

# **Responses to Public Comments and Peer Reviews**

Phase III: Malathion 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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## Responses to Comments

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

<b>Term</b>	<b>Definition</b>
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 <sub>x</sub>	The chemical concentration that has an effect on <i>x</i> % of the test population.
K <sub>oc</sub>	Organic Carbon Partition Coefficient
LC <sub>50</sub>	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 malathion is one.

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

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 – Paul Whatling, Cheminova, Inc.

**COMMENT 1-1:** To derive an acute or chronic criterion using an SSD method, the methodology states that a minimum of five effects metrics from five different families are required (TenBrook et al. 2009). These include: 1) a salmonid, 2) a warm water fish, **3)** a planktonic crustacean, of which one must be in the family Daphniidae in the genus Ceriodaphnia, Daphnia or Simocephalus, 4) a benthic crustacean, and 5) an insect (aquatic exposure). Faria et al. (2009) stated that acceptable acute toxicity data were available for only four of the five required taxa. A member of the benthic crustacean family was unavailable. Thus, they concluded that the SSD approach could not be applied. Instead, a more conservative approach was used to derive the acute criterion. The approach involved dividing the lowest mean acute value (1.5 ppb for *Chironomus tentans*) by an assessment factor of 5.1 to extrapolate to a HC5 and then dividing the result by a safety factor of 2 to obtain the final acute criterion value of 0.15 ppb. The safety factor of 2 is applied because 50% effect to the 5th percentile species is not considered acceptable (TenBrook et al. 2009). The derivation of the safety factor of 2 was based on 219 acute toxicity tests with various chemicals. The test results indicated that the mean concentration that did not cause mortality greater than control was 0.44 times the LC50 (34 FR 97, p 21508-21218). The inverse of 0.44 (2.27) was rounded to 2 for deriving acute water quality criteria.

**Response To Comment (RTC) 1-1:** Comment acknowledged.

**COMMENT 1-2:** While Cheminova is generally supportive of SSD methods, it disagrees with the approach taken by the Board for derivation of a WQC for Malathion. The WQC derived using this method is driven primarily by one 96 hour EC50 value of 1.5 ppb for *Chironomus tentans* (Belden and Lydy, 2000), which is not a species mean acute value (SMAV). Additional studies that were performed in Dr. Lydy's lab (Pape-Lindstrom and Lydy 1997) resulted in a 96 hour EC50 of 19.1 ppb. These data were excluded in the Board's data reduction process (i.e., "1. More sensitive endpoint available"), although we found little difference in the endpoint used in the two studies (unable to perform normal swimming motion -vs- failure of the midges to execute three figure-eight motions). It appears that this data was discounted erroneously or the data reduction process is seriously flawed. When this data is included, the SMAV for *Chironomus tentans* would then be 10.7 ppb.

**RTC 1-2:** The *Chironomus tentans* value from Pape-Lindstrom & Lydy (1997) has been added back to the final acute data set and the *Chironomus tentans* SMAV has been updated to be 5.35 µg/L, which is the geometric mean of 1.5 and 19.01 µg/L. The criteria have been re-calculated based on the lowest SMAV in the final data set of 1.7 µg/L (*Neomysis mercedis*) to be 0.17 and 0.028 µg/L.

**COMMENT 1-3:** Nevertheless, there are unique field and laboratory data for Malathion that directly measure the potential for community-level effects, whereas the Board's approach provides only an indirect and highly conservative method of assessing community-level effects.

The Alabama field study and mesocosm data clearly indicate that there are not community-level effects at concentrations of up to 30 ppb and the goal of the water quality criteria are to prevent such community-level effects. Also, there were no effects to any biota at 5 ppb in the mesocosm study. Therefore, Cheminova recommends basing the acute WQC on the NOEC in the mesocosm study of 5 ppb.

