

Responses to Public Comments and Peer Reviews

Phase III: Diazinon 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
CDFG	California Department of Fish and Game
CVRWQCB	Central Valley Regional Water Quality Control Board
DPR	California Department of Pesticide Regulation
EC _x	The chemical concentration that has an effect on x% of the test population.
K _{oc}	Organic Carbon Partition Coefficient
LC ₅₀	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
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 six the 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 six additional pesticides, of which diazinon is one.

The diazinon criteria report was submitted to peer review, conducted by experts from academia and sister agencies, including 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 – Lenwood Hall, University of Maryland

COMMENT 1-1: Page 5, Ecotoxicity Data, parag 1 - The number of studies evaluated is mentioned (~250). How many different test species were included in these 250 studies? Only studies rated relevant and reliable (RR) were included Appendix C. Data from studies that were evaluated but have lower ratings should also be included in an appendix so the reader can see the reasons (failed parameters) that lead to study rejection. This will make the process much more transparent.

Response To Comment (RTC) 1-1: Data with lower ratings (RL, LR, and LL) is included in Table 8 of the criteria report. It can be seen that in Table 8 there are 39 species in the supplemental data set, of which 32 are not included in the acceptable data set. Data summaries for the supplemental studies (RL, LR, and LL) and the unacceptable studies (N) have been added in Appendix D so that every study that was reviewed for this report is now available with explanations for its rating and if relevant, why it was excluded.

COMMENT 1-2: Page 5 bottom of page and top of page 6 – It is not clear from this section how studies rated RL, LL, or RL can be used as reliable supplemental information if they are flawed (see Table 8). How will these studies actually be used? Can studies with unacceptable ratings be used to influence the final criteria?

RTC 1-2: Clarification on the use of supplemental data (studies rated RL, LR, or LL) in criteria adjustment has been added to this section. Section 3-6.0 of the methodology, titled “Check criteria against ecotoxicity data,” describes how the criteria are evaluated to ensure they are protective to: 1) particularly sensitive species, 2) ecosystems, and 3) threatened and endangered species (TenBrook *et al.* 2009). Supplemental data are used to evaluate the criteria, particularly for sensitive species, as described in section 3-6.1 of the methodology, because there may be particularly sensitive species in the supplemental data set that are not well-represented in the acceptable data set (studies rated RR), from which the criteria are calculated. It is stated in this section (3-6.1): if the calculated criterion is higher than toxicity values reported for particularly sensitive species, then the criterion may require downward adjustment (TenBrook *et al.* 2009). The criteria would never be adjusted upward because the various percentiles are calculated to provide a range of robust and more conservative values, and increasing the criterion above the calculated percentiles would likely be underprotective.

COMMENT 1-3: Page 6, parag 2 – It is not clear from this section how the microcosm/mesocosm data will actually be used as supplemental information. For example, if the microcosm/mesocosm data were rated RR can the toxicity values be used to change (i.e., raise or lower) a final criterion?

RTC 1-3: Clarification on the use of microcosm/mesocosm data rated R or L in criteria adjustment has been added to section 13 of the report, titled “Ecosystem and other studies.” Section 3-6.0 of the methodology, titled “Check criteria against ecotoxicity data,” describes how the criteria are evaluated to ensure they are protective to: 1) particularly sensitive species, 2) ecosystems, and 3) threatened and endangered species (TenBrook *et al.* 2009). Ecosystem data are used to evaluate the criteria to judge whether they will be protective of ecosystems, as described in section 3-6.2 of the methodology, because there may be ecosystem-level effects that are not accounted for with single-species studies, from which the criteria are calculated. It is stated in this section (3-6.2): if toxicity values obtained for appropriate endpoints in these studies are lower than the derived criteria, then criteria may need to be adjusted downward (TenBrook *et al.* 2009). The criteria would not be adjusted upward based on ecosystem-level data because the various percentiles calculated using single-species data provide a range of robust and more conservative values, and increasing the criterion above the calculated percentiles would likely be underprotective according to the single-species data.

COMMENT 1-4: Page 6, last parag – There needs to be a consistent process for rounding off the significant digits in the criteria development process. Will the final criterion always be reported with one significant digit for all pesticides? Was this issue addressed in the TenBrook *et al.* 2009 document?

RTC 1-4: Section 3-3.2.6, titled “Calculate criterion from 5th percentile value,” of the methodology describes how the number of significant digits in the final acute criterion are rounded (TenBrook *et al.* 2009). The criterion is not expressed with more significant digits than are in the original toxicity data, which often only have one significant digit. The significant digits of the final criteria are rounded to be consistent with the known variability in the calculated criteria. For example, if the median estimate is used for criterion calculation the last digit that is relatively variable in comparison to the 95% confidence limit is the last significant digit.

Comment 1-5: Page 7, Alternative Approach – After splitting the species into 2 groups, the SSD was then developed with the lower subset (invertebrates) using the log-logistic distribution. This produced an acute value of 0.208 ug/L/2 or 0.104 ug/L. This is confusing as it suggests that 0.1 ug/L and not 0.2 ug/L will be the final acute criterion. Please add text to clarify this issue.

