



Environmental Utilities
Administration
2005 Hilltop Circle
Roseville, California 95747

January 14, 2010

Danny McClure
Regional Water Quality Control Board, Central Valley Region
11020 Sun Center Drive, #200
Rancho Cordova, CA 95670-6114

RE: Comments on Draft Aquatic Life Criteria for Bifenthrin and Malathion Developed by University of California at Davis

Dear Mr. McClure:

The City of Roseville (City), with assistance from Robertson-Bryan, Inc., has reviewed draft water quality criteria derivation reports for bifenthrin and malathion prepared by the University of California at Davis (UCD) while under contract to the Central Valley Regional Water Quality Control Board (Regional Water Board). These draft criteria derivation reports were made available by the Regional Water Board for public review in December 2009 by e-mail notification and the comment period was subsequently extended to January 15, 2010.

The City makes the following comments based on the detailed technical comments prepared by Robertson-Bryan, Inc. (RBI) on the City's behalf, which are provided in the enclosed attachment. This letter, together with the attached Technical Memorandum, contains the City's complete comments at this time.

The City formally requests that the Regional Water Board consider these comments, and the items listed in the enclosed attachment, in light of its own review of the UCD documents and before these draft criteria are utilized for any regulatory planning or enforcement purposes.

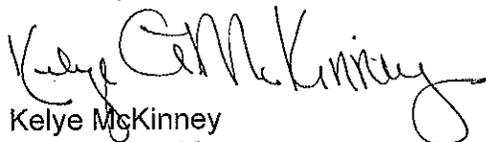
- The City does not accept the validity of chronic criteria derived when utilizing default acute-to-chronic ratios (ACR). The use of default ACRs is not scientifically defensible and, therefore, results in aquatic life criteria unsuitable for regulatory purposes.
- The City disagrees with the assumption of dose additivity. Compliance with criteria should not be based on simplifying, inaccurate assumptions of concentration addition as the principals of concentration addition do not necessarily hold true under possible environmental mixture scenarios. Until clearly demonstrated among specified compounds, assumptions of dose additivity are unsuitable for regulatory purposes and as such allowance for dose additivity should be omitted.
- The City disagrees that bifenthrin compliance should be measured against whole water analysis. Scientific evidence points to freely dissolved bifenthrin as the bioavailable fraction. Compliance should be measured against that portion of bifenthrin that is known to be toxic (i.e., the bioavailable fraction of the total measured amount). The draft bifenthrin criteria report should be revised in a manner that allows for either direct measurement of the bioavailable fraction or allows for some compensating factor accounting for particulate matter effects (i.e., the biologically unavailable fraction).
- The capabilities of commercial laboratories in achieving sufficiently low 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 use, yet at considerable economic expense to the party collecting the data.

Finally, the City requests correction of an apparent derivation error, as described in the enclosed attachment, in which the chronic criterion for bifenthrin appears to have been calculated in a manner that is inconsistent with the UCD methodology. If a chronic criterion is to be derived, which we argue against based on the scientific shortcomings of the methodology, the chronic criterion should at least be derived consistent with the UCD derivation methodology.

Thank you for the opportunity to comment and we look forward to your responses to our comments.

Sincerely,

A handwritten signature in black ink, appearing to read "Kelye McKinney". The signature is fluid and cursive, with a large, stylized initial "K" and "M".

Kelye McKinney
Engineering Manager

Encl.



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TECHNICAL MEMORANDUM

Date: January 14, 2010

To: Delyn Ellison-Lloyd, Kelye McKinney, Art O'Brien (City of Roseville)

From: Michael Bryan, Ph.D., Brant Jorgenson, Ben Giudice, M.S.

Re: Review of Draft Derivation of Bifenthrin and Malathion Water Quality Criteria

1 Introduction

Robertson-Bryan, Inc (RBI) has reviewed and provided comments on draft water quality criteria derivation reports prepared by the University of California at Davis (UCD) while under contract to the Central Valley Regional Water Quality Control Board (Regional Water Board). Specifically, this Technical Memorandum (TM) provides comments based on our technical review of criteria derivation documents for the pyrethroid insecticide bifenthrin and the organophosphate insecticide malathion that were recently released for public review by the Regional Water Board through email notice, and the criteria development methodology employed to derive criteria for these compounds.