**RTC 1-3:** Single-species toxicity data is used for water quality criteria calculation by methodologies from around the world, including the USEPA (1985), and it has been demonstrated that criteria calculated based on single-species data are protective of ecosystems (TenBrook & Tjeerdema 2006). The Alabama field study (Kuhajda *et al.* 1996) was a field monitoring study that did not test specific concentrations, and no dose-response effects were not observed. This study is not conclusive of ecosystem-level effects due to malathion exposure. The above-mentioned mesocosm study (Ebke, 2002) was not received from the USEPA before the malathion water quality criteria report was finalized, and therefore cannot be included in criteria derivation. Data requests from the US EPA through the Freedom of Information Act (FOIA) process can take several months to receive, but if the malathion criteria are re-evaluated in the future, this study should be included.

**COMMENT 1-4:** Faria *et al.* (2009) determined that the five taxa requirement was also not met for the chronic SSD method. Specifically, no chronic studies were available for benthic crustaceans or insects exposed to Malathion. Instead, the chronic criterion was calculated by applying an acute-to-chronic ratio to the acute water quality criterion value. Three acute-to-chronic ratios (ACRs) for fish could be calculated from the available data: bonytail (*Gila elegans*) (ACR=10.8); Colorado squawfish (*Phytocheilus lucius*) (ACR = 3.7); and flagfish (*Jordanella floridae*) (ACR=36.0). No ACR values were available for invertebrate species (Faria *et al.* 2009). A default ACR of 12.4 was thus included in the ACR data set to account for the missing invertebrate data (TenBrook *et al.* 2009). The species mean ACR (SMACR) was determined by taking the geometric mean of the three data-based ACRs and the default ACR (SMACR =

11.8). Dividing the previously obtained acute HC5 (1.5 ppb / 5.1 = 0.29 ppb) by the SMACR resulted in a chronic criterion of 0.03 ppb.

**RTC 1-4:** Comment acknowledged.

**COMMENT 1-5:** Cheminova disagrees with the SMACR developed by the Board. The flagfish study is old and used a product with unknown impurities (Hermanutz, 1978). Therefore, it does not provide a reliable basis to estimate an ACR. Without the flagfish study, the SMACR is 7.8.

**RTC 1-5:** The Hermanutz (1978) study reports that it tested malathion with 95% purity. The year a study was published is not a factor in determining the reliability of the study, reliability is determined based on documentation and acceptability of test parameters. The Hermanutz (1978) study is included in the final malathion criteria report, and the ACR for this species is included in the calculation of the final multispecies ACR.

**COMMENT 1-6:** Cheminova recommends using the Board's procedures, but with the proposed acute criteria value of 5 ppb from the mesocosm study. Applying the SMACR results in a chronic criteria value of 0.6 ppb (5 ppb / 7.8).

**RTC 1-6:** The UC-Davis methodology uses single-species laboratory test results to calculate criteria, not mesocosm test results.

**COMMENT 1-7:** More broadly, Cheminova believes that setting a chronic WQC for Malathion is unnecessary given its rapid degradation in the environment (see mesocosm study). Therefore, exposure over a chronic duration is unlikely.

**RTC 1-7:** The UC-Davis methodology derives both acute and chronic criteria for a given pesticide. Chronic effects due to malathion exposure have been observed in many laboratory tests (see Table 5 of the malathion criteria report).

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

(Comments that were unrelated to malathion are not reported in this document)

**COMMENT 2-1:** 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.

**RTC 2-1:** The default ACR was calculated using a procedure described and utilized by the US EPA (USEPA 2003, Host *et al.* 1995). The use of a default ACR is accepted by the US EPA for derivation of water quality criteria (USEPA 2003).

**COMMENT 2-2:** 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.

**RTC 2-2:** The malathion report does not recommend use of the concentration addition model for criteria compliance.

**COMMENT 2-3:** 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.

**RTC 2-3:** The derivation of water quality criteria do not take into account reporting limits of commercial laboratories or other economic feasibility issues. These considerations are taken into account when setting water quality objectives, while water quality criteria are derived with only the objective of the protection of aquatic life.

**COMMENT 2-4:** 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.

**RTC 2-4:** See RTC 2-1.

**COMMENT 2-5:** The UCD methodology has been used to derive criteria for pesticides (e.g., chlorpyrifos and diazinon) for which the US. 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.

