STATE OF CALIFORNIA CALIFORNIA REGIONAL WATER QUALITY CONTROL BOARD CENTRAL COAST REGION 895 Aerovista Place Suite 101 San Luis Obispo, CA 93401-7906

SCIENTIFIC PEER REVIEW COMMENTS AND STAFF RESPONSE FOR TOTAL MAXIMUM DAILY LOADS FOR TOXICITY AND PESTICIDES IN THE SANTA MARIA WATERSHED IN SANTA BARBARA, SAN LUIS OBISPO AND VENTURA COUNTIES, CALIFORNIA (DRAFT PROJECT REPORT, MARCH 12, 2012)

PREFACE

California Health and Safety Code Section 57004 requires all California Environmental Protection Agency organizations to submit for external scientific review the scientific basis and scientific portion of all proposed policies, plans and regulations. The peer reviewer's responsibility is to determine whether the scientific findings, conclusions, and assumptions are based upon sound scientific knowledge, methods, and practices.

Three individuals were selected to review this document for scientific adequacy: Dr. Jonathan Maul, Professor (Department of Environmental Toxicology), Texas Tech University; Linda S. Lee, Department Head (Ecological Science and Engineering Interdisciplinary Graduate Program and Professor (Environmental Chemistry) Purdue University and Dr. Jeffrey Jenkins, Professor (Environmental and Molecular Toxicology), Oregon State University. These researchers collectively have substantial research experience in environmental chemistry and toxicology.

Peer reviewer selection was facilitated through the University of California. The detailed step-by-step guidance for setting up and obtaining reviews appears as Exhibit F¹ in an Interagency Agreement between the California Environmental Protection Agency and the University of California. A January 7, 2009 Supplement to the Guidelines², in part, provides guidance to ensure confidentiality of the process. No person may serve as an external scientific peer reviewer if that person participated in the development of the scientific basis or scientific portion of the proposed rule, regulation, or policy³.

The California Health and Safety Code states that if the external scientific peer reviewers find that a State agency failed to demonstrate that the scientific portion of the proposed rule is based upon sound scientific knowledge, methods, and practices, the reviewer's report shall state that finding, and the reasons explaining the finding⁴.

Central Coast Regional Water Quality Control Board staff (Water Board staff) asked the reviewers to comment on whether the scientific portions of the Total Maximum Daily Load (TMDLs) project report are based upon sound scientific knowledge, methods, and practices.

Specifically, the reviewers were asked to comment on five specific areas related to the document:

1. Numeric Targets

- 2. Source Analysis
- 3. TMDLs and Allocation
- 4. Implementation
- 5. Monitoring

The Central Coast Regional Water Quality Control Board appreciates the thorough comments provided by the reviewers. Their comments and insight have prompted us to clarify and improve technical information in TMDL project in several areas.

Note that in the following sections of this document, we reproduce direct transcriptions of the comments from each reviewer and insert staff responses using **bold**, **blue italic text**. Some of the reviewer comments were underlined or bolded by staff to clarify the component reviewed or the main topic or question from the reviewer.

SCIENTIFIC PEER REVIEW COMMENTS OF

Jeffrey Jenkins, Ph.D.

Professor

Oregon State University Department of Environmental and Molecular Toxicology

Prepared for Central Coast Regional Water Quality Control Board

Comments Received by Water Board Staff November 7, 2012 Staff responses are inserted in **bold, blue italic text**.

1) Numeric Targets

The primary scientific issue is the scientific basis for the assignment of numeric targets for specific pesticides addressed in the TMDL.

In the Central Coast Regional Water Quality Control Board memo from Christopher Rose dated June 28, 2012, Attachment Five – Water, Sediment, and Fish Tissue Chemistry Numeric Targets – lists water chemistry numerical targets for the organophosphate (OP) insecticides chlorpyrifos, diazinon, and malathion; the synthetic pyrethroid insecticides bifenthrin, cyfluthrin, and λ -cyhalothrin; and the legacy organochlorine (OC) insecticides DDT, DDD, DDE, chlordane, dieldrin, and toxaphene.

Sediment chemistry numerical targets are provided for the OP chlorpyrifos; the synthetic pyrethroids bifenthrin, cyfluthrin, λ -cyhalothrin, cypermethrin, permethrin, and esfenvalerate; and the legacy OCs DDT, DDD, DDE, chlordane, dieldrin, toxaphene, and endrin.

Fish tissue numeric targets are provided for the legacy OCs – chlordane, DDTs, dieldrin, and toxaphene.

The numeric targets in Attachment Five are listed as concentrations (with units) for a given endpoint (CMC, CCC, etc.), along with a reference for that supports the derivation of the numerical target.

The water chemistry numeric targets for the OPs chlorpyrifos and diazinon have been previously derived by the California Department of Fish and Game (CDFG 2000), and further evaluated in the California Regional Water Quality Control Board Central Coast Region project report "TMDLs for Chlorpyrifos and Diazinon in the Lower Salinas River Watershed" (CCRWQCB 2011). These numeric targets are considered sufficiently "peer reviewed with a known record by a recognized expert or expert body." Similarly, as the legacy OC water chemistry numeric targets are derived from the concentration established by the U.S. Environmental Protection Agency (EPA 2000), no further review will be provided. For the sediment and fish tissue chemistry no additional peer review will be conducted for the legacy OCs as references (WDOH, 1995 and OEHHA, 2008) for the numerical targets are deemed sufficiently peer reviewed.

For the pesticides – the OP malathion and the synthetic pyrethroids – evaluation of the scientific basis for the assignment of numeric targets will largely rely on the review of methodologies conducted by TenBrook and Tjeerdema (2006), and subsequent derivation and application of the UC-Davis methodology for specific pesticides (TenBrook et al., 2009), as these reports are considered current, highly relevant, and comprehensive.

