

**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**

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Executive Summary

The goal of this project is to develop a methodology for derivation of pesticide water quality criteria for the protection of aquatic life in the Sacramento River and San Joaquin River basins. The project will be accomplished in three phases. Phase I (TenBrook & Tjeerdema 2006) was a comparison of existing methodologies. This is a report of the results of Phase II, in which a new methodology is developed. Phase III will be to apply the new methodology to derive criteria for up to five pesticides including diazinon and chlorpyrifos, two organophosphate insecticides of particular concern in the Sacramento River watershed due to listings under 303(d) of the federal Clean Water Act.

This report is organized into four chapters. The first is an introduction to this phase of the project with a discussion of the approach taken to develop the new methodology. The second chapter is an evaluation and selection of methods for inclusion in the new methodology. Twelve pesticide data sets, including a chlorpyrifos set collected according to procedures in the new methodology, were used to evaluate various techniques. Particular attention was given to the assessment of distributional assumptions used in species sensitivity distribution (SSD) methods, and to determination of appropriate duration and frequency components of criteria statements. Results of these evaluations, together with findings from the Phase I report, were used to select elements to include in the new methodology. For criteria derivation with small data sets, Chapter 2 includes derivation of assessment factors, based on existing pesticide data, as well as derivation of a default acute-to-chronic ratio (ACR) for use when chronic data are lacking.

Chapter 3 presents the new methodology in a step-by-step format. Major features include: guidance for collection, evaluation, and reduction of data; a SSD method to derive criteria when five or more data are available; an assessment factor (AF) method to derive acute criteria when fewer than five acute toxicity data are available; an ACR method 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; methods for quantifying relationships between toxicity and water quality parameters, such as pH and temperature; techniques for assessing whether derived criteria might harm particularly sensitive species, lead to bioaccumulation, harm ecosystems, harm threatened and endangered species, or lead to unacceptable levels of pesticides in other environmental compartments. Finally, a template is given for how to state final criteria in terms of magnitude, duration and frequency. The appendices include flow charts for data collection and criteria derivation processes, a blank data summary sheet, and tables of data sources, physical-chemical test methods, data rating schemes, critical values for assessing outliers, assessment factors, and examples of quantitative structure activity relationships.

In Chapter 4 the new methodology is used to derive acute and chronic criteria for chlorpyrifos. Although this was originally to part of Phase III of the project, it was included here to facilitate review of the proposed methodology. Using data sets collected, evaluated and reduced according to guidance in Chapter 3, the SSD method was used to derive an acute criterion and the ACR method was used to derive a chronic criterion. An ACR of 2.2 was calculated for chlorpyrifos. The appendices include tables of data rated acceptable for criteria derivation or for use as supporting information, as well as data summary sheets for all studies rated acceptable for criteria derivation. The final criteria statement follows:

Aquatic life in the Sacramento River and San Joaquin River basins should not be affected unacceptably if the four-day average concentration of chlorpyrifos does not exceed 10.5 ng/L more than once every three years on the average and if the one-hour average concentration does not exceed 11.5 ng/L more than once every three years on the average.

These values are lower than the USEPA chlorpyrifos acute and chronic freshwater criteria of 83 and 41 ng/L, respectively (USEPA 1986). They are also lower than current water quality objectives for the lower San Joaquin River (CVRWQCB 2005) and those proposed for the Sacramento and San Joaquin River Delta (CVRWQCB 2006). Acute and chronic objectives for both of these water bodies are 25 and 15 ng/L, respectively. Differences between established values and those derived by the new methodology are attributed to differences in the data sets used to derive them. The new criteria data sets include data points from studies conducted since the older criteria and objectives were derived, and exclude data points that were used in prior derivations, but did not pass the data evaluation scheme developed for the new methodology. It is important to note that four acute values in the new data set are below the USEPA criterion of 0.083 µg/L.

References

TenBrook PL, Tjeerdema RS. 2006. Methodology for Derivation of Pesticide Water Quality Criteria for the Protection of Aquatic Life in the Sacramento and San Joaquin River Basins. Phase I: Review of Existing Methodologies. Final Report Prepared for the Central Valley Regional Water Quality Control Board, Rancho Cordova, CA.

