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TECHNICAL MEMORANDUM

Date: December 1, 2014

To: Delyn Ellison-Lloyd, Kelye McKinney, Ken Glotzbach (City of Roseville)

From: Paul Bedore, M.S.

Reviewed by: Art O'Brien, P.E., Michael Bryan, Ph.D.

Re: Review of the October 2014 Draft Pyrethroid Basin Plan Amendment Language

1 Introduction

Robertson-Bryan, Inc. (RBI) has reviewed language drafted by the Central Valley Regional Water Quality Control Board (Regional Water Board) that would amend the Water Quality Control Plan for the Sacramento River and San Joaquin River Basins (Basin Plan) by adopting water quality objectives for pyrethroid pesticides along with implementation and monitoring language associated with the newly adopted pyrethroid water quality objectives. The numeric water quality objectives (referred to as "criteria" by researchers at the University of California at Davis (UCD) that developed them) for pyrethroids will apply basin-wide. Acute and chronic water quality objectives are proposed for the following pyrethroid pesticides, based on criteria derivation work performed by UCD:

- Bifenthrin
- Cyfluthrin
- Lambda-Cyhalothrin
- Cypermethrin
- Esfenvalerate
- Permethrin

In addition to numeric water quality objectives, the Regional Water Board has also proposed an additivity-based water quality objective for pyrethroids. The additivity-based water quality objective is described in detail below.

Pyrethroid water quality criteria derivation reports were prepared by UCD researchers. Throughout this technical memorandum (TM), the UCD reports are referred to as "draft criteria reports" or "final criteria reports." The draft criteria reports were issued to the Regional Water Board, who posted them for public comment and peer review. Following public comment and peer review, the UCD researchers issued final criteria reports to the Regional Water Board. The final criteria reports contain

the authors' recommendations for acute and chronic pyrethroid criteria, and these recommended criteria are equivalent to the numeric water quality objectives in the draft Basin Plan Amendment. Final criteria reports are available for bifenthrin, cyfluthrin, lambda-cyhalothrin, cypermethrin, and permethrin (Palumbo et al. 2010; Fojut et al. 2010a; Fojut et al. 2010b; Fojut et al. 2011a; Fojut et al. 2011b). The draft criteria report for esfenvalerate was recently issued (Trunnelle et al. 2014) and a final criteria report is forthcoming.

The draft Basin Plan Amendment also includes provisions establishing a Total Maximum Daily Load (TMDL) for water bodies in the Central Valley Region that are currently listed as impaired on the Clean Water Act Section 303(d) list due to pyrethroid insecticide-related toxicity. Sections of Pleasant Grove Creek, South Branch Pleasant Grove Creek, and Kaseberg Creek are 303(d)-listed and are subject to the TMDL provisions of the draft Basin Plan Amendment. The Regional Water Board has proposed two numeric targets for the TMDL – a sediment toxicity numeric target and a water quality-based numeric target equivalent to the proposed additivity-based water quality objective. Thus, the draft Basin Plan Amendment and proposed water quality objectives are particularly relevant to the City of Roseville's (City) wastewater and stormwater management operations.

This TM specifically reviews the draft Basin Plan Amendment language that was recently released for public review by the Regional Water Board for the pyrethroid pesticides listed above. While the official public comment period on the draft Basin Plan Amendment will occur in early 2015, the Regional Water Board is requesting stakeholder feedback to refine the draft language prior to peer review. Regional Water Board staff requested that comments on the draft Basin Plan Amendment be submitted by December 1, 2014. At Regional Water Board staff's request, we have also drafted questions to be directed to the peer review panel which we believe to be most relevant in determining the validity of the science supporting the proposed water quality objectives and implementation language.