RTC 1-5: Text has been added to clarify which value is the final acute criterion.

COMMENT 1-6: Page 10, Chronic criterion calculation – ACRs were developed for 3 species with the corresponding acute LC50 values and the MATCs (chronic values). The MATC (maximum acceptable toxic concentration) is the geometric mean of the NOEC and the LOEC. These NOEC, LOEC and MATC values have a high degree of uncertainty as they are determined by the range of test concentrations (dilution series) and the sample size used in the toxicity test. The peer reviewed literature has a number of papers that discuss the uncertainty associated with using NOEC, LOEC and MATC values in the regulatory process because these values have no statistical confidence (Newman, 2010; Risk Sciences, 2001 among others). In cases where a suboptimal design is used higher NOEC and LOEC values may be reported due to low statistical power and high error variance. In contrast, when a superior study design is used lower NOEC and LOEC values could be reported. Values such as EC50s, EC25s or EC20s should be used to represent chronic values.

RTC 1-6: The method discusses by MATC values are used instead of ECx values for derivation of chronic criteria (section 3-2.1.1.2, TenBrook *et al.* 2009). This section states that chronic ECx values may be used for criteria derivation if studies are available to show what level of x is appropriate to represent a no-effect level. It is acknowledged that poor design of hypothesis tests may lead to overestimation of NOEC values and underestimation of LOEC values. Another concern with the use of ECx values is that most chronic tests report MATC values, so requiring the use of ECx values would further reduce chronic data sets, which are typically small already. The use of ECx values is not prohibited by the methodology, but there is currently not enough chronic ECx data for diazinon to use for criteria derivation.

COMMENT 1-7: A chronic criterion of 0.2 ug/L is calculated using the 5th centile/50 % confidence limit (0.358949). This value is then divided by the ACR of 2.3 to obtain a chronic criterion of 0.2 ug/L. This would seem to be the end of the chronic calculation. However, the authors continue with additional calculations using acute values from the entire data set and the lower 95th confidence interval. The 5th centile, 95% confidence limit of 0.167165 ug/L is divided by the ACR of 2.3 to obtain a value of 0.0836 or a final chronic criterion on 0.1 ug/L. Additional calculations are also conducted using the more sensitive subset of species and a log-logistic distribution (5th centile, 50% confidence limit of 0.208136 ug/L divided by the ACR of 2.3) to obtain a chronic value of 0.1 ug/L. These last two calculations used to drive the original chronic criterion of 0.2 ug/L to a lower chronic value of 0.1 ug/L add yet another level of overprotection and need to be justified.

RTC 1-7: The additional chronic criterion calculations referred to in Comment 1-7 are shown because it is the goal of the report to be transparent and give environmental managers relevant information about the level of protection, accuracy, and confidence of the derived criteria. It is recommended to adjust the chronic criterion downward from the median 5th percentile of the whole data set because the supplemental data set shows that the chronic criterion of 0.2 µg/L could be underprotective of Cladocerans (see section 12. Sensitive Species of the Diazinon Criteria Report). The other more conservative percentiles calculated may be used when the median 5th percentile does not appear to be protective of all species, which is the case for diazinon.

COMMENT 1-8: Page 10, mixtures – Joint toxicity definitions of antagonism, additivity and synergism should be provided to the reader upfront in this section. Antagonism is phenomenon is which the toxicity of a mixture of chemicals is less than would be expected from a simple summation of the toxicities of the individual chemicals present in a mixture (i.e., algebraic subtraction of effects). Additivity is when the toxicity of a mixture of chemicals is approximately equivalent to that expected from simple summation of the known toxicities of the individual chemicals present in the mixture (i.e., algebraic summation of effects). Synergism is a phenomenon in which the toxicity of a mixture of chemicals is greater than would be expected from a simple summation of the toxicities of individual chemicals in a mixture.

RTC 1-8: A note has been added to the mixtures section describing where definitions of the phenomena can be found.

COMMENT 1-9: The assumption that OP insecticides are often detected in the environment concurrently is often misstated. For example, it is unlikely to have diazinon and chlorpyrifos measured in the same water sample because these two OPs are not generally used at the same time to control pest pressure.

RTC 1-9: In a ten year comprehensive study by the United States Geological Survey, pesticide mixtures were detected much more often than individual pesticides in surface waters (Gilliom 2007). The four most common insecticides detected in mixtures were diazinon, chlorpyrifos, carbaryl, and malathion – three of which are organophosphates.

COMMENT 1-10: Page 13, Sensitive Species, last parag – The lack of logic in the last paragraph of this section is troubling. In summary, the authors used chronic cladoceran toxicity data from studies they judged to be unacceptable to lower the chronic criterion from 0.2 µg/L to 0.1 µg/L. Scientific rationale is needed to support this action.

RTC 1-10: See RTC 1-2.

COMMENT 1-11: Page 15, Ecosystem and other studies – Why can't the acceptable Giddings et al. 1996 microcosm study (LOEC = 9.2 ug/L and NOEC = 4.3 ug/L) be used as justification for keeping the original chronic criterion at 0.2 ug/l rather than lowering it to 0.1 ug/L based on unacceptable toxicity data. This would seem to be excellent rationale to support the original 0.2 ug/L chronic criterion.