**RTC 2-5:** The UC-Davis methodology was developed to be able to accommodate data sets of varying size and diversity – including those that meet all of the data requirements of the USEPA (1985) methodology. The UC-Davis methodology uses different distributions than the USEPA methodology that better characterize large data sets than the log-triangular distribution used in the USEPA methodology (section 2-3.1.1, TenBrook *et al.* 2009).

**COMMENT 2-6:** 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.

**RTC 2-6:** See RTC 2-1.

**COMMENT 2-7:** 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.

**RTC 2-7:** See RTC 2-2.

### **2.3. Comment Letter 3 – Nasser Dean, Western Plant Health Association**

**COMMENT 3-1:** We request that the UCD authors of this Method (Faria et al.) clearly define the proposed numeric criteria which do not have a "detrimental physiological responses" in aquatic life.

**RTC 3-1:** Detrimental physiological responses are measured in toxicity tests that test for effects on survival, growth or reproduction. A dose-response relationship must be observed for the effects, and the responses of exposed organisms are always compared to those of control organisms. The goal of numeric criteria is to derive concentrations at which organisms in the environment will not experience adverse effects on their survival, growth, or reproduction, using toxicity data.

**COMMENT 3-2:** Impurities in older materials may contribute to toxicity. For older studies, the quality of malathion would be very different from that currently produced by the major registrant. Studies should be screened thoroughly to determine the source and purity of the test material. This should include identifying and quantifying levels of any impurities, and those not equivalent should be discarded. Many studies performed by the major registrant of malathion determined to be acceptable by US EPA were not included by the UCD authors. Registrant studies follow Good Laboratory Practice (GLP) requirements and standard study guidelines. These studies are reviewed stringently by US EPA based on meeting the guideline requirements and GLP. This should take precedence in the development of the Method.

**RTC 3-2:** In the UC-Davis methodology, only studies that test a pesticide of > 80% purity are used for criteria derivation. All studies are screened using the same data evaluation process, as described in the methodology (section 3-2.2.2, TenBrook *et al.* 2009). Data summary sheets for all studies evaluated are provided in the final malathion criteria report; the summaries list the relevancy and reliability scores for each study.

**COMMENT 3-3:** The removal of certain taxa (e.g., rotifers, annelids, and mollusks) from consideration is inconsistent with the goal of a representative "unbiased" species sensitivity distribution (SSD). The purpose of the SSD is to represent the entire community. The CVRWQCB and UCD authors should consider a broader range of statistical distributions for estimating SSDs, including polynomial, Fisher Tippet, Weibull and Gompertz distributions.

**RTC 3-3:** In the UC-Davis methodology, no taxa that are excluded from the use in SSDs. Rotifers, annelids, and mollusks are not required for use of a SSD, but if high quality data are available for these species, they are included in the SSD data set. We agree that the purpose of an SSD is to represent the whole community, which is why the use of the Burr Type III distribution and log-logistic distributions are used in the UC-Davis methodology, instead of the log-triangular distribution (used in the USEPA methodology), which emphasizes the fit to the

sensitive end of the data set. The Burr Type III distribution used in the UC-Davis methodology, as well as the ANZECC & ARMCANZ (2000) methodology, fits three distributions (reciprocal Weibull, reciprocal Pareto, Burr III) to the data set and chooses the one that best fits the data. The choice of distributions has been thoroughly reviewed by the peer review and public comment processes, but may be revised in the future.

**COMMENT 3-4:** The UCD authors of this Method incorrectly imply that the disappearance of a single species will lead to community-wide effects in an ecosystem. In fact, such occurrences are rare and for malathion, there is specific data to rebut this claim. Mesocosm and field studies demonstrated that at relatively high malathion concentrations (up to 30 ppb) there were no community-level effects in aquatic ecosystems. This appears to have been overlooked or not considered by the UCD authors. These studies should be considered in a multiple lines of evidence (MLOE) approach.

**RTC 3-4:** The Phase I report (section 5.2, TenBrook & Tjeerdema 2006) describes in detail that the assumption that ecosystems can sustain some level of damage from toxicants and subsequently recover with no lasting harm is not completely supported in the literature. The goal of the UC-Davis method is not just to maintain function or structure of an ecosystem, but to maintain healthy populations of all resident species in an ecosystem. Mesocosm studies are not used to derive water quality criteria because they are typically not reproducible, do not follow standard methods, and there are relatively few mesocosm studies available in the literature.