Under its contract, UCD has prepared methodology and draft aquatic life criteria for a list of pesticides that the Regional Water Board has identified as posing high risks for adversely impacting water quality. The proposed methodology allows for the derivation of acute and chronic aquatic life criteria for pesticides with limited toxicity datasets. Although these criteria do not represent water quality objectives or standards at present, they may be implemented as quantitative interpretations of Basin Plan narrative toxicity objectives, and thus are of particular relevance to local agencies who manage discharges to water bodies known to be, or potentially, impacted by pesticides. The Regional Water Board recently adopted and submitted to the State Water Board for its approval, Clean Water Act Section 303(d) listings for pyrethroid insecticide-related toxicity on Pleasant Grove Creek, South Branch Pleasant Grove Creek and Kaseberg Creek making the development of these draft insecticide criteria particularly relevant to the City's wastewater and storm water operations.

Incorporated throughout the UCD criteria derivation documents is reference to a recently developed criteria development methodology. Review of the criteria derivations requires review and comment on the methodology used to derive the criteria and, therefore, review of the methodology also was conducted and comments on the methodology relative to its application for deriving draft criteria are provided herein.

2 Draft Criteria and Background

Draft aquatic life criteria statements for bifenthrin and malathion are provided below. Specific comment on the criteria values and means of measuring compliance are provided in Section 3 and 4 of this TM.

“Aquatic life in the Sacramento River and San Joaquin River basins should not be affected unacceptably if the four-day average concentration of bifenthrin does not exceed **0.3 ng/L**¹ more than once every three years, on the average, and if the one-hour average concentration of bifenthrin does not exceed **4 ng/L** more than once every three years on the average.” (Palumbo *et. al.* 2009a)

and,

“Aquatic life in the Sacramento River and San Joaquin River basins should not be affected unacceptably if the four-day average concentration of malathion does not exceed **0.03 µg/L** more than once every three years, on the average, and if the one-hour average concentration of malathion does not exceed **0.15 µg/L** more than once every three years on the average.” (Faria *et. al.* 2009)

These criteria, and draft criteria for the insecticides chlorpyrifos and diazinon and the herbicide diuron, were developed following a methodology published in September 2009. In *Methodology for Derivation of Pesticide Water Quality Criteria for the Protection of Aquatic Life, Phase II: Methodology Development and Derivation of Chlorpyrifos Criteria* (TenBrook *et al.*, 2009), a new method of criteria derivation is formalized and a step-by-step procedure for deriving criteria from small toxicity datasets is provided. A new criteria derivation methodology was necessary because these limited datasets are deficient in one manner or another for use with the existing EPA methodology (EPA, 1985). The draft criteria derivation reports, which are the principal subject of this review, follow this step-by-step procedure.

The UCD methodology has been revised based on comments received from both peer review and public comment. In general, the UCD methodology developed for the task of deriving aquatic life criteria for pesticides of concern is scientifically sound. The UCD methodology is rather unique in that it lays a foundation for a regional regulatory body to develop criteria from toxicity data sets found to be incomplete by the conventional EPA method (EPA, 1985), which is most commonly used for criteria derivation purposes. Although principally intended for use on limited toxicity datasets, draft criteria were developed for some pesticides meeting the acceptability criteria of the conventional EPA derivation methodology (e.g., chlorpyrifos and diazinon).

The specific manner in which this new methodology is applied in the derivation of specific aquatic life criteria is of key importance. The UCD methodology provides more than a means to derive numeric criteria; it also considers factors of bioavailability, mixture effects, and the effect of other tangential water quality parameters on pesticide toxicity (e.g., temperature and pH). Considering these other factors is complex, and caution is warranted in how assumptions are employed in developing final criteria statements and execution of those statements.