RTC 1-11: Each type of ecotoxicity data is evaluated separately to determine if the calculated criteria would be protective based on the available data. The chronic criterion was lowered because it was determined to be underprotective based on Cladoceran data in the supplemental data set, and therefore the criterion will not be increased as it would compromise protection of the sensitive Cladocerans.

COMMENT 1-12: Page 17/18 – Limitations, assumptions and uncertainties – Chronic data were lacking for two of the five required taxa (benthic crustaceans and insects) and this was stated as a source of uncertainty. It would therefore seem prudent to allow the registrant to fund the necessary high quality toxicity studies that would allow these data gaps to be filled. I would suggest starting this type of dialogue with the registrant. This would promote a data driven process and reduce the uncertainty associated with use of an ACR approach (see previous comments on the uncertainty associated with the use of NOEC, LOEC and MATC values).

RTC 1-12: Diazinon registrants have been contacted with regards to the data gaps and no responses have been received as of yet.

COMMENT 1-13: Page 18, parag 1 – As stated previously, the authors are using unacceptable toxicity data from cladocerans to drive their original chronic criterion from 0.2 to 0.1 ug/L to ensure protection of cladocerans. The authors also use the bimodality argument to drive a lower chronic value as well. These actions need to be justified.

RTC 1-13: See RTC 1-2 and RTC 1-7.

COMMENT 1-14: It is noteworthy that the acute diazinon toxicity data screening process resulted in only 13 species values that were judged to be acceptable for use in the SSD. This seems like a rather minimal data set given the large toxicity data set for diazinon. I suspect this is the result of the data screening process that I have previously addressed in my review of the diuron water quality criteria document (see Hall, 2009). These previous comments also apply to this draft water quality criteria document for diazinon and are included below.

In my view, the step by step process for reviewing the toxicity data is cumbersome, somewhat flawed and needs to be revised. In the current format, a total of 4 forms need to be completed if the relevance score in Table 3.6 is ≥ 70 (see TenBrook et al., 2009). It would be more logical to first establish criteria that **must** be acceptable before conducting any other evaluation of documents containing the toxicity data. These “Kill Switch Criteria” that must be met for an acceptable study are as follows: (1) Is the control endpoint (survival or growth) acceptable?; (2) Is the document under review the (primary) original source of the data?; (3) Were adverse effects evaluated using exposures of a single pesticide?; (4) Was the duration of exposure reported?; (5) Were the effects reported for relevant endpoints (e.g., survival, growth, or reproduction)?; (6) Was more than one dose/concentration used in the toxicity test?; (7) Was the test species reported?; (8) Was the chemical form (% active ingredient) of the test material reported?; and (9) Was a dose response relationship evident? For example, in the current data review process a study with unacceptable control survival receives a 7.5 point reduction (see Table 3.6 in TenBrook et al. 2009) and can still be rated acceptable for criteria development. In contrast, studies published in the peer reviewed literature with page space limitations, which often lack details for various water quality parameters (i.e., hardness, alkalinity, dissolved oxygen, conductivity and pH) resulting in point deductions in the scoring system, may be rated non-acceptable. Page space limitations in published papers may also result in lack of details on tolerance values for test species to various water quality parameters, dilution water information, and information on prior contaminant exposure which can cause scoring reductions that may lead to data rejection (see Table 3.8 in TenBrook et al. 2009). The exclusion of data that may be valid in the above scenarios is problematic and could result in the use of safety factors that have a high degree of uncertainty.

RTC 1-14: The data evaluation process of the methodology has been thoroughly reviewed by both peer review and public comment processes, but may be revised in the future.

2.2. Comment Letter 2 – Nasser Dean, Western Plant Health Association

Comment 2-1: WPHA restates for the written record our previous concerns about the CVRWQCB embarking so quickly and narrowly focused policy toward developing an excessively conservative WQC Method for 7 active ingredients to then be applied to listed “waterbodies” just within the Central Valley.

RTC 2-1: The comparison of criteria outcomes of the UCD methodology, US EPA, and CDFG reports for diazinon and chlorpyrifos indicate that the UCD methodology derives criteria very similar to those of other agencies, which are regarded as reasonable water quality criteria, and not excessively conservative. For example, the proposed acute diazinon criterion is actually higher than the previously adopted water quality objectives, so this method actually gave a less conservative water quality criterion than those previously adopted.

Comment 2-2: WPHA is quite concerned about using the unacceptable toxicity data from cladocerans to support the author's (Palumbo et al.) chronic criteria from the scientifically established 0.2 mg/L to 0.1 mg/L in an effort to protect cladocerans (water fleas).

RTC 2-2: See RTC 1-2.

Comment 2-3: The results from the Giddings et al. 1996 microcosm study should be used as the scientific justification for maintaining the original chronic value of 0.2µg/L rather than the lower value of 0.1µg/L.

RTC 2-2: See RTC 1-11.