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

- Guidance for collection, evaluation, and reduction of data;
- A species sensitivity distribution (SSD) method to derive criteria when data are available for five representative taxa - 1) a warm water fish, 2) a fish in the family Salmonidae, 3) a planktonic crustacean – Ceriodaphnia, Daphnia, or Simocephalus, 4) a benthic crustacean, and 5) an insect (aquatic exposure).
- An assessment factor (AF) method to derive acute criteria when fewer than five acute toxicity data are available;
- A default acute-to-chronic ratio (ACR) to derive chronic criteria when fewer than five chronic data are available;
- Methods for assessing bioavailability;
- Methods for assessing compliance in cases of mixtures of chemicals with similar modes of toxic action and for mixtures that exhibit non-additive toxicity;
- Techniques for assessing whether derived criteria might harm particularly sensitive species, lead to bioaccumulation, harm ecosystems, harm threatened and endangered

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

3) any breakdown products of these materials that threaten beneficial uses."

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

Review of the scientific basis for the assignment of numeric targets for malathion

The selected malathion water chemistry numerical target was derived using the UC-Davis methodology as described in Faria et al., 2010. The UC-Davis methodology derived numeric targets were used as there are no Clean Water Act (CWA) National Standards for malathion. However, for comparison, using the same data set, the malathion numerical targets were derived using National Standard methodology (USEPA 1985).

As acute data for the all of the 5 representative taxa were not available for malathion, the SSD method could not be used. Instead the AF method was used to estimate the median 5th percentile value (acute value) of the SSD, which was subsequently used to calculate the acute criterion. Employing the AF method, using LC50 or EC50 data for 4 of the 5 representative taxa, resulted in an acute criterion = 0.17ug/L. As the AF method may be considered more conservative¹ than the SSD method, <u>in the absence of a complete data set</u>, use of the AF method is considered appropriately protective of <u>aquatic life</u>.

As chronic data for only 3 of the 5 representative taxa were available for malathion, the ACR method was used to calculate the chronic criterion by pairing chronic toxicity values (MATC) with an appropriate corresponding acute toxicity value (LC50) in order to calculate an ACR; resulting in the ACR-derived chronic criterion = 0.028 ug/L. <u>As with the acute criterion derived from the AF method, in the absence of a complete data set, the ACR method is considered conservative and appropriately protective of aquatic life.</u>

Exposure Scenario	Species	Exposure Duration	Toxicity Reference Value
	Freshwat	er Fish	
Acute	Bluegill sunfish	69hr	LC50 = 30 ug/L
Chronic	Rainbow trout	97 day	NOEC 21 ug/L
	Freshwater In	vertebrates	
Acute	Water flea, Daphnia magna	48hr	EC50 = 1.0 ug/L

Table 1. USEPA OPP aquatic toxicity reference values for malathion

Chronic	Water flea, Daphnia magna	21 day	NOEC = 0.06 ug/L	
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Malathion products are registered for use in California by the USEPA Office of Pesticide Programs (OPP) in partnership with California EPA Department of Pesticide Regulation. The Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) requires that pesticides registered by EPA do not pose

¹Critical to this approach is the use of sufficiently conservative procedures to minimize false negative outcomes i.e., for every statistical comparison, there is always a defined probability that a difference will not be designated as significant, when in fact it is (Type I error or false negative when there is a null hypothesis of some adverse effect).

"unreasonable adverse effects on the environment"². EPA periodically evaluates pesticide use practices to determine if they meet this requirement. The most recent Reregistration Eligibility Decision (RED) for malathion was published in 2006 (EPA 738-R-06-030). In this decision EPA compared edge-of-field surface water expected environmental concentrations (EECs) with aquatic life levels of concern (LOC). USEPA OPP aquatic toxicity reference values for malathion used in this analysis are shown in Table 1.

Using the risk quotient (RQ) method, EECs are divided by the malathion aquatic toxicity reference values (TRV). In determining LOCs, for acute exposures RQ=0.5; for chronic exposures RQ=1, and for endangered species protection RQ=0.05. If LOCs are expected to be exceeded then EPA may choose to cancel a registered use or require additional mitigation measures. Using the malathion TRVs for freshwater invertebrates and the associated RQs, the acute LOC is 0.5 ug/L and the chronic LOC is 0.06 ug/L. These levels are roughly 2X the proposed acute and chronic numeric targets for malathion, suggesting that additional mitigation measures may be required to reduce surface water loading associated with labeled malathion use practices.

In 2008 the National Marine Fisheries Service issued a biological opinion³, under the authority of section 7(a)(2) of the Endangered Species Act (ESA), on the effects of the USEPA registered pesticide products containing the active ingredients chlorpyrifos, diazinon, and malathion on endangered and threatened salmonid species, and critical habitat that has been designated for those species. In that opinion, risks to salmonid evolutionary significant units (ESUs), including steelhead whose critical habitat includes the South-Central California Coast, associated with exposure to malathion were evaluated. Effect concentrations were determined for salmon swimming behavior, fish reproduction and growth, salmon survival, and prey survival. Effect concentrations were lowest for prey survival, ~0.2 ug/L. The proposed malathion acute criterion of 0.17 ug/L is consistent with this finding.

Staff comment: Staff concurs with the reviewer.

Conspicuously absent from this analysis is consideration of any malathion breakdown products that threaten beneficial uses. It is widely known that the organophosphate insecticides, including malathion, are transformed in the environment to the more toxic oxon degradate. In addition, research suggests that organophosphate oxon degradates are more stable in the atmosphere than the parent compound. Studies investigating the airborne transport of organophosphate pesticides from the central valley of California to the Sierra Nevada Mountains often found levels of the oxon degradate at higher levels than the parent compound.^{4,5} Dry and wet deposition can result in the occurrence of both the parent organophosphates and oxon degradates in surface waters⁶.

Consequently, for water bodies currently listed as impaired for water column toxicity and malathion detections, additional monitoring should include malathion oxon.

Staff comment: Malathion oxon appears to be significantly more toxic than the malathion. The TMDL report will include a requirement for monitoring malathion oxon (Maloxon) in surface waters impaired for water column toxicity and with malathion detections.