USEPA. 1986. Ambient water quality criteria for chlorpyrifos. EPA 440/5-86-005. US Environmental Protection Agency, Washington, DC.

Table of Contents

Title	i
Executive Summary	ii
Table of Contents	iv
List of Acronyms	viii
List of Tables	x
List of Figures	xii
Chapter 1. Introduction and Approach	
1-1.0 Introduction	1-1
1-2.0 Approach to methodology development	1-1
1-3.0 Notes about numeric criteria	1-4
1-4.0 Format of this report	1-4
1-5.0 References	1-4
Chapter 2. Evaluation and Selection of Methods	
2-1.0 Introduction	2-1
2-2.0 Data	2-1
2-2.1 Data collection	2-1
2-2.1.1 Kinds of data	2-1
2-2.1.1.1 Acute vs. chronic toxicity data	2-2
2-2.1.1.2 Hypothesis tests vs. regression analysis	2-3
2-2.1.1.3 Non-traditional endpoints	2-4
2-2.1.1.4 Multispecies (field/semi-field, laboratory) data	2-6
2-2.1.1.5 Data from multipathway exposures	2-6
2-2.1.1.6. Toxicity data that incorporate time	2-7
2-2.2 Filling data gaps with estimation techniques	2-7
2-2.2.1 Estimating acute and chronic toxicity	2-8
2-2.2.1.1 Quantitative Structure Activity Relationships (QSARs)	2-8
2-2.2.1.2 Interspecies correlations for estimation of toxicity	2-8
2-2.2.2 Estimating chronic from acute toxicity data	2-9
2-2.2.2.1 Time-concentration-effect (TCE) models	2-9
2-2.3 Data sources and literature searches	2-10
2-2.4 Data summaries of ecotoxicity data	2-10
2-2.5 Data evaluation	2-11
2-2.5.1 Physical-chemical data	2-11
2-2.5.2 Ecotoxicity data evaluation	2-12
2-2.6 Data quantity—ecotoxicity	2-14
2-2.7 Data reduction	2-17
2-3.0 Criteria Calculation	2-19
2-3.1 SSD methodology	2-20
2-3.1.1 Appropriate distribution	2-20
2-3.1.2 Percentile cutoff	2-37

2-3.1.3	Level of confidence	2-38
2-3.1.4	Aggregation of taxa and outliers	2-39
2-3.1.5	Comparison of methods	2-39
2-3.1.5.1	Assumptions common to all models	2-40
2-3.1.5.2	USEPA (1985, 2003a)	2-40
2-3.1.5.3	RIVM (2001; formerly MHSPE 1994)	2-41
2-3.1.5.4	ANZECC & ARMCANZ (2000)	2-42
2-3.1.5.5	Results and discussion of SSD model comparison	2-43
2-3.1.5.6	SSDs in the new methodology	2-45
2-3.2	AF methodology	2-45
2-3.2.1	Appropriate use of assessment factors	2-47
2-3.2.2	Toxicity values	2-49
2-3.2.3	Magnitude of factors	2-49
2-3.2.3.1	Acute factors	2-49
2-3.2.3.2	Acute-to-chronic ratios (ACRs)	2-52
2-3.2.3.2.1	Single-chemical, multispecies ACR based on measured data	2-52
2-3.2.3.2.2	Single-chemical, multispecies ACR based on measured and assumed values	2-53
2-3.2.3.2.3	Default ACRs	2-53
2-3.3	Averaging periods	2-54
2-3.3.1	Acute averaging period	2-55
2-3.4	Allowable frequency of exceedance	2-56
2-3.4.1	Review of the literature	2-57
2-3.4.2	Allowable frequency of exceedance-conclusion	2-60
2-3.5	Water quality effects	2-61
2-3.5.1	Bioavailability	2-61
2-3.5.2	Mixtures	2-65
2-3.5.2.1	Additivity	2-66
2-3.5.2.1.1	Concentration addition—for similar modes of action	2-66
2-3.5.2.1.2	Response addition—for independent modes of action	2-68
2-3.5.2.2	Non-additivity; synergism and antagonism	2-69
2-3.5.2.3	Combined models	2-70
2-3.5.2.4	Conclusions on mixtures	2-72
2-3.5.3	Other water quality effects	2-72
2-3.6	Other considerations after criteria have been derived	2-72
2-3.6.1	Sensitive species	2-73
2-3.6.2	Bioaccumulation/secondary poisoning	2-73
2-3.6.3	Ecosystem and other studies	2-75
2-3.6.4	Threatened and endangered species	2-75
2-3.6.5	Harmonization/coherence across media	2-76
2-4.0	Guideline format	2-78
2-5.0	Conclusion	2-78