**COMMENT 3-5:** We strongly disagree with the UCD author's conclusion – that 3 years is required before recovery following a contaminant pulse. Even in the citations provided to justify this point, most studies show recovery on the order of days to weeks. Mesocosm data available for malathion show rapid recovery of sensitive invertebrate species such as daphnids.

**RTC 3-5:** The three-year frequency of exceedance was chosen to allow for full recovery from effects of an excursion above either acute or chronic criteria for all species, including those with long life-cycles (section 2-3.4.2, TenBrook *et al.* 2009).

## 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 malathion (diethyl 2-dimethoxyphosphinothioylsulfanybutanedioate) defined in this draft report was derived using methodology recently developed by Tenbrook *et al.* (2009)<sup>1</sup>. The methodology considers relevance of the endpoints and quality of the data in derivation of the criteria. This methodology was motivated by the California Regional Water Quality Control Board's desire to employ rigorous methods to develop criteria for protection of the Sacramento and San Joaquin River Watershed.

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

#### **Review 1-2: Basic information and physical-chemical data**

The report provides a comprehensive summary of the physical-chemical data for malathion. 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., moderate 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 acknowledgement.

#### **Review 1-3: Human and wildlife dietary values**

The FDA has not set action levels for malathion in fish tissue.

Avian mortality is a concern for malathion. Reported subacute dietary toxicity values for malathion to mallard ducks vary widely (i.e., LD<sub>50</sub>s of 1,200-1,485 mg/kg). This report presents these oral doses as LC<sub>50</sub> values whereas they should be should be LD<sub>50</sub>s (this is a dietary dose reported as mg/kg, not a water-based exposure). No-effect doses are not reported.

**RTR 1-3:** The dietary toxicity values are reported as LC<sub>50</sub>s because they are a concentration in feed.

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<sup>1</sup> 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.

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

The authors evaluated 200 published studies of malathion toxicity to develop the proposed criteria. Relevance was determined using the aforementioned criteria<sup>1</sup> 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. Thirty-six acute, 9 chronic, and 2 mesocosm studies were found to contain relevant and reliable data.

**RTR 1-4:** Comment acknowledged.

**Review 1-5: Acute criterion calculation**

The acute criterion for malathion was calculated using methods defined by Tenbrook *et al.* (2009). Due to the lack of data for benthic crustaceans, the five taxa required for the species sensitivity distribution (SSD) was not available and the SSD method could not be used. Instead, the Assessment Factor (AF) method was used to calculate the acute criterion. Using an estimate of the median 5<sup>th</sup> percentile value of the SSD and then applying an assessment factor of 5.1, a lowest acute value of 0.29 µg/L was derived. Applying a safety factor of 2 yields a final acute criterion of 0.15 µg/L. Although, this calculation appears to have been performed correctly, the lowest acute value (i.e., 0.29) is not explicitly listed.

**RTR 1-5:** The calculation of the acute criterion has been written more explicitly in the final criteria report. The acute criterion has been recalculated in the final report because the lowest SMAV was changed. The final acute criterion is 0.17 µg/L. The criterion is rounded to two significant digits because all of the SMAV used to calculate the criterion has two significant digits; most data in the data set also report two significant digits.

**Review 1-6: Chronic criterion calculation**

The acute-to-chronic ratio (ACR) method was used to derive the chronic criterion using data for three fish species. Because chronic data were not available for invertebrate species, ACRs could only be calculated for the 3 fish species. Accordingly, the use of a default ACR (i.e., 12.4) is appropriate. A species mean acute to chronic ratio (SMACR) was calculated by deriving the geometric mean for the 3 fish species plus the default ACR.

The presentation of this approach lacks clarity due to inconsistent use of descriptors. Specifically, the term “final acute value” appears to be the “lowest acute value” defined in the acute calculation on page 6. This value (i.e., 0.29) does not appear in the description of the acute criteria derivation, which makes its first appearance in the chronic derivation confusing. The final chronic value (i.e., 0.03 µg/L) appears to have been

rounded up from a value of 0.0246, which does not appear to be an appropriate rounding. The basis for the 0.03 µg/L value should be defined.