² FIFRA section 2(bb) defines "unreasonable adverse effects on the environment" to mean, in part, "any unreasonable risk to man or the environment, taking into account the economic, social, and environmental costs and benefits of the use of any pesticide...."(<u>http://www.epa.gov/pesticides/health/risk-benefit.htm</u>)

³ http://www.nmfs.noaa.gov/pr/pdfs/pesticide_biop.pdf

 ⁴ Zabik, J. M., and J. N. Seiber. 1993. Atmospheric transport of organophosphate pesticides from California's Central Valley to the Sierra Nevada mountains. Journal of Environmental Quality 22:80-90.
⁵Aston, L. S. and J. N. Seiber. 1997. The fate of airborne organophosphate pesticides transported to the Sierra Nevada mountains in summer. Journal of Environmental Quality 26:1483-1492.

⁶ McConnell, L. L., J. S. LeNoir, S. Datta, and J. N. Seiber. 1998. Wet deposition of current-use pesticides in theSierra Nevada mountain range, California, USA. Environmental Toxicology and Chemistry 17:1908-1916.

Review of the scientific basis for the assignment of numeric targets for the synthetic pyrethroids: bifenthrin, cyfluthrin, λ -cyhalothrin, cypermethrin, esfenvalerate, and Permithrin

The scientific basis for the assignment of water chemistry numeric targets for synthetic pyrethroids bifenthrin, λ -cyhalothrin, and cyfluthrin are contained in the water quality criteria Reports, prepared for the Central Valley Regional Water Quality Control Board, which derive acute and chronic water quality criteria using the UC-Davis methodology.

Bifenthrin

The acute criterion for bifenthrin was derived using the SSD method as at least five acceptable acute toxicity values were available and fulfilled the five taxa requirements of

the SSD method. The resulting acute criterion, based on the median 5th percentile value, is 0.004 ug/L. This value is considered acceptable for its intended purpose.

Details of the application of the SSD method are as follows:

"The log-logistic SSD procedure (section 3-3.2.2, TenBrook et al. 2009a) was used for the acute criterion calculation because there were not more than eight acceptable acute toxicity values available in the bifenthrin data set (Table 2). The log-logistic SSD procedure was used to derive 5th percentile values (median and lower 95% confidence limit), as well as 1st percentile values (median and lower 95% confidence limit). The median 5th percentile value is recommended for use in criteria derivation by the methodology because it is the most robust of the distributional estimates (section 3-3.TenBrook et al. 2009a). Comparing the median estimate to the lower 95% confidence limit of the 5th percentile values, it can be seen that the first significant figures of the two values are different (0.00803 vs. 0.000391 μ g/L). Because there is uncertainty in the first significant digit, the final criterion will be reported with one significant digit (section 3-3.2.6, TenBrook et al. 2009a).

The ETX 1.3 Software program (Aldenberg 1993) was used to fit the log-logistic distribution to the data set, which is plotted with the acute values in Figure 2. This distribution provided a satisfactory fit (see Appendix A) according to the fit test described in section 3-3.2.4 of TenBrook et al. (2009a). No significant lack of fit was found (χ 22n = 0.2417) using the fit test based on cross validation and Fisher's combined test (section 3-3.2.4, TenBrook et al. 2009a), indicating that the data set is valid for criteria derivation."

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

As chronic toxicity values from fewer than five different families were available the ACR procedure was used to calculate the bifenthrin chronic criterion. Because an ACR could not be calculated with the available data, the chronic criterion was calculated with the default ACR value of 12.4 = 0.0006 ug/L. <u>Use of the default ACR value is considered</u> conservative and appropriately protective of aquatic life.

Staff comment: None

λ-cyhalothrin

For λ -cyhalothrin The Burr Type III SSD procedure was used for the acute criterion calculation because more than eight acceptable acute toxicity values were available in the λ -cyhalothrin data set. This procedure, roughly equivalent to the CWA National Standard methodology, the acute criteria=0.001 ug/L is based on the median 5th percentile acute value. This value is considered acceptable for its intended purpose.

As chronic data for only 3 of the 5 representative taxa (including a saltwater species) were available for λ -cyhalothrin, the ACR method was used to calculate the chronic criterion by pairing chronic toxicity values (MATC) with an appropriate corresponding acute toxicity value (LC50) in order to calculate an ACR; resulting in the ACR-derived chronic criterion = 0.0005 ug/L. This value is considered conservative and appropriately protective of aquatic life.

Staff comment: Comment noted.

Cyfluthrin

The acute criteria for cyfluthrin was derived using the SSD method as at least five acceptable acute toxicity values were available and fulfilled the five taxa requirements of the SSD. The resulting acute criterion= 0.002 ug/L, based on the median 5th percentile acute value. However, further "sensitivity analysis" determined that this acute criterion is not protective of the sensitive species H. azteca. This determination was based on comparing the result of the SSD analysis – the median 5th percentile acute value – to the lowest acute value for H. azteca. Consequently the median 1st percentile estimate was used to derive the acute and chronic criteria. Use of this less reliable acute value estimate is inconsistent with the derivation of other acute and chronic criteria for which there is sufficient data to use the SSD approach. Given the premise for use of the SSD approach in the UC-Davis Methodology – a robust statistical analysis using all of the available toxicity values that meet data quality criteria - it seems arbitrary to use the median 1st percentile estimate for the sole purpose of deriving a toxicity value that is less than the H. azteca lowest acute value, a single value of unknown significance. If a goal of the SSD approach is to reduce the probability of both Type I and Type II error in estimating the acute value, use of the median 5th percentile acute value is consistent with other assessments and appropriate for its intended purpose, regardless of whether the result is greater than an independent acute value of unknown significance.

Alternatively, if H. azteca is significantly more sensitive than taxa required for use of the SSD approach in the UC-Davis methodology, and is ultimately the driver in determining criteria, then it should be included as a required species for SSD analysis. Otherwise, the statistical power that is derived from the SSD approach may not be appropriate for determination of water quality criteria for some contaminants.

Staff Comment: Staff contacted one of the authors of the UC Davis report, Tessa Fojut PhD., for a response to the reviewers comments (personal communication with Tessa Fojut PhD. via email dated December 11, 2012). Dr. Fojut's response is as follows in italics:

Hyalella azteca <u>was</u> included in initial criteria calculation in the species sensitivity distribution, and satisfied the required taxon of benthic crustacean. Although Hyalella azteca is not always the most sensitive species for all pesticides, they are known to be relatively sensitive to pyrethroids.