2 Summary of Conclusions

The following is a summary of our review of the draft Basin Plan Amendment language. The adoption of pyrethroid water quality objectives into the Basin Plan is **premature** for the reasons listed below:

- The proposed chronic objectives are overly stringent and were derived using acute-to-chronic ratios (ACR), an approach that is based on assumptions that have little scientific basis for pyethroids. The chronic criteria are unsuitable for adoption as water quality objectives until they can be derived using a more rigorous and scientific approach. Furthermore, different values for the ACR were used to derive the chronic criteria for esfenvalerate, bifenthrin, cypermethrin, and cyfluthrin without adequate scientific justification for the specific ACRs used.

- The proposed acute objective for cyfluthrin of 0.3 ng/L is unnecessarily overly stringent. In the final cyfluthrin criteria report, an acute criterion of 2 ng/L was derived, and then this criterion was adjusted downward to 0.3 ng/L to be protective of sensitive species. However, the acute cyfluthrin criterion of 2 ng/L is already protective of the sensitive species and thus the adjustment down to 0.3 ng/L lacks adequate scientific justification. Further discussion on this matter is provided below. .

- The proposed additivity-based water quality objective would constitute the lowest of the proposed pyrethroid water quality objectives. The use of the additivity formula as a water quality objective was not developed consistent with any known state or federally issued guidance, is inconsistent with the Basin Plan's intended use of the additivity formula, and is not supported by any scientific data that show beneficial uses will be impacted by mixtures of pyrethroid pesticides below the proposed numeric objectives for the individual pyrethroids.

- The draft Basin Plan Amendment lacks any corresponding implementation language describing how stormwater and wastewater dischargers will determine "cause and contribute" exceedances or whether there is "reasonable potential" to exceed the additivity-based water quality objective.

- Implementation language pertaining to discharges of stormwater from industrial/commercial facilities and construction sites were omitted from the Basin Plan Amendment. Because these facilities and sites are areas of pyrethroid pesticide applications and they can contribute substantial stormwater loads to a given municipal separate storm sewer system (MS4), depending on land use, their exclusion could adversely affect attainment of the water quality objectives or TMDL numeric targets by MS4s.

- The monitoring requirements of the draft Basin Plan Amendment will place dischargers in the position of collecting data using commercial methods and techniques that have not been approved by the United States Environmental Protection Agency (USEPA). Compliance with the proposed water quality objectives cannot be assured or determined using methods that lack standardization, which is especially important for pyrethroids, for which only the most prudent commercial labs can measure with consistent accuracy. Regional Water Board staff review and Executive Officer approval of pyrethroid analytical methods is wholly insufficient to guard against the collection of inaccurate and unreliable data, based on the current status of analytical techniques for measuring pyrethroids at the levels required.

3 Proposed Pyrethroid Water Quality Objectives Derived from UCD developed Criteria

3.1 Proposed Chronic Pyrethroid Objectives

The draft chronic criteria developed by UCD are unsuitable for adoption as water quality objectives in the Basin Plan at this time because considerable uncertainty is associated with the method in which the chronic criteria were derived, yet substantially more robust criteria could be derived with a reasonable amount of effort.

In cases when data from fewer than five taxa are present, the UCD methodology requires that ACRs be used to derive the chronic criterion. ACRs for a given pesticide can vary considerably among species. In general, ACRs have been found to vary from 1 to 20,000 (Chapman et al., 1998). The authors of the UCD method acknowledge that "*…there is no evidence that default ACR values are appropriate for pesticides in general*." They go on to conclude that, nevertheless, some means of calculation of an ACR is necessary, and so accept a default value of 12.4 based on the 80th percentile of ACRs for eight pesticides, including five organochlorine pesticides and three organophosphate pesticides (Tenbrook et al. 2009). ACRs for pyrethroids have been found to vary between 2 and 415 for a variety of species (Solomon et al. 2001), a fact that has been noted by the UCD authors of the criteria reports.

For lambda-cyhalothrin and cyfluthrin, ACRs were derived from pyrethroid-specific datasets that contained toxicity values from a number of different species. However, *Hyalella azteca* is the most sensitive species and the one that drives the acute value. There is no ACR in the datasets for this species or its taxon. Furthermore, for cyfluthrin, the concentrations at which ACRs are derived are approximately two orders of magnitude higher than the acute value. For these reasons, the ACR methodology used by the UCD researchers does not provide a scientifically appropriate means of deriving chronic criteria, particularly in the case of cyfluthrin. For cyfluthrin, the derived chronic criterion is 332 times lower than the most sensitive chronic value in the available dataset.