The remainder of this review summarizes specific findings in the development and execution of these draft aquatic life criteria. Only brief effort was made to review the toxicity value screening procedure because conducting a thorough review of this aspect of the methodology was beyond the scope of this

¹ This value is believed to be in error; see Section 3.7.

review effort. However, it should be noted that the screening of available toxicity values largely determines the criteria derivation outcome and, therefore, a thorough review of the toxicity value screening procedure by an outside party is recommended.

3 Assessment of Methodology and Draft Derivation of Bifenthrin and Malathion Criteria

3.1 Uncertain Need for New Criteria

The UCD method was developed specifically to address data shortages that precluded the use of the established U.S. EPA methodology (EPA, 1985). Since ample data is available and multiple criteria have already been developed for diazinon and chlorpyrifos using several different methods, it is unclear why it is necessary to derive additional criteria for these compounds by this new methodology, which uses smaller data sets. Any new published data since the last derivation using the conventional EPA methodology could have been used with that EPA methodology to update previously derived criteria. and, by itself, does not necessitate wholly new criteria using a new derivation methodology.

3.2 Use of Safety Factors and Small or Limited Toxicity Datasets

Use of safety factors in derivation of aquatic life criteria is standard practice. However, in the development of draft criteria utilizing the UCD methodology, several safety factor iterations are employed in order to compensate for inherent informational deficiencies in limited datasets. In the case of the draft diuron criteria derivation report (Fojut *et al.*, 2009), an acute criterion was derived by taking the single most sensitive acute result of 12 mg/L and dividing it by an assessment factor of 36 (due to only 2 taxa being available—as per Table 3.13 in the methods), dividing by a further factor of 2 to convert from an LC50/EC50 to an assumed NOEC, then dividing by 2 again to both account for uncertainty in the assessment factor approach, which was not developed for herbicides, and to protect the most sensitive species. Ultimately, the compounded safety and assessment factor of 144 was used to correct for a data set that had been limited to a great degree by the screening procedures outlined in the UCD methodology. This is compounded on the fact that an assessment factor approach for diuron is inconsistent with the published methodology, which in section 3-3.3 states, “For herbicides (or if plants are most sensitive), however, another procedure should be used as described in section 3-4.3” (TenBrook *et al.*, 2009). Section 3-4.3 refers to derivation of chronic criteria and does not address acute derivation.

While it is true that derivation of criteria using sparse datasets does more to meet the water quality protection goal than no criteria at all, when criteria are based on the single most sensitive data-point in a data set and then divided by a safety factor of 144, the resulting criteria has very little scientific defensibility. Such criteria represent more of a conservative “guess” at the NOEC than a data-derived calculation or estimate of the NOEC. The draft diuron criteria, as it is presented in its attending report, should not be considered for application until data are sufficient to derive criteria with fewer compounded safety factors.

The case of diuron illustrates the inherent short-comings of the UCD methodology when applied to datasets that inherently prove themselves too limited, too small, or too encumbered. Certainly under the data screening procedures of the methodology itself, this is the case.

In the case of malathion, data were found insufficient to develop an acute criterion based on a species sensitivity distribution. As a result, the lowest acute toxicity value was divided by an assessment factor of 5.1 per Table 3.13 of the UCD methodology, and then further divided by a safety factor of 2 for a total compounded factor of 10.2. The case of malathion represents a much more scientifically defensible derivation, with reasonable safety factors that are scientifically derived from data on similar compounds.

3.3 Implementation of Acute to Chronic Ratios

In cases when data from fewer than five taxa are present, the methodology requires that acute-to-chronic ratios (ACRs) be used. The specific method of implementation of this procedure varies between the 5 pesticides for which the authors have derived criteria. In the case of chlorpyrifos and diazinon, an increasing trend of ACR with species mean acute value (SMAV) was detected, so ACRs were calculated using only those ACRs for SMAVs within a factor of 10 of the acute criterion. Because diuron is a herbicide, the ACR approach was not employed—instead, the lowest NOEC available was used. For malathion, invertebrate data were unavailable, so a default ACR of 12.4 was included in the data set of ACRs for the final calculation of a geometric mean ACR. In the case of bifenthrin, initial chronic data requirements were not met, so a default ACR of 12.4 was selected.