The median 5th percentile is initially recommended for all criteria calculations because it is usually a good estimate of a "no-effect concentration" for the entire ecosystem. When data are relatively sparse, such as for cyfluthrin, there is a higher likelihood that the median 5th percentile may not be a good estimate of the "no effect concentration" because there is less of a chance that the true species sensitivity distribution is represented. When there are relatively few (5-8) data, a log-logistic distribution is fit to the data because there are less degrees of freedom and a lower chance of over-fitting the data set. As an additional way to check that the 5th percentile is a good estimate of a no-effect concentration, it is compared to the toxicity data for the most sensitive species. In the case of cyfluthrin, the lowest toxicity value was approximately equal to the 5th percentile, indicating that the 5th percentile was not a good estimate of a "no effect concentration," because the toxicity values are LC50s, which means that this concentration was lethal to 50% of the exposed population.

We know that Hyalella azteca are relatively sensitive to pyrethroids and they are endemic in California, so adjusting the criteria to be protective of this species is reasonable. All laboratory test species are intended to be indicators of what might be happening out in the environment. There are many more species in the ecosystem that we are not able to test in the laboratory, and it is not known if some of those could be equally or more sensitive than Hyalella azteca or other indicator test species.

Staff response: Based on the author's response, the numeric criteria UC Davis developed for cyfluthrin is a sufficiently protective TMDL target.

The scientific basis for the assignment of sediment chemistry numeric targets for the synthetic pyrethroids

The scientific basis for the assignment of sediment chemistry numeric targets for the synthetic pyrethroids bifenthrin, cyfluthrin, λ -cyhalothrin, esfenvalerate, and permithrin is contained in the publication by Amweg and Weston (2005)⁷. The scientific basis for the assignment of sediment

⁷ Amweg EL, Weston DP, Ureda NM. 2005. Use and toxicity of pyrethroid pesticides in the Central Valley, California, USA. Environ Toxicol Chem 24:966–972; Correction: 24:1300–1301.

chemistry numeric target for cypermethrin is contained in the publication by Maund et al. (2002)⁸. The scientific basis for the assignment of sediment chemistry numeric targets for the organophosphate chlorpyrifos is contained in the publication Amweg and Weston (2007)⁹.

Relying on a single study to derive CWA criteria is not the preferred approach. In addition to the paucity of data that may be derived from a single studies, of concern is that research studies whose specific aim(s) are not designed to meet regulatory needs, may not be adequate to provide the scientific basis for the assignment of numeric targets. Sufficient data to allow the use of a "weight of the evidence" approach, such as described in the UC-Davis Water Quality Reports prepared for the Central Valley Regional Water Quality Control Board, is generally preferred by risk assessors and best serves stakeholders. In addition, a common general criticism is often studies are not conducted according to Good Laboratory Practice (GLP), part of the testing guidelines developed by regulators around the world, outlining basic standards for equipment calibration and the storage of raw data. In general, when called on by state and federal regulators to test the safety of a substance, the chemical industry has relied on private labs to carry out studies using GLP; academic researchers rarely conduct such studies. Consequently, while the studies listed above employ the appropriate EPA methods for sediment toxicity¹⁰, I suspect that the research conducted by Maund et al., (2002) was conducted under GLPs, but not the research of Amweg and Weston (2005, 2007). However, in their deliberations about protecting water quality, state and federal agencies are expected to examine all the evidence, GLP or not.

Considering the concerns described above, in critiquing these studies for suitability as scientific basis for the assignment of sediment chemistry numeric targets, I provide the following:

While expressing the numeric target as a value normalized for the organic carbon (ug/g)o. c.) is useful in addressing bioavailability, this approach introduces the potential for significant variability depending on how the organic carbon (OC), as a surrogate for organic matter, is considered. For example, in Maund et al., (2002) they state that "Predictions of aqueous concentrations at the LC50 in sediments (based on Koc) compared well to each other and to effect concentrations from studies in water alone, suggesting that equilibrium partitioning theory could be used reasonably to predict and normalize the toxicity of cypermethrin across sediments of differing OC content." However they go on to state that "Theoretically, Koc should be a constant for a particular chemical, that is, an increase in OC content should lead to a direct increase in adsorption. However, adsorption probably also is affected by the physical nature of the OC present in the sediment and the surface area available for adsorption (the latter being a function of particle size distribution within the soils). Organic carbon that is present in small, often cominuted particles or coating the surface of mineral particles is likely to present a greater potential for adsorption than larger intact particles of OC, because of increased surface area." However, the methods of analyzing for OC content generally do not take surface area into account, because OC is digested from the sediment in its entirety.

⁸ Maund, S.J., Hamer, M.J., Lane, M.C.G., Farrelly, E., Rapley, J.H., Goggin, U.M., Gentle, W.E., 2002. Partitioning, bioavailability, and toxicity of the pyrethroid insecticide cypermethrin in sediments. Environ Toxicol Chem 21, 9-15.

⁹ Amweg, E.L., Weston, D.P., 2007. Whole-sediment toxicity identification evaluation tools for pyrethroid insecticides: I. Piperonyl butoxide addition. Environmental Toxicology and Chemistry 26, 2389-2396.
¹⁰ U.S. Environmental Protection Agency. 2000. Methods for measuring the toxicity and bioaccumulation of sediment-associated contaminants with freshwater invertebrates, 2nd ed. EPA/600/R-99/064. Washington, DC.