Comment 2-3: WPHA finds it quite interesting that the author's acute diazinon toxicity data screening process only yielded 13 species values that were deemed acceptable for use in the Species Sensitivity Distribution (SSD). This appears to be rather sparse in comparison with the robust toxicity data set for diazinon.

RTC 2-3: See RTC 1-14.

Comment 2-4: WPHA believes that the numerous deficiencies in the author's (Palumbo et al.) outlined process to review toxicity data require revision. For example, a total of 4 forms need to be completed if the relevance score in Table 3.6 is to be greater than or equal to 70 (TenBrook et al. 2009). It is more appropriate to first establish criteria that must be scientifically acceptable before conducting subsequent evaluation of toxicity data documents. This could lead to inaccurate and unsupportable conclusions.

RTC 2-4: See RTC 1-14.

Comment 2-5: WPHA expresses our concern regarding the exclusion of data that may be valid in the author's WQC Method for diazinon. Such omissions could result in the use of additional safety factors based on a high degree of uncertainty. We appreciate the fact that published peer-reviewed literature is constrained by page space limitation requirements. However, this type of limitation may result in a lack of important details on

tolerance values for test species subject to various water quality parameters, dilution water information, and information on prior contaminant exposure which may cause inappropriate scoring reductions that may be lead to data rejection (see Table 3.8 of TenBrook et al. 2009).

RTC 2-5: See RTC 1-14.

2.3. Comment Letter 3 – Daniel McClure, Central Valley Regional Water Quality Control Board

COMMENT 3-1: The authors have done a thorough review of the toxicology literature, and applied the criteria derivation methodology developed by Tenbrook, et al., in a sound and transparent manner to derive criteria that should be protective of aquatic life.

RTC 3-1: Comment acknowledged.

Comment 3-2: The initial chronic criteria concentration is calculated as 0.2 ug/L. The available toxicity data in the supplemental data set, however, indicate that there may be toxic effects to cladocerans at concentrations between 0.1 and 0.2 ug/L. Therefore the authors recommend to using one of the lower values for calculating the chronic criteria, either using the 5th percentile with a 95% confidence limit, or using the 5th percentile and the 50% confidence limit for the more sensitive subset of the data. Both of these calculations yield a chronic criterion concentration of 0.1 ug/L. This use of a more conservative chronic criterion by the authors to ensure protective criteria is rational and consistent with the criteria derivation methodology.

RTC 3-2: Comment acknowledged.

Comment 3-3: In section 7, the determination of the species sensitivity distribution (SSD) used for calculating the acute criteria is somewhat confusing. The discussion should explain why the Reciprocal Weibull distribution was used. Since it was not used, the inclusion of the Reciprocal Pareto distribution for comparison may be more confusing than informative.

RTC 3-3: This section has been revised to explain the choice of the Reciprocal Weibull distribution. The BurrliOz software is used to fit the Burr Type III family of distributions to the data set. The Burr Type III family of distributions consists of three different distributions, of which the Reciprocal Weibull fit the data best. The section that previously discussed the Reciprocal Pareto distribution has been removed for clarity.

Comment 3-4: The Criteria statement indicates that the recommended criteria would be protective of aquatic life in the Sacramento and San Joaquin River Basins. The specificity of these criteria to those basins should not be over-emphasized. It would be useful to note in the criteria statement that these criteria should also likely be protective of aquatic life in freshwater ecosystems 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.

RTC 3-4: The final criteria statement has been revised to state that these criteria should also be protective of aquatic life in other freshwater ecosystems in North America, which is also stated in the methodology (TenBrook *et al.* 2009) that was used to derive these criteria.

Comment 3-5: The discussion of uncertainty in section 17 should review the following information gaps:

- The genera that would be needed to do a full species sensitivity distribution.
- The lack of directly applicable information on the synergistic effects of the combination of diazinon with other compounds, especially those for which there are indications of synergistic effects such as pyrethroids.

RTC 3-5: Section 17 of the criteria report has been amended to describe which taxa were missing from the chronic data set to meet the requirements to use the species sensitivity distribution approach for criteria calculation (benthic crustacean and insect). This section has also been amended to note the lack of directly applicable information on the synergistic effects of the combination of diazinon with other compounds.

Comment 3-6: In section 18, the comparison of criteria using other data sets and/or methodologies should be clarified. The document should state the chronic criteria that would result from using the EPA methodology on the data set used in sections 7 and 8 to derive the draft criteria.

RTC 3-6: The criteria report has been amended with a section titled “Comparison to the National Standard Methods,” in which the US EPA (1985) criteria derivation methodology was used to calculate acute and chronic criteria with the data set collected using the TenBrook *et al.* (2009) methodology. The acute and chronic criteria calculated using the USEPA (1985) methodology would be 0.087 and 0.076 $\mu\text{g/L}$, respectively. The chronic criterion calculated using the USEPA (1985) method is slightly lower, but similar to that calculated by the UC-Davis methodology (TenBrook *et al.* 2009) of 0.1 $\mu\text{g/L}$.

Comment 3-7: The first paragraph on page 1 should state that the criteria are for the Sacramento **and San Joaquin** Valleys.

RTC 3-7: This paragraph has been amended to state that the criteria are applicable to the Sacramento River and San Joaquin River watersheds.