In the case of bifenthrin, cypermethrin, and permethrin, chronic criteria were derived entirely using the default ACR of 12.4, which incorporates no data on pyrethroids, but instead is 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 for esfenvalerate was developed more recently than criteria for the other pyrethroids (in February 2014) using an updated default ACR of 11.4. Fujot et al. (2014) updated the default ACR to include the chemical-specific ACRs for lambda-cyhalothrin and cyfluthrin. Notwithstanding, the inadequacies of using a default ACR, the updated default ACR was derived predominantly on classes of pesticides whose structures are different, environmental fate is different, and modes of toxic action are mostly different than pyrethroids. The sensitive species

analyses contained in the final criteria reports indicate that the default ACRs consistently produced overly stringent chronic criterion.

Given the wide range in pyrethroid ACRs, lack of scientific support for the use of default ACRs derived from pesticides other than pyrethroids, and clear evidence that the draft chronic criteria are overly stringent, the Regional Water Board should not adopt chronic criteria until the criteria are derived with a scientifically robust and technically valid approach. An additional 17 chronic toxicity studies are needed to satisfy the five taxa requirement to use the more robust species sensitivity distribution (SSD) approach of the UCD methodology. Within a reasonable amount of time, this data could be generated or compiled from recently published studies, and the chronic criteria derived using the SSD approach could be adopted at a later date. The time and fiscal resources necessary to derive scientifically valid chronic criteria are minimal compared to the unnecessary resources dischargers will spend to comply with overly stringent chronic criteria that were derived based on assumptions that have insufficient scientific basis.

3.2 Cyfluthrin Acute Criterion

Because of comments received during the public comment period, the recommended acute criterion for cyfluthrin was recalculated prior to issuance of the final criteria report. The final cyfluthrin criteria report recommended an acute criterion of 0.3 ng/L (Fojut et al. 2010b), which constitutes the lowest acute criterion of the six pyrethroids by a factor of three. The recommended acute cyfluthrin criteria is overly conservative as a result of subjective decisions made by the final criteria report's authors to derive the criterion using the median 1st percentile, rather than the median 5th percentile, of the log-logistic distribution fit of the acute data set. The use of the median 1st percentile was based on the determination that the criterion developed using the median 5th percentile was not protective of the sensitive species. The acute criterion based on the median 5th percentile is 2 ng/L. This criterion is lower than the species mean acute value (SMAV) for *H. azteca* (2.3 ng/L), the sensitive species, but it is not lower than one of the three EC50s for *H. azteca* in the acute toxicity dataset from which the SMAV was calculated (1.7, 2.3, and 3.1 ng/L). On this basis, the authors of the criteria document determined it was necessary to adjust the acute criterion lower; thus they selected the median 1st percentile and derived a recommended acute criterion of 0.3 ng/L. This adjustment to the median 1st percentile has no scientific basis and thus was arbitrary. Moreover, it is not consistent with the UCD methodology, as discussed further below. The downward adjustment of the acute criterion also resulted in a substantially lower chronic criterion because the chronic criterion was calculated using an ACR. As a result, the chronic criterion for cyfluthrin of 0.05 ng/L is overly restrictive in that it is 34 times lower than any toxicity value for freshwater species listed in the "reliable" toxicity datasets and five times lower than a published chronic toxicity value for *Americamysis bahia*, a salt water species.

Comparison of the calculated acute criterion to toxicity studies of the most sensitive species is one of the last steps of criterion derivation required by the UCD methodology (Tenbrook et al. 2009). However, the methodology does not mandate that the criterion be adjusted, nor does it provide any objective basis on which to make this determination. On p. 2-76 the methodology states:

> "*Derived criteria should be compared to studies of the most sensitive species in the data set to ensure that these species will be protected. If a calculated criterion is higher than toxicity values reported for a particularly sensitive species, then the criterion may require downward adjustment, for example, by using the lower 95% or 99% confidence interval estimate of the 5th percentile, rather than the median.*" (Tenbrook et al. 2009).

