default ACR values, resulting in a cypermethrin chronic criterion = 0.0003 ug/L. Discussion of the rationale for use of this surrogate data is missing and seems appropriate. EPA has conducted a cumulative human health

risk assessment⁵ in which pyrethroid relative potency factors (RPFs) are reported based on studies in mammals. A cypermethrin RPF of 0.19 indicates that it is less potent than cyfluthrin (RPF=1.15) and λ -cyhalothrin (RPF=1.63). While RPFs take into consideration both target site sensitivity and pharmacokinetics and dynamics, as the pyrethroids have a common mode of action across taxa – disruption of voltage-gated sodium channels leading to alteration of neuronal membranes and ultimately neurotoxicity – these findings suggest that the use of cyfluthrin and λ -cyhalothrin ACRs in determining the cypermethrin chronic criterion may be overly conservative while protective of aquatic life. In addition, ACRs as a function of potency should be addressed.

However, further “sensitivity analysis” determined that this acute criterion is not protective of the sensitive species *H. azteca*. This determination was based on comparing the result of the SSD analysis – the median 5th percentile acute value – to the lowest acute value for *H. azteca*. Consequently the median 1st percentile estimate was used to derive the acute and chronic criteria, resulting in final cyfluthrin criteria of acute = 0.00004 ug/L and chronic = 0.00001 ug/L. While this value is considered acceptable for its intended purpose, see discussion above regarding use of the median 1st percentile to estimate of bifenthrin acute criterion.

Esfenvalerate

As at least five acceptable acute toxicity values were available and fulfilled the five taxa requirements and more than eight acceptable acute toxicity values were available the Burr Type III SSD procedure was used to determine the median 5th percentile acute value, resulting in esfenvalerate acute criterion = 0.002 ug/L. This value is considered acceptable for its intended purpose.

As chronic toxicity values for 3 different families were available, the acute-to-chronic ratio (ACR) method was used to calculate the chronic criterion. As acceptable acute and chronic data was only available for 1 species, the final multi-species ACR was obtained by calculating the geometric mean of the daphnid ACR with two default ACR values (surrogate data for cyfluthrin and λ -cyhalothrin), resulting in a esfenvalerate chronic criterion = 0.0003 ug/L. Discussion of the rationale for use of this surrogate data is missing and seems appropriate. EPA has conducted a cumulative human health risk assessment³ in which pyrethroid relative potency factors (RPFs) are reported based on studies in mammals. An esfenvalerate RPF of 0.36 indicates that it is less potent than cyfluthrin (RPF=1.15) and λ -cyhalothrin (RPF=1.63). While RPFs take into consideration both target site sensitivity and pharmacokinetics and dynamics, as the pyrethroids have a common mode of action across taxa – disruption of voltage-gated sodium channels leading to alteration of neuronal membranes and ultimately neurotoxicity – these findings suggest that the use of cyfluthrin and λ -cyhalothrin ACRs in determining the esfenvalerate chronic criterion may be overly conservative while protective of aquatic life. In addition, ACRs as a function of potency should be addressed.

However, further “sensitivity analysis” determined that this acute criterion is not protective of the sensitive species *H. azteca*. This determination was based on comparing the result of the SSD analysis – the median 5th percentile acute value – to the lowest acute value for *H. azteca*. Consequently the median 1st percentile estimate was used to derive the acute and chronic criteria, resulting in final esfenvalerate criteria of acute = 0.0002 ug/L and chronic = 0.00003 ug/L. While this value is considered acceptable for its intended purpose, see discussion above regarding use of the median 1st percentile to estimate of bifenthrin acute criterion.

⁵ http://epa.gov/pesticides/cumulative/common_mech_groups.htm#pyrethrins

Permethrin

As at least five acceptable acute toxicity values were available and fulfilled the five taxa requirements and more than eight acceptable acute toxicity values were available the Burr Type III SSD procedure was used to determine the median 5th percentile acute value, resulting in permethrin acute criterion = 0.006 ug/L. This value is considered acceptable for its intended purpose.