Comment 3-8: A table of contents would make the document easier to read.

RTC 3-8: A table of contents has been added to the final report.

Comment 3-9: If possible, it would be useful to display the toxicity information in data tables in order of species sensitivity.

RTC 3-9: The toxicity data are displayed in order of species because when there are multiple toxicity values for a species, the geometric mean of those values is calculated to give the final species mean toxicity value. If the data were displayed in order of sensitivity, all of the values for a given species would not be adjacent and the calculation would be less clear, and it would be more difficult to compare the range of toxicity values for a given species.

Comment 3-10: We appreciate the tremendous effort that has gone into development of this document and look forward to seeing it finalized.

RTC 3-10: Comment acknowledged.

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 diazinon (O,O diethyl O-[6-methyl-2-(1-methyl)-4-pyrimidinyl] phosphorothioate) 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.

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 chlorpyrifos criteria.* Report prepared for the Central Valley Regional Water Quality Control Board, Rancho Cordova, CA.

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 diazinon. This data set is straightforward and indicates that this pesticide has moderate solubility, low volatility, moderate ability to bioaccumulate, and is somewhat persistent in aqueous environments (i.e., relatively low rates of hydrolysis, photolysis, and biodegradation). Accordingly, 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 diazinon in fish tissue.

Avian mortality is a concern for diazinon. Reported subacute dietary toxicity values for diazinon to mallard ducks vary widely (i.e., LD₅₀s of 32-3,912 mg/kg). This report presents these oral doses as LC₅₀ values whereas they should be should be LD₅₀s (this is a dietary dose reported as mg/kg, not a water-based exposure). The (only) reported no-effect level for mallard ducks is 8.3 mg/kg. However, acute LD₅₀s (intubation and gavage) have been reported to be as low as 1.44 mg/kg. The reason for this discrepancy is not clear.

RTR 1-3: With regard to avian mortality, the report has been revised to only report values from studies rated as Core by the USEPA (fulfilling the required EPA study guidelines), which is a much smaller range of dietary toxicity values (32 and 191 mg/kg feed vs. the previously reported range of 32-3,912 mg/kg feed). Some of the higher reported LC₅₀ values were from studies that were rated poorly by the USEPA for reasons such as inappropriate test methods, unacceptable confidence interval, and unacceptable organism age (USEPA 2004). The dietary exposures are reported as LC₅₀s, as done by the USEPA, because they are concentrations in feed, whereas the oral toxicity values are reported as LD₅₀s because they are tests that administered pure diazinon to the birds via oral intubation or oral gavage. As for the discrepancy between the dietary NOEC value of 8.3 mg/kg feed and the oral toxicity LD₅₀ of 1.44 mg/kg body weight, it is expected that oral toxicity by oral intubation would result in a lower toxicity value than a dietary study because the diazinon is diluted in feed in the dietary study. Also, because these values are from different types of tests with different exposure regimes, they are not directly comparable.

Review 1-4: *Ecotoxicity data and data reduction*

The authors evaluated 250 published studies of diazinon toxicity to develop the proposed criteria. Relevance was determined using the

aforementioned criteria¹ and data for studies that were deemed acceptable were evaluated. Adequate and reliable data is available for determining acute toxicity using animal studies and exclusion criteria appear to have been applied properly.

Mean acute toxicity values were determined when multiple toxicity values were available for the same species. The final acute and chronic data sets consist of 13 and 5 species mean acute values. Less sensitive species or endpoints were excluded from the data reduction process. This is acceptable.

RTR 1-4: Comment acknowledged.

Review 1-5: *Acute criterion calculation*

The acute criterion for diazinon was calculated using methods defined by Tenbrook *et al.* (2009). Due to the high level of uncertainty in the significance of the toxicity values, the recommended value is reported as a single significant digit (i.e., 0.2 µg/L). This is appropriate. The entire data set (i.e., 13 species mean acute values) was used to derive the criterion based on the results of a fit test. This is also appropriate.

RTR 1-5: Comment acknowledged.

Review 1-6: *Alternative approach: Bimodal distribution*

Because the acute toxicity values indicated a bimodal distribution of data, the more sensitive subset of data was used to derive a lower acute criterion of 0.1 µg/L. Although this approach makes intuitive sense, there does not appear to be a precedent for this calculation. The authors should consider bolstering the justification for this approach as it provides the basis for lowering the existing acute criterion. The fit to a Burr Type III distribution further confuses this issue as it produces an even lower acute value of 0.035 µg/L. The significance of this latter approach is not discussed and must be addressed. The reason(s) why was this criterion not considered as the final value must be discussed.

RTR 1-6:

The bimodal distribution has been removed from the report as it was unnecessary according to the methodology (TenBrook *et al.* 2009). This section added confusion to the acute criterion calculation instead of clarity, and it was therefore removed.

Review 1-7: *Chronic criterion calculation*

The acute-to-chronic ratio (ACR) method was used to derive the chronic criterion using eight values from the data set. The entire data set yields a chronic criterion of 0.2 µg/L, while the value derived from the 95th confidence interval of the estimates as well as the more sensitive subset

yields a chronic criterion of 0.1 µg/L. These values are consistent with the acute values.