In the case of cyfluthrin, the acute criterion based on the median 5th percentile (2 ng/L) is protective of the *H. azteca* in terms of the SMAV and should not have been adjusted downward on the basis that the criterion was higher than one of the EC50s in the dataset. The SMAV is the geometric mean of the chemical-specific EC50 and LC50s for the species. The geometric mean is a measure of the central tendency of a dataset and is biased to the dataset's low values in comparison to the arithmetic mean. Because a geometric mean gives greater weight to low EC50s, the SMAV is the preferred threshold with which to compare the acute criterion. However, if further adjustment of the calculated criterion downward is deemed warranted, it should be based on the methodology quoted above, rather than the arbitrary use of the median 1st percentile.

In the case of cypermethrin, the draft acute criterion (1 ng/L) was higher than the minimum EC50 for cypermethrin in the supplemental data set. The acute criterion was not adjusted downward in this case because the minimum EC50 was from a study that was: 1) not based on measured concentrations, and 2) the species was represented in the relevant and reliable data set, which means the data were acceptable for criteria derivation, with a SMAV that indicated it was protected by the acute criterion (Fojut et al. 2011). In this case, the fact that the cypermethrin acute criterion was lower than the SMAV was used in part to substantiate the claim that the acute criterion was protective.

Further, previously adopted water quality objectives support not adjusting the cyfluthrin criterion downward. For example, at 100 mg/L $CaCO_3$, the acute California Toxics Rule (CTR) criterion (CMC) for "total" copper (13 µg/L) is protective of *Ceriodaphnia dubia* in terms of the SMAV (24.00 µg/L), even though the individually published EC50s range from 2.73 to 80.7 µg/L (USEPA 2001).

Based upon the foregoing discussion, the recommended acute criterion for cyfluthrin should be derived based on the median 5th percentile of the distribution of acute toxicity values. The ensuing acute criterion would be 2 ng/L (not 0.3 ng/L as proposed), a value which is protective of *H. azteca*, the sensitive species.

3.3 Additivity-Based Water Quality Objective

The additivity formula should not be used as a water quality objective, or as guidance for determining compliance with the chemical-specific water quality objectives for pyrethroids. The current proposal to include the additivity formula as a water quality objective is problematic for several reasons.

Inclusion of the additivity formula into the draft Basin Plan Amendment has been made on the basis of the Pesticide Discharges section of the Water Quality Control Plan for the Sacramento River and San Joaquin River Basins (Basin Plan; p. IV-35.00):

> *In conducting a review of pesticide monitoring data, the Board will consider the cumulative impact if more than one pesticide is present in the water body. This will be done by initially assuming that the toxicities of pesticides are additive. This will be evaluated separately for each beneficial use using the following formula:*
>
> $$S = \frac{C_1}{O_1} + \frac{C_2}{O_2} + \cdots + \frac{C_i}{O_i}$$
>
> *Where:*
>
> *C = The concentration of each pesticide.*
> *O = The water quality objective or criterion for the specific beneficial use for each pesticide present, based on the best available information. Note that the numbers must be acceptable to the Board and performance goals are not to be used in this equation.*
> *S = The sum. A sum exceeding one (1.0) indicates that the beneficial use may be impacted.*
>
> *The above formula will not be used if it is determined that it does not apply to the pesticides being evaluated. When more than one pesticide is present, the impacts may not be cumulative or they may be additive, synergistic or antagonistic. A detailed assessment of the pesticides involved must be conducted to determine the exact nature of the impacts.*