**RTR 1-6:** The calculation of the chronic criterion has been written more clearly in the final criteria report. The final acute value is now defined in the acute criterion calculation section. The final chronic criterion has been re-calculated in the final report to be 0.028 µg/L. The chronic criterion is rounded to two significant digits to be consistent with the significant digits of the acute criterion.

**Review 1-7: *Bioavailability***

Insufficient data is available to assess the effects of water chemistry bioavailability of malathion. Due to this compound's relatively low log Kow value, its tendency to sorb to dissolved and particulate organic material is also low. Accordingly, the recommendation that compliance with criteria should be based on total concentration is conservative and appropriate.

**RTR 1-7:** Comment acknowledged.

**Review 1-8: *Mixtures***

Additive and synergistic toxicity effects in the presence of other pesticides have been reported for malathion. In some cases, antagonistic effects have also been reported. Because a variety of potential interactions is possible, it is not practical to apply a single model to predict toxicity.

**RTR 1-8:** Comment acknowledged.

**Review 1-9: *Temperature, pH effects***

Malathion is subject to pH-dependent hydrolysis and the products of hydrolysis are less toxic than the parent compound. Although insufficient data exists to generalize the influence of pH or temperature on toxicity, these variables appear to have little influence on toxicity and will not create a situation in which the criterion is underprotective of aquatic life.

**RTR 1-9:** Comment acknowledged.

**Review 1-10: *Sensitive species***

The calculated acute and chronic criteria (0.15- and 0.03-µg/L, respectively) are both below the lowest reported acute value of 0.21 mg/L reported for a chironomid. The chronic criterion is also below the lowest reported maximum acceptable toxicant concentration of 0.08 µg/L reported for a daphnid. The conclusion that both the calculated acute and chronic criteria derived in this report should be adequately protective is appropriate.

**RTR 1-10:** Comment acknowledged.

**Review 1-11: *Bioaccumulation***

Malathion has a relatively low  $K_{ow}$  and therefore a low 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 rapidly. Due to these properties, malathion has little potential to undergo significant food-web transfer and little or no potential for biomagnification.

A calculation to determine the water concentration of malathion required to produce a toxic dose to mallards via food web transfer results in a concentration that far exceeds the acute criterion value. Accordingly, food-web transfer of malathion to terrestrial species does not appear to pose a significant ecological risk.

**RTR 1-11:** Comment acknowledged.

**Review 1-12: *Ecosystem and other studies***

The authors reviewed several studies that evaluated potential ecosystem impacts of malathion in mesocosms and ecosystems. Impacts on invertebrates were only noted at concentrations of malathion that exceeded the proposed acute and chronic criteria.

**RTR 1-12:** Comment acknowledged.

**Review 1-13: *Threatened and endangered species***

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

**RTR 1-13:** Comment acknowledged.

**Review 1-14: *Harmonization with air and sediment criteria***

Sediment and air quality standards for malathion do not exist. Although malathion has a relatively low partition coefficient, partitioning into the water column can serve as a proxy for sediment burdens.

**RTR 1-14:** Comment acknowledged.

**Review 1-15: *Limitations, assumptions, and uncertainties***

The authors correctly point out that the major source of uncertainty in this evaluation stems from the lack of viable malathion toxicity data for benthic crustaceans. The approaches used (i.e., ACR and Assessment Factor) were appropriate given this limitation.

**RTR 1-15:** Comment acknowledged.

**Review 1-16: Comparison to national standard methods**

EPA (1985) methods were also used to derive acute and chronic criteria for malathion. The EPA method faces the same limitation encountered in this report, that is, lack of data for all required taxa. The acute criterion proposed in this study is significantly higher than the EPA-derived value for invertebrates (0.15 µg/L vs. 0.005 µg/L, respectively). This result is due to the fact that the EPA method included data that was deemed to be of low relevance and reliability. The authors' rationale for exclusion of these data is sound (e.g., lack of controls, non-reporting of chemical purity).