RTR 1-7: Comment acknowledged.

Review 1-8: *Bioavailability*

Insufficient data is available to assess the effects of water chemistry bioavailability of diazinon. The recommendation that compliance with criteria should be based on total concentration is conservative and appropriate.

RTR 1-8: Comment acknowledged.

Review 1-9: *Mixtures*

Additive, synergistic and antagonistic toxicity effects have been reported for diazinon. Because a variety of potential interactions is possible, it is not practical to apply a single model to predict toxicity.

RTR 1-9: Comment acknowledged.

Review 1-10: *Temperature, pH effects*

There is insufficient evidence to support generalized effects of temperature or pH on diazinon toxicity.

RTR 1-10: Comment acknowledged.

Review 1-11: *Sensitive species*

The calculated acute and chronic criteria of 0.2 µg/L is essentially equivalent to the lowest acute values in the data set that contains the most reliable data. However, some data from the less reliable data sets is slightly lower than the proposed criteria. In addition, relatively little data exists for Cladocerans, which appear to be the most sensitive taxon. Accordingly, the conclusion that the value of 0.2 µg/L may be underprotective is reasonable and the recommendation to use the lower chronic value of 0.1 µg/L is prudent.

RTR 1-11: Comment acknowledged.

Review 1-12: *Bioaccumulation*

Diazinon has a moderately high K_{ow} and therefore a moderate potential to bioaccumulate in aquatic organisms. Reported bioconcentration factors are consistent with this K_{ow} and studies in fish indicate that it is eliminated and/or metabolized in a matter of days when contaminated fish are transferred to clean water.

The potential risks posed by food-chain transfer of diazinon from aquatic ecosystems was determined by calculating the water concentration that would be required to produce a dietary exposure of 8.3 mg/kg, which is the lowest NOEC reported for mallard ducks. The NOEC calculation was derived using a biomagnification factor of 2. The value of 186 appears to be a bioconcentration factor, but the origin of this value is not clear. However, the value of 186 does appear to represent an upper conservative value of the BCF and yields a final NOEC for water of 22.3 µg/L, which is two orders of magnitude greater than the chronic water criterion. Accordingly, diazinon bioaccumulation and its transfer through the food-chain does not appear to pose a significant ecological risk.

RTR 1-12: The report has been revised to use a BCF of 188 in this calculation, which is a BCF reported in Table 2 for *Poecilia reticulata* (Keizer *et al.* 1993), to yield a NOEC for water of 22.1 µg/L. It appears the use of the BCF of 186 was a typographical error. This alteration did not change the conclusions of this section.

Review 1-13: *Ecosystem and other studies*

The authors reviewed several studies that evaluated potential ecosystem impacts of diazinon in microcosms and field work (e.g, stormwater runoff). Toxicity was reported at relatively high values of diazinon and one study reported effects at a level of 0.3 µg/L, which is slightly above the derived criteria. The authors' conclusion that the proposed criteria would appear to be protective is tempered by concerns over observed impacts at this slightly higher level.

RTR 1-13: Comment acknowledged.

Review 1-14: *Threatened and endangered species*

None of the plants and animals that are listed as endangered in California is represented in the data set. However, data for congeners that are relatively insensitive to diazinon indicates that endangered species would be protected by the proposed criteria.

RTR 1-14: Comment acknowledged.

Review 1-15: *Harmonization with air and sediment criteria*

Sediment and air quality standards for diazinon do not exist. Partitioning into the water column can serve as a proxy for sediment burdens.

RTR 1-15: Comment acknowledged.

Review 1-16: *Limitations, assumptions, and uncertainties*

The authors correctly point out that the major source of uncertainty in this evaluation stems from the general paucity of viable data on the chronic toxicity of diazinon. Only data from the most sensitive species (i.e.,

Cladocerans) was used to derive the chronic criterion of 0.2 µg/L. Given that data deemed less reliable points to possible toxicity at concentrations of diazinon lower than this value, the conclusion that a lower value should be considered has merit.

RTR 1-16: Comment acknowledged.

Review 1-17: Final criteria statement

The derived acute and chronic criteria were compared to EPA Benchmarks. The derived acute value is essentially the same as the EPA value (0.2- vs. 0.17-µg/l) and the apparent difference can be attributed to rounding. However, a more conservative chronic value of 0.1 µg/L would be lower than the EPA value of 0.17 µg/L.

Overall, the recommended criteria are in agreement with existing state and federal standards. Minor differences resulted from data acceptance criteria and mathematical rounding. Given the relatively high degree of variability that accompanies toxicity data derived from studies conducted at low concentrations of toxicants, these slight differences are to be expected.

RTR 1-17: Comment acknowledged.

Review 1-18: Errata

The following error should be corrected in the final version of the report:

1. Page 7, line 4: Figure 2 is cited here. There does not appear to be a Figure 1.

RTR 1-18: Figure 1, the structure of diazinon, can be found on page 1.