2-6.0 References	2-79
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Chapter 3. Methodology

3-1.0 Introduction	3-1
3-2.0 Data	3-1
3-2.1 Collect data	3-1
3-2.1.1 Definitions of acute and chronic toxicity data	3-1
3-2.1.2 Toxicity values	3-2
3-2.1.3 Endpoints	3-2
3-2.1.4 Multispecies (field/semi-field) data	3-3
3-2.2 Fill chronic toxicity data gaps with estimation techniques	3-3
3-2.3 Evaluate data	3-4
3-2.3.1 Physical-chemical data	3-4
3-2.3.2 Ecotoxicity data	3-4
3-2.4 Reduce data	3-5
3-3.0 Derive acute criterion	3-8
3-3.1 Species sensitivity distribution (SSD) method	3-8
3-3.1.1 Data requirements	3-8
3-3.1.2 Procedure	3-9
3-3.1.2.1 Median estimate	3-9
3-3.1.2.2 Calculation of confidence limits	3-10
3-3.1.2.3 Procedure in cases of 8 or fewer values in the data set	3-10
3-3.2 Assessment factor (AF) method	3-12
3-4.0 Derive chronic criterion	3-12
3-4.1 SSD method	3-12
3-4.2 Chronic criterion using an acute-to-chronic ratio (ACR)	3-12
3-4.2.1 Single-chemical, multispecies ACR based on measured data	3-13
3-4.2.2 Single-chemical, multispecies ACR based on measured and/or assumed values	3-13
3-4.2.3 Default ACR	3-14
3-4.2.4 Calculation of the chronic criterion	3-14
3-5.0 Water quality effects	3-14
3-5.1 Bioavailability	3-14
3-5.2 Mixtures	3-15
3-5.2.1 Concentration addition—for pesticides with similar modes of action	3-16
3-5.2.1.1 Toxic unit approach	3-16
3-5.2.1.2 Relative potency factor (RPF) approach	3-16
3-5.2.2 Non-additivity: synergism and antagonism	3-17
3-5.3 Temperature, pH and other effects (USEPA 1985, 2003a)	3-18
3-5.3.1 Regress toxicity values vs. water quality values by species	3-18
3-5.3.2 Assess of relevance and reasonableness of data and regressions	3-18
3-5.3.3 Normalize toxicity and water quality values and	

re-do regression	3-19
3-5.3.4 Combine species to obtain a pooled slope	3-19
3-5.3.5 Calculate toxicity values at Z for each species	3-19
3-6.0 Other considerations after criteria have been derived	3-20
3-6.1 Sensitive species	3-21
3-6.2 Bioaccumulation/secondary poisoning	3-21
3-6.3 Ecosystem and other studies	3-23
3-6.4 Threatened and endangered species	3-23
3-6.5 Harmonization/coherence across media	3-24
3-7.0 Final criteria statements	3-25
3-8.0 References	3-26
Appendix A. Figures	3-A1
Appendix B. Tables	3-B1
Appendix C. Software documentation	3-C1

Chapter 4
Criteria derivation
Chlorpyrifos draft

4-1.0 Basic information	4-1
4-2.0 Physical-chemical data	4-1
4-3.0 Human and wildlife dietary values	4-3
4-4.0 Ecotoxicity data	4-3
4-5.0 Data reduction	4-5
4-6.0 Acute criteria calculation	4-5
4-7.0 Chronic criteria derivation	4-6
4-8.0 Bioavailability	4-7
4-9.0 Mixtures	4-7
4-10.0 Temperature, pH, other water quality effects	4-9
4-11.0 Sensitive species	4-9
4-12.0 Bioaccumulation	4-10
4-13.0 Ecosystem and other studies	4-11
4-14.0 Threatened and endangered species	4-12
4-15.0 Harmonization/coherence across media	4-13
4-16.0 Final criteria statement	4-14
4-17.0 References	4-15
Appendix 4A Tables	4-A1
Appendix 4B Data summary sheets for acute and chronic studies in final sets	4-B1