The draft Basin Plan Amendment has codified the additivity formula as a water quality objective for pyrethroids, as follows:

$$S = \frac{C_{bif}}{O_{bif}} + \frac{C_{cyf}}{O_{cyf}} + \frac{C_{cyp}}{O_{cyp}} + \frac{C_{esf}}{O_{esf}} + \frac{C_{lcy}}{O_{lcy}} + \frac{C_{per}}{O_{per}} \leq 1$$

The Basin Plan does not discuss or imply that the additivity formula should be used as a water quality objective. Rather, it states that the Regional Water Board will initially assume "that the toxicities of pesticides are additive." The additivity formula itself is not evidence that beneficial uses *are* being impacted because the impacts of multiple pesticides may not be cumulative or they may be additive, synergistic, or antagonistic. Thus, the additivity formula is to be used as a "trigger" to direct the Regional Water Board to conduct a detailed assessment of the pesticides involved to determine the exact nature of the impact.

The final pyrethroid criteria reports from UCD include discussions of published studies pertinent to determining whether pyrethroid toxicity is dose-additive, but these discussions alone are not sufficient to be considered "detailed assessments," nor do they address the requirements of the Basin Plan. The additivity formula stated above, which is proposed as a water quality objective, has not been developed consistent with any state or federal guidance. In contrast, the individual acute and chronic pyrethroid criteria were issued under separate criteria reports using the UCD methodology. Both the criteria reports and criteria derivation method have undergone public comment and peer review. No such process has occurred for the derivation of the additivity formula as a water quality objective, even though it would constitute the most stringent of all of the proposed pyrethroid objectives.

The Basin Plan's requirement to perform a detailed assessment of the impacts of multiple pesticides is important because each of the individual pyrethroid water quality objectives are not simply toxicity end points (e.g., EC50, LC50). While the various pyrethroids have the same modes of action, it is unknown whether mixtures of pyrethroids at levels less than water quality objectives actually impact beneficial uses. The individual pyrethroid criteria are more sensitive than known toxicity end points and have different levels of safety because the criteria were developed using small datasets and different assumptions based upon the availability of data (e.g., use of default or chemical-specific ACRs). The Regional Water Board needs to provide the necessary scientific information and data to determine whether mixtures of pyrethroids at concentrations less than the individual criteria would actually impact beneficial uses before adopting the additivity objective. As proposed, it lacks the scientific justification necessary for setting water quality objectives.

In the final bifenthrin, lambda-cyhalothrin, and cyfluthrin criteria reports (Palumbo et al. 2010, Fojut et al. 2010a; Fojut et al. 2011b), the authors made definitive statements regarding the use of dose-additivity in compliance determination, e.g., *"The additivity of pyrethroid mixture toxicity has not been clearly defined in 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. 2010a). In the final permethrin and cypermethrin criteria reports, the authors state that results of *"…several studies have demonstrated that the toxicity of pyrethroid mixtures is additive and is well-predicted by the concentration addition model."* (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 final reports as they did in the final reports for bifenthrin, lambda-cyhalothrin, and cyfluthrin, and so it is unclear why differing definitive statements are made regarding the dose-additivity of pyrethroid mixtures.

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 additive toxicity at low toxicant concentrations, well below expected LC50 values (i.e., in the range of the recommended acute criteria). There is enough inherent uncertainty in the use and applicability of concentration addition models, be they toxic unit or relative potency factor approaches, that water quality objectives should not be based on assumed additivity.

If the additivity formula is retained as a water quality objective, despite its lack of adequate scientific justification, it is unclear how a stormwater discharge would be determined to "cause and contribute" to an exceedance of the additivity criterion. Consider the following scenario: A toxic unit of one is exceeded in the receiving water from detections of bifenthrin and permethrin, but no other pyrethroids are detected in the receiving water. The corresponding stormwater discharge sample contained cyfluthrin above the cyfluthrin criterion, and by definition, the additivity criterion was also exceeded. Yet, cyfluthrin did not measurably cause or contribute to an exceedance of the additivity equation in the receiving water. Clear guidance is not provided pertaining to the use of the additivity criterion in determining whether a discharge has caused or contributed to an exceedance of the additivity water quality objective. Similar arguments could be made for discharges of wastewater and the determination of "reasonable potential." The draft Basin Plan Amendment language does not clearly state how reasonable potential for discharges from wastewater treatment facilities using the additivity formula will be determined.