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

REVIEW 2-1: Your proposed acute and chronic criteria for diazinon are 0.2 µg/L and 0.1 µg/L, respectively. The most sensitive species in the data set used to generate these criteria is the cladoceran *Ceriodaphnia dubia*. The Genus Mean Acute Value for *C. dubia* is 0.36 µg/L, based on 9 different tests. There is little variation within this dataset (0.21 to 0.507 µg/L) with no obvious outliers. It is generally accepted that toxic effects to an organism can be demonstrated at approximately ½ the LC50 value. This would mean that toxic effects to *C. dubia* may be expected at concentrations as low as 0.1 µg/L.

RTR 2-1: The species mean acute value (SMAV) for *Ceriodaphnia dubia* has been re-calculated in the final report to be 0.34 µg/L, because two LC₅₀ values were added to the data set (from Bailey *et al.* 1997).

The most robust toxicity value for *Ceriodaphnia dubia* is the SMAV of 0.34 µg/L. While there is one *Ceriodaphnia dubia* toxicity value (0.21 µg/L) in the RR data set that is very close to the proposed acute criterion, the SMAV is the most robust toxicity value to represent a species. The *Ceriodaphnia dubia* SMAV is based on eleven separate tests, and is therefore a more robust and reliable value than a single test value. A SMAV is calculated for use in the SSD so that no single species or single test for a species receives undue weight in the derivation process (section 2-2.7, TenBrook *et al.* 2009). The goal of a SSD is to utilize the whole data set to derive protective estimates, not to simply choose the lowest toxicity value and divide it by a factor of 2. In this case, it is not recommended that the acute criterion be adjusted downward based on one of eleven toxicity values for *Ceriodaphnia dubia*, because the SMAV indicates that the acute criterion of 0.2 µg/L will be protective of this species. Downward adjustment of criteria can be recommended when a proposed criterion is higher than toxicity values for a sensitive species (section 3-6.1, TenBrook *et al.* 2009), especially when there is very little data for a species, but it is not recommended in this case because there is ample data highly rated data for *Ceriodaphnia dubia*.

The USEPA has demonstrated that a concentration of ½ of the LC₅₀ of an organism is a good approximation of a no-effect concentration in experimental stream studies (USEPA 1991). The USEPA (1985) methodology states that the final acute value is divided by 2 “to result in a concentration that will not severely adversely affect too many of the organisms,” (p. 17). The safety factor of 2 was derived based on 219 acute toxicity tests with various chemicals, which showed that the mean concentration that did not cause mortality greater than control was 0.44 times the LC₅₀. The inverse of 0.44 (2.27) was rounded to 2 for use in EPA methods (USEPA 1985). In the EPA method, the safety factor of 2 is applied to the final acute value determined by the log-triangular distribution; they do not simply take the lowest LC₅₀ in the data set and divide it by 2. The safety factor is an approximation of a no-effect level; it is not an exact ratio for across all species and chemicals.

Review 2-2: The narrative criterion of the Basin Plan states “Waters shall be maintained free of toxic substances in concentrations that produce detrimental physiological responses in human, plant, animal, or aquatic life”. Adherence to this narrative criterion and protecting fish and wildlife would likely prevent the acute criterion from being above 0.1 ug/L. Cladocerans are an important component of freshwater invertebrates in the upper Sacramento-San Joaquin Estuary and their numbers have been in decline since the early 1970s. Having similar acute and chronic criteria for diazinon is substantiated by there being little difference between the acute and chronic toxicities of most organophosphates to invertebrates.

RTR 2-2: The protection goal of the criteria calculation methodology used to calculate these criteria is based on language in the Basin Plan. The acute criterion determined by the UC-Davis methodology of 0.2 µg/L should be protective of all species in the Sacramento and San Joaquin River ecosystems based on the available toxicity data. See RTR 2-1 for additional discussion of the protection of Cladocerans. It would not be unreasonable to have acute and chronic criteria of the same value, but the data and the fit of the distribution demonstrate that an acute criterion of 0.2 µg/L should not be underprotective of Cladocerans.

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

REVIEW 3-1: The diazinon water quality criteria were derived by applying a new methodology developed by the University of California, Davis. Explicitly following the data evaluation criteria of the methodology, the author(s) identified 22 acute toxicity studies and 8 chronic toxicity values that were reliable and relevant for criteria derivation from 250 original studies. As acute toxicity data were acceptable from five required taxa (i.e., a warm water fish, a cold water fish, a planktonic crustacean, a benthic crustacean, and an insect), species sensitivity distribution (SSD) procedures were applied for the acute water quality criterion derivation that yielded a recommended acute value of 0.2 µg/L. Since the data were available from only 3 of 5 required taxa, the chronic criterion was calculated by using the acute-to-chronic ratio (ACR) method that yielded a recommended value of 0.1 µg/L.

RTR 3-1: Comment acknowledged.

REVIEW 3-2: For the chronic water criterion, the limitation was primarily due to the lack of data from more sensitive species of required taxa in the chronic toxicity data set. In fact, the criterion was derived from only one value of *Daphnia magna* because of the large range of ACR values between fish and *D. magna* (46-80 times difference). The author(s) considered the limitation and supplemental values that suggested lower acute toxic (0.2-0.25 µg/L) and MATC (0.07-0.13 µg/L) values (Sánchez et al. 2000), and recommended a lower chronic value of 0.1 µg/L that was calculated from the lower confidence limit of the whole data set and the median estimate of the lower subset data. The recommendation appears appropriate and ensures protection.