List of acronyms and abbreviations

ACE	Acute-to-Chronic Estimation
AChE	Acetylcholinesterase
ACR	Acute to Chronic Ratio
AF	Assessment Factor
ANZECC	Australia and New Zealand Environment and Conservation Council
APHA	American Public Health Association
ARMCANZ	Agriculture and Resource Management Council of Australia and New Zealand
ASTM	American Society for Testing and Materials
BAF	Bioaccumulation Factor
BCF	Bioconcentration Factor
BMF	Biomagnification Factor
BSAF	Biota Sediment Accumulation Factor
CAS	Chemical Abstract Service
CCME	Canadian Council of Ministers of the Environment
CDFG	California Department of Fish and Game
CEAM	Center for Exposure Assessment Modeling
CEMC	Canadian Environmental Modeling Center
CSIRO	Commonwealth Scientific and Industrial Research Organization, Australia
CVRWCB	Central Valley Regional Water Quality Control Board
CWA	Clean Water Act
DHM	Dissolved Humic Material
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter
DPR	Department of Pesticide Regulation
EC _x	Concentration that affects x% of exposed organisms
ECB	European Chemicals Bureau
EU	European Union
EXAMS	Exposure Analysis Modeling System
FACR	Final Acute to Chronic Ratio
FAV	Final Acute Value
FCV	Final Chronic Value
FDA	Food and Drug Administration
FIFRA	Federal Insecticide Fungicide and Rodenticide Act
GMAV	Genus Mean Acute Value
HC _x	Hazardous Concentration potentially harmful to x% of species
IC _x	Inhibition concentration; concentration causing x% inhibition
ICE	Interspecies Correlation Estimation
IUPAC	International Union of Pure and Applied Chemistry
K	Interaction Coefficient
K _H	Henry's law constant
K _{ow}	Octanol-Water partition coefficient

K_p or K_d	Solid-Water partition coefficient
LC_x	Concentration lethal to $x\%$ of exposed organisms
LD_x	Dose lethal to $x\%$ of exposed organisms
LFER	Linear Free Energy Relationship
LOEC	Lowest Observed Effect Concentration
LOEL	Lowest Observed Effect Level
MATC	Maximum Acceptable Toxicant Concentration
MHSPE	Ministry of Housing, Spatial Planning and the Environment
NOEC	No Observed Effect Concentration
OECD	Organization for Economic Co-operation and Development
QSAR	Quantitative Structure Activity Relationship
pK_a	Acid dissociation constant
RIVM	National Institute of Public Health and the Environment, Bilthoven, The Netherlands
RPF	Relative Potency Factor
SETAC	Society of Environmental Toxicology and Chemistry
SMACR	Species Mean Acute to Chronic Ratio
SMAV	Species Mean Acute Value
SSD	Species Sensitivity Distribution
TBT	Tributyltin
TCE	Time Concentration Effect
TE	Toxic Equivalent
TEF	Toxic Equivalency Factor
TES	Threatened and Endangered Species
TFM	3-trifluoromethyl-4-nitrophenol
TGD	Technical Guidance Document
TMDL	Total Maximum Daily Load
TSD	Technical Support Document for Water Quality-based Toxics Control
TTE	Time To Event
TU	Toxic Unit
US	United States
USEPA	United States Environmental Protection Agency