As chronic toxicity values from fewer than 5 different families were available the acute-to-chronic ratio (ACR) method was used to calculate the chronic criterion. While chronic toxicity data was available for one freshwater species and one saltwater, however only the saltwater species data met data quality requirements and could be paired with acute data to determine the ACR. Surrogate (default) data for cyfluthrin and λ -cyhalothrin were used to meet data requirements of the ACR method. The final multi-species ACR was obtained by calculating the geometric mean of the saltwater species with two default ACR values, resulting in a permethrin chronic criterion = 0.001 ug/L. Discussion of the rationale for use of this surrogate data is missing and seems appropriate. EPA has conducted a cumulative human health risk assessment³ in which pyrethroid relative potency factors (RPFs) are reported based on studies in mammals. A permethrin RPF of 0.09 indicates that it is significantly less potent than cyfluthrin (RPF=1.15) and λ -cyhalothrin (RPF=1.63). While RPFs take into consideration both target site sensitivity and pharmacokinetics and dynamics, as the pyrethroids have a common mode of action across taxa – disruption of voltage-gated sodium channels leading to alteration of neuronal membranes and ultimately neurotoxicity – these findings suggest that the use of cyfluthrin and λ -cyhalothrin ACRs in determining the permethrin chronic criterion may be overly conservative while protective of aquatic life. In addition, ACRs as a function of potency should be addressed. However, Permethrin acute and chronic criteria are considered acceptable for their intended purpose.

3. The proposed TMDL loading capacity, allocations, and margin of safety are clearly described and consistent with attaining water quality objectives that are protective of the beneficial use(s) most sensitive to pyrethroid pesticides.

The use of urban point source discharge allocations to address pyrethroid TMDL loading capacity impairment objectives is typical and practicable. For non-point source pyrethroid discharge from agricultural lands assigning allocations is not feasible or practicable at this time. Assigning TMDL allocations for non-point source discharge from agricultural lands requires detailed spatial-temporal information on pesticide distribution and fate at the watershed scale and beyond. Effective implementation will require monitoring and modeling technologies that currently not available for this purpose, such as GIS-based ecohydrologic models that incorporate agronomic practices. However, the Clean Water Act (CWA) category 4(b) alternative, as described in Section 6.2, is a viable approach to in meeting water quality objectives that are protective of the beneficial use(s) most sensitive to pyrethroid pesticides. This approach relies on sufficiently stringent provisions of the Irrigated Lands Regulatory Program, including best management practices designed to reduce surface water loading, as well as monitoring to evaluate BMP performance.

As required by the CWA, TMDLs must also include a margin of safety (MOS) to account for the uncertainty in predicting how well pollutant reduction will result in meeting water quality standards, and account for seasonal variations. As point source allocations are concentration-based (the alternative being mass-based) and water quality objectives are concentrations, a MOS is implicit regarding seasonal variations in discharge or volume of receiving waters. In addition, the UC-Davis Methodology used to derive the criteria is sufficiently conservative to address other areas of uncertainty.

4. For determining compliance with water quality objectives it is scientifically sound and protective of beneficial uses to consider the 6 pyrethroid pesticides additively if more than one is detected in a water sample. Based on current information available, it is not scientifically sound to assume additive toxicity of other constituents with pyrethroid pesticides.

Pyrethroid use practices and monitoring data indicate that the co-occurrence of pyrethroids in the surface waters of the Sacramento and San Joaquin Basins is likely. As the pyrethroids have shared structural characteristics and a common mode of action – disruption of voltage-gated sodium channels leading to alteration of neuronal membranes and ultimately neurotoxicity – their toxicity to aquatic life should be considered jointly. Since Bliss (1939)⁶ three basic types of action for combinations of chemicals have been defined:

- Similar action (dose/concentration addition)
- Dissimilar action (independent action), and
- Interactions (agonist, antagonist)

Consideration of chemical mixtures with a common mode of action is of interest as the mixture may exceed an adverse effect threshold even when the individual chemicals are at concentrations that are below their threshold. The Staff report provides a detailed appraisal of the relevant literature and concludes that the pyrethroids have a common mode of action and act jointly by dose/concentration addition. Dose/concentration addition assumes that all components in a mixture contribute to the joint effect, in proportion to their prevalence and individual potency. This implies that individual pyrethroid concentrations in a mixture should be normalized based on their potency – using LC50 values or some other endpoint to determine relative potency factors (RPF) or toxicity equivalency factor (TEF). The Staff Report implies that data was insufficient for potency normalization and that toxicity thresholds varied by no more than a factor of 2. Consequently, acute and chronic water quality objectives for the 6 pyrethroids are based on additive toxicity (normalized for individual acute and chronic criteria), as determined by equations 7 and 8 in Section 5.9. Adequate consideration of the additive toxicity of the pyrethroids jointly with the action all other co-occurring constituents is not justified given the current state of knowledge and would be outside the scope of current regulations. Consequently, assumptions regarding pyrethroid additive toxicity are deemed scientifically sound and protective of beneficial uses. However, in the future the co-occurrence of the pyrethroids with other neurotoxins should be considered in the context of neurological adverse outcome pathways.

⁶ Bliss, CI. 1939. The Toxicity of Poisons Applied Jointly. *Annals of Applied Biology*. 26 (3) 585-615