RTR 3-2: Comment acknowledged.

REVIEW 3-3: However, I felt less confident on the acute water criterion recommended for the following reasons: 1) The recommended criterion was derived by Burr Type III distribution using the whole acute data set. As shown in the report, diazinon toxicity data set has a distinct bimodal distribution. Thus, alternative calculations using the subset of lower toxicity data were processed by applying Log-logistic, log-triangular and Reciprocal Pareto distributions. The alternative calculations suggested lower acute criteria (Section 7 and Appendix B, this report)

RTR 3-3: The acute diazinon data set does exhibit a bimodal trend, but the Burr Type III distribution does fit the whole data set. The distribution did not fail the fit test, and according to the methodology, the entire data set should be used if the distribution has an acceptable fit (section 3-3.2.4, TenBrook *et al.* 2009).

REVIEW 3-4: 2) On section 12, Sensitive species (Page 13, 1st paragraph), only one acute value (0.21 µg /L) for *Ceriodaphnia dubia* was reported similar to the recommended acute criterion. In fact, Bailey *et al.* (1997) reported 4 acute values from the same study. Two 96 h LC₅₀ values were included in the report but two 48 h LC₅₀ values (0.25 and 0.29 µg /L) that were in the ballpark of the criterion were excluded. When there are three values with 95% confidence intervals bracketing the recommended criterion, it is difficult to ignore them. Two values by Sánchez *et al.* (2000) were also discussed with the acute criterion. These values were derived from a 21 days multi-generation test; they should be treated as chronic values that may not be taken into considerations for acute criteria derivation.

RTR 3-4: The 48-hr LC₅₀ values from tests 3 and 4 by Bailey *et al.* (1997) have been added back to the final acute RR data set (table 3). The *Ceriodaphnia dubia* SMAV has been re-calculated to be 0.34 µg/L (instead of 0.36 µg/L), and the SSD was re-fit to the revised data set. The discussion of the 21-d *C. dubia* values (Sanchez *et al.* 2000) has been removed from the sensitive species section, because they are not appropriate to compare to 48 and 96-h tests.

The most robust toxicity value for *Ceriodaphnia dubia* is the species mean acute value (SMAV) of 0.34 µg/L. While there is one *Ceriodaphnia dubia* toxicity value in the RR data set that is very close to the proposed acute criterion (0.21 µg/L), and two that are near it (0.25 and 0.29 µg/L), the SMAV is the most robust toxicity value to represent a species. The *Ceriodaphnia dubia* SMAV is based on eleven separate tests, and is therefore a more robust and reliable value than a single test value. A SMAV is calculated for use in the SSD so that no single species or single test for a species receives undue weight in the derivation process (section 2-2.7, TenBrook *et al.* 2009). In this case, it is not recommended that the acute criterion be adjusted downward based on one of eleven toxicity values for *Ceriodaphnia dubia*, because the SMAV indicates that the acute criterion of 0.2 µg/L will be protective of this species. Downward adjustment of criteria can be recommended when a proposed criterion is higher

than toxicity values for a sensitive species (section 3-6.1, TenBrook *et al.* 2009), especially when there is very little data for a species, but it is not recommended in this case because there is ample data highly rated data for *Ceriodaphnia dubia*.

REVIEW 3-5: Data for density and melting point were cited from the same source (Tomlin 1994, 2003) but different editions. Should the newer edition be used?

RTR 3-5: The melting point has not changed in the new edition.

REVIEW 3-6: Page 7-9, Section 7, the figures 3 and 4 were not referred in the text. It creates some difficulties for readers to follow through.

RTR 3-6: Figures 3 and 4 are referenced in the text of section 7 of the final report.

REVIEW 3-7: Page 8 and 9, Figure 3 and 4, inconsistency between the graph label and the caption: Burr III is labeled in the graph but named Reciprocal Weibull or Pareto distribution in the captions. Reciprocal Weibull distribution does not seem to be described in the text.

RTR 3-7: The Reciprocal Weibull is one of the three distributions of the Burr Type III distribution. The Reciprocal Weibull is the distribution given by the BurrliOZ software program as the best fit the data of the three distributions that the program fits to the data set. This has been clarified in the text of section 7. The Reciprocal Pareto distribution was the distribution that best fit the lower subset, but this graph has been removed from the final report.

REVIEW 3-8: Page 13, 1st paragraph, line 3, 'Table 4' should be 'Table 3'.

RTR 3-8: The table reference in this section has been corrected in the final report.

REVIEW 3-9: Page 18, paragraph 2, line 7, the log-triangular calculation should be referred to the Appendix B. The calculation wasn't described in the Section 7 of this report.

RTR 3-9: The calculation of the log-triangular distribution has been added to the text of the report (section 18 Comparison to the national standard methods) in the final criteria report.

4.0 References

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