The sorption of a particular pesticide to a soil is measured in a laboratory by mixing water, pesticide, and soil. After equilibrium has been reached, the amount of pesticide remaining in solution is measured. The concentration of pesticide sorbed to the soil in the mixture is divided by the pesticide concentration still in solution. This yields the distribution coefficient, Kd. A low distribution coefficient indicates that more of the pesticide is in solution; a higher value indicates that the pesticide is more strongly sorbed to soil. The Kd is soil and pesticide specific; for a given pesticide the Kd is largely dependent on the soil's clay content and the type of clay – which determines surface area, as well as the organic matter attached to the clay surface. The sorption coefficient (Koc) is used to compare the relative sorption of pesticides. Koc is the distribution coefficient Kd divided by the amount of organic carbon in the soil (soils are tested for organic carbon – soil organic carbon is directly proportional to soil organic matter, which is primarily responsible for a soil's sorption properties.) While use of Koc allows a reasonable comparison of pesticides for their sorption to soil and sediment, the variation in Koc values is still great depending on the soils used in determining the Kd. For example, in Maund et al., (2002) for the 8 replicates tested the cypermethrin mean Koc values were 238,000 (standard deviation [SD] = 38,000; coefficient of variation [CV] = 16%), 502,000 (SD = 27,000; CV = 5%), and 177,000 (SD = 40,000; CV = 23%) for the 1, 3, and 13% OC sediments, respectively. These data suggests significant variation in pore water concentrations for a given contaminant sediment loading, even when normalized for OC. Consequently, more studies are needed to adequately characterize the relationship between the total sediment loading and the bioavailable fraction to sediment-dwelling aquatic life as estimated by the sediment OC content and the Koc. For example, in the analytical methods section of Amweg and Reston (2005) there is the following statement to explain low recoveries "Though the recoveries among sediments were relatively similar for any given compound, Pacheco Creek sediment consistently had the lowest value of the three sediments. This sediment was atypical in that it contained a large proportion of cow manure from surrounding rangeland, raising the possibility that matrix effects may have reduced extraction efficiency." Use of an "atypical sediment" (1 of 3) to derive a sediment chemistry numeric target may not be appropriate.

Staff response: The sediment numeric targets were described as interim targets in the draft report provided to the reviewers. Since the review, the targets have been changed to invertebrate survival and the numeric targets were changed to numeric guidelines.

2) Source Analysis

Section 4 of the Santa Maria Watershed TMDL Final Project Report describes pesticide source analysis. Source analysis is based, in part, on findings of the study conducted by UC Davis that confirmed the association of unknown toxicity to currently applied pesticides (Phillips, 2010). The procedures used to indentify pesticides most likely contributing to water and sediment toxicity are considered current, highly relevant, and comprehensive. Those current use pesticides (OPs and synthetic pyrethroids) for which numeric targets are proposed are listed above. The California pesticide use reporting system is unique, and with the exception of urban use, has provided valuable information on pesticide use in the Santa Maria Watershed. Consultation with local UC Extension has allowed comparison of pesticide use data with cropping practices and pest pressure to construct likely pesticide use patterns in space and time. In the absence of urban pesticide use reporting, procedures described to estimate pesticide use patterns in urban areas are considered thorough and comprehensive, within the limits of the available data and its quality. In addition, the discussion of source analysis of OC pesticide pollution provides a comprehensive outline of the history of OC use. both in agriculture and for mosquito control. However, a discussion of the development of pest resistance to the OCs which resulted in label changes allowing significant increase in application rates and frequency might also be of interest.

Staff responses: Comment noted.

SCIENTIFIC PEER REVIEW COMMENTS OF

Jonathan D. Maul, Ph.D.

Professor Texas Tech University Department of Environmental Toxicology

Prepared for Central Coast Regional Water Quality Control Board

Comments Received by Water Board Staff October 22, 2012 Staff responses are inserted in **bold**, **blue italic text**.

Numeric Targets

 It would be very helpful to report information or data on the quantities of suspended solids in the various reaches of the system. Background information could be presented in the Watershed Description under the Problem Identification.

Suspended sediments and organic matter, as well as dissolved organic matter and organic carbon, would be among the most important water quality parameters in these systems that would influence bioavailability of the more hydrophobic pesticides included within the TMDL, particularly organochlorines and pyrethroids, and to some extent chlorpyrifos.

Staff response: Staff agrees that data on suspended solids and dissolved organic matter in the impaired reaches would be of value and we recommend it as an additional study or parameter to monitor for the watershed.

2) For the water column numeric targets for pyrethroids and organochlorines it should be described how the sampling will occur to compare to the numeric target. Perhaps this is discussed in the monitoring section and I missed it (See comment in Monitoring Section). The point is if the water sample is filtered so that suspended particles are removed, this may not be consistent with the conditions under which the toxicity data was generated that are used for the numeric target. Suspended particles can have a significant effect on bioavailability. In terms of chemical analysis, filtering suspended particles can reduce the amount of chemical detected in samples. Alternatively, extracting water samples that are unfiltered could result in a measured aqueous concentration that is actually above the concentration that is readily bioavailable and will contribute to toxicity.

Staff responses: Staff clarified in the implementation and monitoring sections of the TMDL Report to monitor freely dissolved concentrations of pyrethroids in surface waters, which is consistent with the targets.

3) Pyrethroid sorption to suspended OM: Is this fraction accounted for in the numeric water column targets? For members of this chemical class bioavailability could be strikingly different with suspended OM present versus a system in which most of the chemical is in the form of the freely dissolved fraction?

Staff response: The researchers that developed the pyrethroid water criteria recommend the freely dissolved concentration of pyrethroids for criteria since research indicates that the dissolved fraction more accurately indicates toxicity of the pesticide. I clarified in the report that the criteria is for freely dissolved fraction and not concentrations bound to suspended solids and dissolved organic material.

4) Table 3-9: It would be useful to identify the species (i.e., Hyalella azteca) in the endpoint column following the text "average 10-d median lethal concentration (LC50)". This is identified as a footnote for Table 3-4, but it is somewhat obscure by only being mentioned there.

Staff response: The table was revised and the species identified in the endpoint.