Acute-to-chronic ratios 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). In the methodology, the authors 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 8 pesticides, including 5 organochlorine pesticides and 3 organophosphate pesticides (TenBrook *et al.*, 2009).

The authors of the draft bifenthrin criteria note that ACRs for pyrethroids have been found to vary between 2 and 425 for a variety of species (Palumbo *et al.*, 2009a). In the case of bifenthrin, the default ACR of 12.4 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.

In the case of malathion, the most sensitive SMAV for fish was 349 µg/L, which is over 1200 times higher than the 5th percentile value (0.29 µg/L). Due to a lack of data, the default ACR of 12.4 was applied for invertebrates and included in the calculation of the geometric mean. Other organophosphate insecticides have invertebrate-specific ACRs of 1.0 (chlorpyrifos, TenBrook *et al.*, 2009) and 2.3 (diazinon, Palumbo *et al.*, 2009b). Acute-to-chronic ratios derived for organophosphate pesticides, and included in the authors' derivation of the default value, are 2.2 (chlorpyrifos), 3.0 (diazinon), and 10 (parathion) (TenBrook *et al.*, 2009). By applying a default ACR derived partially from a different class of chemicals, and by including species whose acute endpoints far exceed the derived acute endpoint, the resulting chronic criterion has a weak scientific basis.

3.4 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 the bifenthrin and malathion criteria reports, in fact all the draft criteria derivation reports, where toxic modes of action are considered the same, the reports state in similar fashion:

“Since compounds in this class have a similar mode of action, either the toxic unit or the relative potency factor approach can be used to determine compliance in cases where pyrethroid mixtures are present in environmental samples” (Palumbo *et al.*, 2009a)

Admittedly, this principal of toxicology holds well, but one must question how *similar* a toxic mode of action must be, how many mixture components there are, and at what concentration ratios for the assumption of additivity to hold true under all likely environmental scenarios. Caution is advised in applying concentration addition models in cases of compliance determination. For example, Trimble *et al.* (2009) investigated 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. There is enough inherent uncertainty in the use and applicability of concentration addition models, be they toxic unit or relative potency factor approaches, that pause should be taken before assessing compliance based on assumed additivity.

3.5 Bioavailability

The UCD criteria derivation methodology should be lauded for including considerations of bioavailability. In Section 11 of the draft bifenthrin criteria report 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. Despite this admission, the draft criteria report recommends that compliance with the bifenthrin criteria be determined based on the total recoverable, whole-water fraction. This recommendation is made rather arbitrarily in an effort to balance error associated in toxicity measurements reporting nominal spiked concentration with that of the error in predicting toxicity with the use of whole-water measurements. By assuming these relative errors to be equal, and thus cancelling, the authors attempt to strike a balance between the over prediction of toxicity when utilizing a total recoverable analytical measurement with the under prediction of toxicity when utilizing a nominal spike concentration in determining LC₅₀'s. There is no justification for this balance, the result of which knowingly biases a compliance measurement in favor of overprotection. Furthermore, the lowest acute toxicity value for *Hyalella azteca* is based on directly measured bifenthrin concentration, not nominal concentration. The *Hyalella azteca* toxicity value already greatly influences the species sensitivity distribution that is used in setting the acute, and by extension,

chronic criterion. Since conservative overprotection is inherently built into the criteria derivation methodology through the use of safety factors and default ACRs, this additional level of protection is unnecessary and only compounds bias upon bias. The direction of science and the direction in Section 3-5.1 of the method development criteria itself should be followed, and compliance measurements for bifenthrin should be based on the dissolved fraction, despite any associated analytical challenges.