**RTR 1-16:** Comment acknowledged.

**Review 1-17: Final criteria statement**

Overall, the recommended criteria are less stringent than existing federal standards. This difference resulted from the less rigorous data acceptance criteria used in derivation of the federal standard. As proposed, the chronic criterion of 0.03 µg/L and the chronic criterion of 0.15 µg/L should be protective of aquatic species in the Sacramento and San Joaquin River basins.

**RTR 1-17:** Comment acknowledged.

### **3.2. Peer Review 2 – Evan Gallagher, Ph.D., University of Washington**

**REVIEW 2-1: Comments on ecotoxicity data and sensitive species.**

The authors identified approximately 200 original studies on the effects of malathion on aquatic life. Single-species effect studies that were rated as relevant (R) or less relevant (L) in accordance with the 2009 data reduction procedures. Malathion studies involving rodents or *in vitro* exposures were deemed irrelevant by an initial screening and were not summarized. The aforementioned approach is justified due to uncertainty surrounding *in vitro* to *in vivo*, and also species extrapolations. Ultimately, 36 acute studies yielding 105 toxicity values were judged reliable and relevant for criteria derivation, whereas there were only 9 chronic studies yielding 6 toxicity values that were judged relevant for criteria derivation.

Of consideration is the application of the criteria to sensitive endangered salmonids in these river basins. The calculated acute and chronic criteria

were below the lowest acute and chronic values in the dataset, and it is reasonable to assume that these values should be adequately protective to sensitive species such as salmonids, at least based upon currently available data from single species toxicity tests. However, a source of uncertainty for salmon is the potential modulating effects of other environmental stress source such as temperature, and dissolved oxygen. Although several studies at the ecosystem level exist for the effects of malathion, the majority were related as an unreliable due to issues with experimental design. Accordingly, ecosystem level and NOEC values were not calculated.

**RTR 2-1:** Comment acknowledged.

**REVIEW 2-2: Issues associated with mixture interactions.** The issue of malathion exposures in the context of mixtures is especially relevant in the Sacramento and San Joaquin River basins, which often contain multiple pesticides. This issue poses a problem with regards to the establishment of water quality criteria, as there is extensive evidence of potentiating interactions among pesticides on toxicity to aquatic life. This issue is particularly relevant to malathion and salmon. The authors are aware of this scenario and site a recent paper cited by the authors of Scholz et al who documented unpredictable and potent toxic interactions among malathion and other organophosphate, such as diazinon and chlorpyrifos. Furthermore, the modulating effects of malathion on diazinon and chlorpyrifos toxicity were among the most prominent among a series of five pesticides tested. However, presently there does not seem to be a clear mechanism of how to incorporate such interactions quantitatively into compliance. The report takes these interactions into consideration, at least in a qualitative sense. However, this is an important area of uncertainty especially given that such pesticide interactions may affect acute toxicity in the field.

**RTR 2-2:** We agree that one of the most important limitations for malathion criteria derivation is that we cannot account for mixture interactions with other organophosphates.

**REVIEW 2-3: Other comments on the acute and chronic criteria calculations.** Acceptable acute toxicity data were available for 4 of 5 of the required taxa for the application of the species sensitivity distribution (SSD). The Assessment Factor (AF) method used to derive the acute criterion requires an acceptable acute toxicity value for a species in the family *Daphniidae*. This criteria was met in the acute toxicity data set. However, due to a lack of relevant studies, there were not 5 taxa available for the required calculation of the chronic species sensitivity distribution (SSD). In turn, the authors calculated chronic criteria using an acute-to-chronic ratio that was outlined in the 2009 manual. In total, 3 acute to

chronic ratios (ACR) could be calculated for data on three species, including bonytail (*Gila elegans*), Colorado squawfish (*Phytocheilus lucius*); flagfish (*Jordanella floridae*). Unfortunately, there were not data available for salmonids, and the available values were all for fish and did not include an invertebrate, which is required by the methodology. This is another source of uncertainty as invertebrates and salmon are often highly sensitive.

**RTR 2-3:** Comment acknowledged.

**REVIEW 2-4: Role of bioavailability and bioaccumulation in the derivation of malathion criteria.** As the authors noted, there are very few studies on the effects of suspended and dissolved organic solids on the bioavailability of malathion to aquatic organisms. There is little evidence that malathion adsorbs to sediments, thus limiting bioavailability. Based upon the limited available information, the authors concluded that malathion appears to be bioavailable, and compliance with criteria should be determined on a total pesticide concentration basis.