5) Synthetic Pyrethroid Sediment Numeric Targets:

- a. It is stated that a specific methodology is described in the implementation section related to identifying a more protective target than the H. azteca 10-d sediment LC50s reported by Amweg et al. (2005) and Maund et al. (2002). I have had difficulty locating this methodology within the implementation section. Is it planned to be included in later drafts of this document? This needs to be explicitly described and would be better placed in the Numeric Targets section of the document. There could potentially be a significant difference between the interim LC50 targets and a more protective target, such as one using an ECXX for invertebrate growth or development.
- b. It should be described in this section the rationale on why H. azteca 10-d sediment LC50s were selected as pyrethroid sediment numeric targets. Are H. azteca the most sensitive species to pyrethroids that has been examined? Similar to that mentioned above, I think a sediment concentration resulting in sublethal concentrations might be more appropriate for protecting aquatic resources.
- c. It should be noted at what temperature the pyrethroid toxicity data used for the numeric targets was conducted. Pyrethroid toxicity is temperature-dependent and there could be a discrepancy in the temperature under which the toxicity data was generated and the average daily temperature for various waterbodies addressed in the TMDL.

Staff response: Based on the comments from the previous reviewer, the synthetic pyrethroids numeric targets were changed to targets based on sediment toxicity to invertebrates.

6) Numeric target for OCs are based on human health risk (i.e., carcinogenicity and are several orders of magnitude below aqueous concentration (at least for DDT and DDT and Toxaphene) that result in sublethal ecological effects on benthic invertebrates and fish. Alternatively, OPs and pyrethroid numeric targets are based on ecological effects of aquatic receptor species. It seems there should be an explanation for why some pesticides within the TMDL human-health based benchmarks are used while for other pesticide benchmarks aquatic receptor species responses are used. This could be as simple as indicating that the human health data just have not been generated yet. However, without some explanation it appears the drivers for numerical targets are very different among pesticides: some driven by human health concern versus others driven by damage to ecosystem services.

Staff responses: The primary concern with the OC impairments in the watershed is for human health. The UC Davis study (Phillips,) determined that the primary source of impairments to benthic invertebrates was currently applied pesticide and they ruled out legacy OC pesticides as a source of toxicity. The OC impairment listings are primarily based on concentrations in fish tissues at levels of human health risks from consumption of the fish. This is why human health risk sediment targets were selected for the TMDL. OPs and pyrethroids impairments are associated with toxicity to invertebrates, which is why the targets protective of impairments to aquatic health were selected for the TMDL. This information is incorporated in the project report.

Source Analysis

1) Within the Problem Identification, under section 2.4. Pollutants Addressed: This reviewer believes that it would be helpful to provide, as an appendix, the initial list of analytes that were tested for in surface water to develop the list of pesticides of concern (i.e., that may impair beneficial uses) in the TMDL. Was the list of pollutants derived from pesticide use survey data? Were any carbamates, such as carbaryl, tested for? It seems that carbaryl may have been used as late as 2010 on some California agricultural crops, but was not included. This question arises because pyrethroids and malathion were not evaluated for the 2008-2010 303(d) list, yet they were included here within the TMDL.

Staff response: For the UC Davis TMDL monitoring in the watershed, the pesticides analyzed in water and sediment were organophosphate and pyrethroids and organochlorine pesticides in sediment. The project waterbodies were subsequently listed as impaired. Consequently, staff gathered data and information regarding these impairments; this is the scope of the project.

2) Also under Pollutants addressed and their sources: it seems possible that fungicide use may occur within the Santa Maria watershed. I am not familiar with the definition of pesticide that is used for the TMDL and the coverage of chemicals intended within that definition; however, fungicides could very well be considered "pesticides". Furthermore, their intended targets and mechanism of action as a fungicide could impair some of the assigned specific beneficial uses. In addition, unintended targets via different mechanisms of toxic action may occur for invertebrate or vertebrate taxa within the watershed. These compounds could potentially be classified under the General Objective for Toxicity described on page 20 of the TMDL document, based on the examples outlined (e.g., "detrimental physiological responses"). Fungicides are commonly applied to crops grown in the Santa Maria watershed. Existing ambient monitoring programs do not specifically monitor for fungicides in surface waters but regular monitoring of toxicity to invertebrates, vertebrates and plants is a surrogate to determine if unknown toxicants are in surface waters.

TMDLs and Allocations

 Any potential anthropogenic activities that may likely influence future flow duration curves should be investigated. Some activities that come to mind include: planned dredging, erosion control measures, changes in irrigation runoff patterns, bridge alterations, weir implementation, dykes, etc.). If these planned activities may or will occur in any of the water bodies within the Santa Maria Watershed, there should be a mechanism in place to recalculate flow duration and load duration curves described in appendix B as the supplement to the concentration-based TMDL.

Staff response: I agree that anthropogenic activities could influence flow duration curves and this is why, the targets and TMDLs are based on concentrations of pesticides in the water or sediment. The flow duration curves are intended to improve our understanding of loading and hydrology of the watershed and have limited importance on the establishment of targets for the watershed, which are the primary goals of the TMDL.

2) 5.7. Seasonal Variation: There could be a problem with the rationale that "since the TMDL is expressed in terms of concentration, seasonal variation is not appropriate". Many of the compounds (i.e., pesticides) listed in the TMDL have been shown to have temperature-dependent toxicity. Pyrethroid toxicity is generally inversely related to temperature, while OP toxicity is generally positively related to temperature. Many of the pesticides listed in the TMDL document (or representatives from the same chemicals classes) have been shown to exhibit temperature-dependent toxicity. If numeric targets are set based on toxicity data that was generated at a continuous 24 °C (i.e., a common standardized temperature for toxicity testing), these numeric targets may not be appropriate for the extremes of seasonal variation. Furthermore, the targets may only be appropriate for a short period of the 24-h daily temperature cycle in some ecosystems. This reviewer recommends that this source of variation on pyrethroid and OP toxicity be mentioned and potentially discussed within the TMDL document. This would also have implications for monitoring (see below) and how the toxicity data used for numeric targets can be highly dependent on water quality conditions (e.g., suspended sediments, dissolved sediments, and temperature). These modifying factors are somewhat accounted for in the sediment numeric targets by using a concentration based on organic carbon mass. This reviewer wonders why this source of variation on bioavailaibity is not accounted for in the aqueous numeric targets.