List of Tables

Table 1.1 Overview of major methodologies .	1-2
Table 1.2 Overview of similarities and differences between key elements of six major criteria derivation methodologies.	1-3
Table 2.1 Acute toxicity data sets.	2-21
Table 2.2 Burr III family distribution fit parameters for data sets in Table 2.1	2-35
Table 2.3 Comparison of log-triangular, log-normal and Burr III distributions for data sets in Table 2.1	2-36
Table 2.4 Results of analyzing pesticide data sets (Table 2.1) with SSD Methods of USEPA (1985), the Netherlands (RIVM 2001), Australia/New Zealand (ANZECC & ARMCANZ 2000).	2-44
Table 2.5 Assessment factors used in existing methodologies.	2-46
Table 2.6 Compilation of 95 th percentile of factors for subsets of 1-5 samples; the median values in the last row are the summary factors for each sample size.	2-51
Table 2.7 Median 5 th percentile toxicity value estimates for sample sizes of 1-5 acute toxicity values using summary pesticide assessment factors.	2-51
Table 2.8 Calculation of default acute-to-chronic ratio (ACR).	2-54
Table 2.9 Default BMF values (BMF 2003) .	2-74
Table 3.1 Data sources.	3-B2
Table 3.2 Web addresses for various electronic resources.	3-B3
Table 3.3 Kinds of data that should be collected for criteria derivation	3-B5
Table 3.4 Acceptable methods for determination of physical-chemical parameters other than the octanol-water partition coefficient	3-B6
Table 3.5 Acceptable experimental and computational techniques for determination of the octanol-water partition coefficient, K_{ow} , and the priority for their use (USEPA 2003a).	3-B7
Table 3.6 Rating of relevance/usability of data for derivation of criteria for the Sacramento and San Joaquin River watersheds	3-B7
Table 3.7 Documentation rating for aquatic laboratory data (adapted from ECOTOX 2006).	3-B8
Table 3.8 Acceptability rating for aquatic laboratory data (adapted from ECOTOX 2006)	3-B9
Table 3.9 Documentation and acceptability rating for aquatic outdoor field Data and indoor model ecosystems (adapted from ECOTOX 2006).	3-B11
Table 3.10 Documentation rating for terrestrial laboratory/field data (adapted from ECOTOX 2006).	3-B12
Table 3.11 Data categories based on reliability and relevance scores.	3-B13
Table 3.12 Critical ratios ($p = 0.05$; one-tailed) for outlier test of samples up $n = 25$	3-B13
Table 3.13 Critical ratios ($p = 0.05$; one-tailed) for testing outliers for sample Sizes of $n = 25-100$	3-B14
Table 3.14 Extrapolation constants, k , for median and lower 95% confidence limit estimates of the 5 th percentile value using a log-logistic distribution	3-B15

Table 3.15 Assessment factors to apply to lowest acute values in data sets of fewer than 5 values	3-B15
Table 3.16 Calculation of default acute-to-chronic ratio (ACR)	3-B16
Table 3.17 Default BMF values (ECB 2003)	3-B16
Table 3.18 QSARS for estimating toxicity from K_{ow} for chemicals acting by narcosis; from OECD (1995a) and RIVM (2001)	3-B17
Table 4.1 Final acute toxicity data set for chlorpyrifos.	4-A2
Table 4.2 Acceptable acute data excluded in data reduction process.	4-A6
Table 4.3 Final chronic toxicity data set for chlorpyrifos.	4-A10
Table 4.4 Calculation of the final acute-to-chronic ratio	4-A11
Table 4.5 Acceptable chronic data excluded in data reduction process.	4-A12
Table 4.6 Studies excluded from criteria derivation (rated RL, LR, or LL).	4-A14
Table 4.7 Acceptable multispecies field, semi-field, laboratory, mesocosm, microcosm studies.	4-A27
Table 4.8 <i>Neomysis mercedis</i> raw acute data from CDFG (1992a).	4-A28
Table 4.9 <i>Neomysis mercedis</i> raw acute data from CDFG (1992e).	4-A29
Table 4.10 Synergistic interactions between chlorpyrifos and other pesticides.	4-A30
Table 4.11 Predicted LC_{50} values for threatened or endangered species; ICE v.1.0.	4-A31
Table 4.12 Level I fugacity model inputs	4-A31
Table 4.13 Level I fugacity model outputs	4-A32

List of Figures

Figure 2.1 Tests for log-normal distribution of data sets	2-24
Figure 2.2 Comparison of fits of pesticide data to log-triangular, log-normal, and Burr Type III distributions	2-28
Figure 3.1 Data flow chart	3-A2
Figure 3.2 Criteria derivation flow chart	3-A3
Figure 3.3 Data summary sheet	3-A4
Figure 4.1 Structure of chlorpyrifos	4-1