**RTR 2-4:** Comment acknowledged.

**REVIEW 2-5: Modulating effects of water quality, temperature and pH.** There's some evidence in the literature for temperature modulation on malathion toxicity, and in general, it appears that malathion toxicity decreases with increasing temperature. The mechanism of this interaction appears to be related to an increased environmental degradation of the compound at higher temperatures, although factors such as metabolism have not been investigated to great detail. Metabolism of pesticides such as malathion greatly differs among aquatic species. While such observations are likely of importance environmentally, especially in the San Joaquin and Sacramento River basins, there does not appear to be enough data for different species to adequately quantify the relationship of toxicity with temperature. Accordingly, only results of tests conducted at standard temperatures used in standard toxicity testing were included in the data set. This appears reasonable.

**RTR 2-5:** Comment acknowledged.

**REVIEW 2-6: Comments on human and wildlife dietary values.** As indicated, food tolerances and FDA action levels have not been clearly established for malathion. With the exception of dietary LC<sub>50</sub> values for Mallard ducks (1200-1485 mg/kg), there is little information on dietary toxicity values for other wildlife species with significant food sources in the water. It was unclear from the document as to the duration (i.e. 48 hr, 96 hr associated with the LC<sub>50</sub> values for Mallards. These data gaps did not appear to hamper the derivation of water quality criteria.

**RTR 2-6:** The exposure duration of the chronic dietary study has been added to this section of the final report.

**REVIEW 2-7:** In table 1 (bioconcentration factors for malathion) there are some missing values missing for data related to target tissue or exposure duration for common carp, salmon, lake trout, shrimp and caddis fly that were evidently used to calculate the log BCF. Is this information available? If so, please add to the table. Conversely, if the data is not available, please clarify in the legend.

**RTR 2-7:** The missing values for the above-mentioned species have been added to Table 1, or indicated that the information was not reported (NR) in the reference.

**REVIEW 2-8:** Figure 3. Histograms of logarithmic values for the malathion dataset: are the probability values for the 6 – 8 ug/L datasets missing, or are the values 0?

**RTR 2-8:** There are no toxicity values in the range of 6-8 µg/L, this is noted in the figure legend in the final report.

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

**REVIEW 3-1:** The malathion water quality criteria were derived by applying a new methodology recently developed by the University of California, Davis. Explicitly following the data evaluation criteria of the methodology, the author(s) identified 36 acute and nine chronic toxicity studies that were reliable and relevant for malathion criteria derivation from over 200 original studies. As acute toxicity data did not meet the requirements for the species sensitivity method, the Assessment Factor (AF) method was chosen to derive the acute water quality criterion of 0.15 µg/L. For the similar reason, the chronic criterion was derived by applying a geometric mean of acute-to-chronic ratios that produced a value of 0.03 µg/L. Although the acute chronic criteria had limitations due to the lack of available data sets, I agree with the author(s) that there is no evidence shown that the derived acute and chronic criteria will be underprotective of aquatic organisms under the current knowledge of malathion toxicity.

**RTR 3-1:** Comment acknowledged.

**REVIEW 3-2:** It also appears justified to exclude the two studies by Rawash et al. (1995) and Wong et al. (1995) that led to much lower EPA

aquatic life benchmark values for invertebrates because the studies were rated non-reliable and low-relevance.

**RTR 3-2:** Comment acknowledged.

**REVIEW 3-3:** The author(s) may consider updating the reference list with the newer edition of “The Pesticide Manual” by Tomlin. It is on its Fourteenth edition in 2006.

**RTR 3-3:** Comment acknowledged.

### **3.4. Peer Review 4 – Stella McMillan, Ph.D., California Department of Fish and Game**

**REVIEW 4-1:** Acute and chronic criteria proposed for malathion are 0.15 and 0.03 µg/L, respectively. Given the available toxicity values, these criteria seem appropriate for the protection of aquatic organisms.

**RTR 4-1:** Comment acknowledged.

## **4.0 References**

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