Staff response: Staff concurs with the reviewer that pesticide and pyrethroids toxicity in particular is temperature dependent. The pyrethroids targets are based on criteria developed by UC Davis (Fojuet et al., 2012). In their criteria report they acknowledge temperature variations and toxicity noting that "Temperature has been reported to be inversely proportional to the aquatic toxicity and bioavailability of pyrethroids." Their criteria are based on aquatic exposure data from other studies and they determined at the time of criteria development, it was infeasible to quantify the relationship between the pyrethroids toxicity and temperature into the criteria due to insufficient data.

Implementation and Monitoring

 Will aqueous samples that are collected as part of monitoring component be filtered? If the water sample is filtered and suspended particles are removed, the conditions may not be consistent with the conditions that the numeric targets were generated under (i.e., the toxicity data). As mentioned above, suspended particles can have a significant effect on bioavailability.

Staff response: The researchers that developed the pyrethroid water criteria recommend the freely dissolved concentration of pyrethroids for criteria since research indicates that the dissolved fraction more accurately indicates toxicity of the pesticide. I clarified in the report that the criteria is for freely dissolved fraction and not concentrations bound to suspended solids and dissolved organic material.

2) Aquatic Habitat Descriptions: Several of the water bodies listed in the section are designated as both a Cold water system and Warm water system. I have similar comments to those mentioned above about the effect of temperature on pesticide risk to aquatic life. It is apparent on pg. 97 that some of the water bodies are designated both cold water and warm water. I assume this represents lower order streams (perhaps in higher elevations) being cold water and flowing into higher order reaches that are designated warm water. If the same numeric targets hold for areas designated either cold or warm, then an argument could be made that a large source of variation exists within the TMDL for protection of those designations. For example, considering bioavailability being equal, pyrethroids would be more toxic to benthic organisms (i.e., the metric that the numeric target is based on) in Cold water systems than Warm water systems.

Staff response: Accounting for the potential variability in toxicity as a function of temperature is discussed in the comment above. With respect to the COLD and WARM water beneficial uses, the Basin Plan does not explicitly define these beneficial uses in terms of temperature. However, staff generally interprets cold fresh water habitat as habitat that should be suitable to support anadromous fish; optimal temperature requirements for anadromous fish are widely understood and accepted. Therefore, if the numeric targets for pesticides in which the toxicity is temperature dependent are revised in the future, the temperature needed to support cold and warm water habitats will be considered.

SCIENTIFIC PEER REVIEW COMMENTS OF

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Prepared for Central Coast Regional Water Quality Control Board

Comments Received by Water Board Staff October 22, 2012 Staff responses are inserted in **bold, blue italic text**.

The specific pollutants to be addressed in the proposed TMDLs are pesticides thought to be associated with water quality impairments based on their presence in water bodies, their presence in associated biota, and various laboratory-based studies assessing toxicities to different target organisms. TMDLs are proposed for water and sediment for currently applied organophosphate (OP) pesticides and synthetic pyrethroids, and water, sediment, and fish for legacy organochlorine pesticides. The report does a thorough job of detailing use and activities that may serve as a source for these pesticides in the Santa Maria Watershed. **Overall, the proposed TMDLs seem reasonable and achievable towards protecting ecosystem and human health, and educating the various stakeholders involved.** Below are a few comments for consideration towards improving the proposed plan.

Comment on OP pesticide evaluation.

For the OP pesticide chlorpyrifos, there is a known major metabolite (3,5,6-trichloro-2-pyridinol, TCP) with toxicity potential that was not mentioned in this report. TCP is ionizable, thus its fate is pH-dependent (Racke, 1993). Although TCP is proposed to be less toxic based on an

extensive review of published ecotoxicological chlorpyrifos data (Barron and Woodburn, 1995), it has 1 to over 2 orders of magnitude greater propensity to exist in the water, thus potentially available at higher concentrations to impact aquatic biota. TCP toxicity to soil bacteria in Microtox system was shown to be higher than that of chlorpyrifos, thus some targets may be equally or more sensitive to TCP. TCP mode of toxicity appears to be distinctly different than chlorpyrifos, acute toxicity tests do show TCP to be slightly to moderately toxic to invertebrates, fish, birds, and mammals (Barron and Woodburn 1995; USEPA 2000). So TCP may or may not be a problem in the Santa Maria Watershed, but given the amount of chlorpyrifos being used in the watershed and what is being detected, it seems reasonable to monitor for TCP to determine if it is a source of impairment, especially in cases where an unidentified source of toxicity was designated and where chlorpyrifos is known to be used (refer to p. 40 of the report).

Barron M.G., and Woodburn K.B. (1995) Ecotoxicology of chlorpyrifos. Reviews of Environmental Contamination and Toxicology, 144, 1-93. Racke, K.D., 1993. 131:1-154. *In* George W. Ware (ed.) Reviews

Environmental Contamination Toxicology. Springer-Verlag New York Inc. USEPA (2000) Human health risk assessment--Chlorpyrifos. US Environmental Protection Agency.

Staff response: Staff concurs with the reviewer that it is important to consider the potential toxicity of pesticide metabolites to impair surface waters. In the case of the chlorpyrifos metabolite, TCP, it is unlikely that TCP would be a source of toxicity to freshwater invertebrates in the Santa Maria watershed because TCP is only slightly toxic and considerably less toxic to invertebrates than chlorpyrifos. Additionally the potential concentrations of TCP are likely to be low and below levels of concern. An aquatic toxicity test of TCP was required by EPA for the risk assessment of chlorpyrifos and TCP was acutely toxic at 10.4 ppm to waterflea (Daphnia magna, as a comparison the corresponding freshwater invertebrate toxicity finding for chlorpyrifos was 0.1 ppb for waterflea Daphnia magna). Of the water monitoring data assessed for the TMDL the highest chlorpyrifos sample was 1.874 ppb and detections were generally much lower concentrations. The EPA TCP toxicity test level is at least several orders magnitude greater than the highest detected levels of chlorpyrifos in the watershed, therefore TCP levels would not likely be at toxic levels.

The primary water toxicity problem in the Santa Maria watershed is water and sediment toxicity to freshwater invertebrates. Toxicity to other test organisms such as vertebrates was evaluated by the ambient water quality monitoring programs in the watershed and impairments were not found. Staff included language in the Project Report reflecting the risks to water quality from pesticide degradates.