3.4 Water Quality Objectives and Pyrethroid Bioavailability

The proposed water quality objectives are for whole-water column concentrations of pyrethroids, yet whole-water column concentrations can be substantially different than the fraction of pyrethroids in the water that are actually bioavailable for uptake and toxic effects in aquatic life. In fact, all of the UCD criteria reports make this point when they describe in detail the propensity of pyrethroid insecticides to sorb to particulate matter, sediments, and laboratory equipment. In the criteria reports, 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 proposed water quality objectives should be based on dissolved pyrethroid water column concentrations because the dissolved fraction is the best predictor of beneficial use impairment.

4 Implementation

The draft Basin Plan Amendment omitted any implementation language that addresses stormwater discharges of pyrethroids from industrial/commercial facilities and construction/development projects. This could be facilitated by including specific language addressing best management practices (BMPs) related discharges of pyrethroids from these facilities and sites. Pyrethroid or pesticide-specific requirements could then be added to the recently adopted Industrial General Permit (Order 2014-0057-DWQ) and the recently amended Construction General Permit (Order 2009-2009-DWQ), both of which contain sections specifically to address discharges to waterbodies that are subject to TMDLs or are 303(d) listed. Without implementation requirements for construction and industrial/commercial stormwater discharges, MS4s will be hindered in their efforts to eliminate discharges of pyrethroids within their jurisdiction.

5 Monitoring

For compliance testing purposes through National Pollutant Discharge Elimination System (NPDES) permits, USEPA-approved (40 CFR 136) analytical methods 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 proposed water quality objective values. Only the most diligent commercial laboratories can achieve reporting limits near the proposed chronic objectives using these analytical methods, and employing good laboratory practices and standard quality assurance. No methods exist for the detection and quantification of cypermethrin, permethrin, and cyfluthrin near the proposed chronic objectives, 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 proposed acute and chronic objectives. This limits the utility of the proposed objectives altogether, and potentially returns the regulated community to a position of providing the Regional Water Board with analytical results containing varied reporting limits. Maximum matrix-specific reporting limits should be considered so as to avoid the potential of reporting false positives and errant detections.

There are no USEPA-approved or commercially available methods in existence for the measurement of dissolved pyrethroids in water. The only practical way currently available to estimate dissolved pyrethroid concentrations is to use the partitioning equation described in the UCD final criteria reports (see equation 1 in Fojut et al. 2011a). Use of the partitioning equation has its drawbacks in that site-specific partition coefficients for organic carbon and dissolved organic carbon are preferred. While pyrethroid partition coefficients developed by academic research laboratories have been published, we are currently unaware of any commercial laboratories that could develop site-specific partition coefficients. Even so, development of site-specific partition coefficients would likely be cost prohibitive.

In summary, the monitoring requirements of the draft Basin Plan Amendment will place dischargers in the position of collecting data using commercial methods and techniques that lack USEPA approval. Compliance with the proposed water quality objectives cannot be assured or determined using methods that lack standardization, which is especially important for pyrethroids which only the most prudent commercial labs can measure with consistent accuracy. Regional Water Board staff review and Executive Officer approval of pyrethroid analytical methods is insufficient to guard against the collection of inaccurate and unreliable data.

6 Questions for Peer Review Panel

The following questions are proposed for the peer review panel:

1. Is there sufficient scientific data and justification presented that reliably show that mixtures of the various types of pyrethroids (Type I and Type II) at concentrations below the proposed individual pyrethroid objectives (both chronic and acute) cause dose-additive toxicity, thereby justifying the proposed additivity-based objective?

2. Should water quality objectives for the pyrethroids be expressed as the dissolved fraction, rather than total as currently proposed, to better reflect pyrethroids propensity to bind to particulate matter?

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