3.6 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 bifenthrin. Only the most diligent commercial laboratories can achieve reporting limits near the acute bifenthrin criterion using these analytical methods and employing good laboratory practices and standard quality assurance. 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 bifenthrin 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. Using such a criterion should consider setting maximum matrix-specific reporting limits so as to avoid the potential of reporting false positives and errant detections.

3.7 Calculation Error

In the bifenthrin draft criteria derivation report (Fojut et al., 2009), the calculation of the final chronic criterion is inconsistent with other criteria derivations and the methodology. According to the methodology Section 3-4.2.4, the criterion is to be taken as a product of the selected percentile value (generally, the 5th percentile value) divided by the calculated ACR (TenBrook *et al.*, 2009). The final acute percentile value was calculated in Section 9 to be 0.007460 µg/L, but in Section 10, the acute criterion of 3.730 ng/L is divided by the ACR to arrive at a chronic criterion of 0.3 ng/L. This is in error as it inappropriately includes the safety factor of 2 that is used to derive the acute criterion. The chronic criterion should in fact be 0.6 ng/L. Derivation of the chronic criterion should be revised accordingly.

4 Summary of Review Findings and Comments

Review findings and comments are summarized as follow.

1. Acute criteria developed for malathion and bifenthrin are within five times the values that would have been derived utilizing the U.S. EPA methodology and the same dataset set of species mean toxicity values. However, through use of default ACRs in deriving chronic criteria, and the attending uncertainties associated with deriving the default ACR from insecticides of dissimilar mode of toxicity, the chronic criteria as derived are of questionable scientific validity and, therefore, are not appropriate for regulatory use.
2. The UCD methodology has been used to derive criteria for pesticides (e.g., chlorpyrifos and diazinon) for which the U.S. EPA methodology is appropriate and has been applied. The UCD

method was developed specifically to address data shortages that precluded the use of the established U.S. EPA methodology. Derivation of new criteria using this new derivation approach is both unnecessary and is not defensible.

3. The UCD methodology has been applied to the derivation of diuron criteria in a manner that is of weak scientific validity. Due to uncertainties with regard to assessment factors for herbicides and inherent informational deficiencies in the diuron data set, a compounded safety and assessment factor of 144 is used to derive the acute criterion. The draft diuron criteria, as it is presented in its attending report, should not be considered for regulatory application until data are sufficient to derive criteria with fewer compounded safety factors and uncertainties.
4. Use of default ACRs should be cautioned and is likely not scientifically defensible in all cases. Acute-to-chronic ratios for a given pesticide can vary considerably (i.e., by orders of magnitude) among species. The default ACR used in criteria derivation for malathion and bifenthrin was developed from a short-list of insecticides that do not all share the same mode of toxic action. In the case of bifenthrin, the default ACR of 12.4 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. Similarly for malathion, by applying a default ACR derived partially from a different class of chemicals, and by including species whose acute endpoints far exceed the derived acute endpoint, the resulting chronic criterion has a weak scientific basis.
5. For all derived criteria, the assumption of dose additivity among pesticides of similar mode of toxicity is assumed. Caution is advised in applying concentration addition principals to compliance measurements unless additivity among specified compounds has been clearly demonstrated. Dose additivity is not settled science because additivity is not always observed, and its accuracy as a model predictor is sensitive to many variable factors. Where science is not settled, compliance should not be based on simplifying assumptions.
6. The current scientific understanding regarding pesticide bioavailability should be applied to criteria compliance determinations. The freely dissolved fraction of pyrethroid insecticides, including bifenthrin, is the fraction that is bioavailable. Compliance 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 accounting for pyrethroid sorption to particulate matter.
7. Achieving commercially available analytical reporting limits below the draft bifenthrin criterion utilizing EPA approved analytical methods is currently lacking or limited. Defensible maximum matrix-specific reporting limits should be defined so as to avoid the potential of reporting false positives and errant detections.
8. The chronic criterion for bifenthrin should be corrected. A clerical error appears to have been made in dividing the acute *criterion* by the default ACR when in fact the 5th percentile acute *value* should have been divided by the default ACR.

5 References

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