Comment on sediment-borne pesticides.

The report several times notes the contribution of sediment (soil) running off of irrigated land being a likely source of pesticides especially legacy pesticides, but this applies to any run off scenario including poorly managed drip irrigation. What was not clear to me

in the proposed draft of TDMLs is what the current TMDL is for solids loading into the targeted water bodies and/or if this is going to be generically addressed since it is the heart of the problem for many of the highly sorbed pesticides being targeted including legacy DDT and its metabolites. A solution to minimize particle-bound pesticides (which included phosphorus as well) running off into the various water bodies would contribute generically to reducing loadings of both known and unknown compounds contributing to impaired waters.

Emphasis needs to be placed on erosion control management plans in general since I believe data shows that this is often the source of pesticides entering the water body for most of the pesticides delineated in the current proposed pesticide TMDLs. In addition, Storm water and irrigation run-off monitoring in all scenarios should also be emphasized.

Staff response: The loads are expressed in terms of concentrations of pesticide in the sediment. Staff agrees that the overall reduction in sediment loading would be lead to an improvement in water quality and would address additional water quality problems from pollutants such as phosphorus, which are sorbed to sediment like many pesticides. Staff has added language in the implementation plan describing the importance of sediment control.

Comment on aerial applications.

In terms of pesticides that are applied via spraying, it was not clear to me if the % contribution of this particular activity was assessed. The latter may not have been possible with the limited data collected, e.g., water monitoring before and after spray application activities. Is there clear documentation that the currently recommended buffer strips, when employed properly address minimizing this contribution? Is there a plant height requirement in the buffer zone and has this value been assessed. The relative need for the latter is a function of the % contribution to the load from spraying activities.

Staff response: The percent of pyrethroid loading from aerial applications was not assessed.

USEPA referenced and USDA/NRCS publication "Conservation Buffers to Reduce Pesticide Lossess" for information on buffer effectiveness (USDA/NRCS, 2000). Staff reviewed the publication and vegetative buffers have been found to reduce the movement of pesticides.

Comment on legacy organochloro-pesticides.

It is not clear if something can be or should be implemented to manage effectively or reduce existing sediment loads already present in streams and canals, or if the plan will just be to monitor, educate, and reduce additional loads.

Staff response: Staff recommends that stakeholders in the Santa Maria Watershed form a watershed planning group to address organochlorine pesticide water quality problems, which are associated with erosion and sedimentation. The purpose of the group would be to develop implementation plans, implement practices and monitor effectiveness and progress towards achieving TMDL goals. Whether something can be done to address the existing loads will be a question the planning group can address.

Comment on OC-normalized sediment loadings.

Overall it appeared from what I know and what was presented in the report that organic carbon (OC) normalized TMDLs are more protective than just sediment concentrations. Numeric targets (Table 3-9) for sediments towards achieving the water quality objectives are primarily listed on an OC-normalized basis as well as loading capacities (chapter 5 of the report) except for sediment concentration-based TMDLS for DDT and derivatives (Tables 5.3 & 5.4), which are not proposed on an OC-normalized basis unlike what is being proposed for the currently used pesticides. I may have missed the logic for this, but wanted to note the apparent inconsistency.

Staff response: Staff noted the inconsistency between the tables and clarified in the report that both the targets and the loads are OC-normalized.

Comment on sources:

In a few places in the report, the % use of a specific pesticide, e.g., chlorpyrifos, was high for strawberry production, but was considered a lower risk source than other sources because irrigation in strawberries is via drip irrigation. While the latter is designed to optimize water use by plants, thus minimizing run off, this is not always achieved. I have observed constant water running off these fields, specifically in the Santa Maria watershed where much of the area is sloped. This water may run off the surface or flow to a shallow impermeable layer an exit at a lower elevation. Ideally, all this should be minimized in drip irrigation, but reality is not always so. Commercial strawberry production allows land that has little value in terms of soil fertility to be used, because the growing media is provided to the plant through raised beds and then all the nutrients and water the plants needs are provided anthropogenically. However, this scenario when not operated under strict conditions also increases risk of this source for nutrients, sediment, and pesticides into the watershed.

Staff responses: In the chlorpyrifos source assessment section of the TMDL (under Section 4.1), the application of chlorpyrifos to strawberries was identified as a potential source of pollution. The reviewer is correct that in reality there could be irrigation runoff from strawberry fields that pose a threat to water quality. however, relative to other crop types and the application and irrigation practices used for them, e.g. cole crops, the relative risk is lower when used on strawberries.

BMP Tracking and Assessment

It didn't appear to be that this included directly land management, but just irrigation and pesticide management (p. 105). Land management may be inherent, but should be explicitly specified where appropriate. I assume standard irrigation and sediment BMPs for irrigated agriculture when applied correctly should reduce sediment movement from farms.

Staff comment: The reviewer is referring to erosion and sediment control when referring to "land management." Staff revised the report to also include the tracking and assessment of erosion and sediment control management practices.

Comment on Education

Stage 1 Education for Minimizing pesticides in Urban runoff (p. 107) is to develop reduce risk practice fact sheets for the general public that discusses pesticide use and water quality protection. It is not clear to me where these will be distributed or made available to optimize exposure of the information (e.g., stores selling to urban home owners at check out). This should be explicitly delineated.

Staff response: Comment noted. Water Board staff do not specify means of compliance, as part of the stormwater permitting process, to the level indicated by the reviewer. However, Water Board staff will coordinate with implementing parties responsible for stormwater allocations to maximize results of the education component of implementation. For example, staff can discuss observations and the results of data analysis gathered during TMDL development to better inform implementing parties how to maximize their implementation efforts.

General comment:

I am not trained as a toxicologist, I found the approach proposed to address compound mixtures when the mode of action is known to be similar is a reasonable first approach and is not overly burdensome. Having this in the proposed TMDLs is commendable and will set a model for future efforts in this area even with so much still unknown about mixtures.

Staff response: Comment noted.

References

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