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Aquatic Life Water Quality Criteria for Selected Pesticides

Ronald S. Tjeerdema
Editor

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Special Foreword

California's Central Valley has been a leader in agricultural productivity since it was first settled by European immigrants in the nineteenth century. Drained by both the Sacramento and San Joaquin River Systems, its fertile farmlands represent the most productive region in the USA today. Key to that productivity is the use of modern agrochemicals, including fertilizers and pest control agents. However, while enormously useful as tools, they also present their share of risks to both human health and the environment.

The Central Valley also contains a rich, endemic flora and fauna—both terrestrial and aquatic. Thus, the challenge for many years has been how to enhance agricultural productivity in the region while maintaining environmental quality, as agricultural residues pose a risk to not only the valley, but also the San Francisco Bay-Delta Region. In recent years, the California State Water Resources Control Board, through its Regional Water Quality Control Board (RWQCB; Central Valley Region), has sought to better characterize the risk to endemic aquatic organisms posed by agricultural pesticides used in the valley. Such characterization would assist in guiding the continued use of pesticides in an environmentally safe manner. However, methods for assessing the risk of pesticides to aquatic species have been slow to develop. Therefore, the RWQCB approached us a number of years ago with the request that we develop an advanced method for assessing such risk, and then apply it to develop criteria for the continued safe use of many of the most effective agents available today.

In response, we first surveyed the methods currently available worldwide—published in *Reviews of Environmental Contamination and Toxicology* (Volume 199). We subsequently developed an advanced method (the University of California—Davis Methodology)—also published in *Reviews* (Volume 209)—which significantly built upon the early progress of others. We then applied the methodology to develop risk criteria for representative agents from three pesticide classes: organophosphates, pyrethroids, and substituted ureas. Those papers are the subject of this volume—providing guidance on the safe use of pesticides, not only in California's Central Valley but potentially worldwide. It should be noted that the assessment of risk is not a one-time task but an ongoing process, as criteria

can be continually refined by the addition of new, and potentially high-quality, data to decrease uncertainty in the derived values over time. In fact, to our knowledge water quality criteria for the pyrethroids have not been previously derived in the USA. Thus, the wide-ranging review of each chemical presented in the subsequent papers represents a good foundation for future refinements.

Another useful aspect of the risk assessment process is that data gaps can be identified—which may stimulate new research to fill them. For instance, there is currently a lack of chronic toxicity data for all seven targeted pesticides (chlorpyrifos, diazinon, malathion, bifenthrin, cyfluthrin, cypermethrin, lambda-cyhalothrin, permethrin and diuron), and because of this the uncertainty of the derived chronic criteria could not be quantified. High-quality tests using flow-through exposure systems which generate calculated toxicity values based on measured concentrations are needed for all the agents but particularly the pyrethroids, which are highly sorptive. The influence of both temperature and nonadditive mixture effects also need further documentation so that they may be incorporated into criteria compliance.

The authors of the papers presented in this volume (Tessa Fojut, Amanda Palumbo, Patti TenBrook, and Isabel Faria) possess a wealth of experience in toxicology and environmental chemistry—as well as environmental risk assessment. It is through their tireless efforts that these criteria are now available with the hope that their application will facilitate the continued use of the subject agents in an environment-friendly manner. I am particularly grateful to Tessa Fojut for her many efforts in preparing the final criteria manuscripts for publication.

Davis, CA, USA Ronald S. Tjeerdema

Foreword

International concern in scientific, industrial, and governmental communities over traces of xenobiotics in foods and in both abiotic and biotic environments has justified the present triumvirate of specialized publications in this field: comprehensive reviews, rapidly published research papers and progress reports, and archival documentations. These three international publications are integrated and scheduled to provide the coherency essential for nonduplicative and current progress in a field as dynamic and complex as environmental contamination and toxicology. This series is reserved exclusively for the diversified literature on "toxic" chemicals in our food, our feeds, our homes, recreational and working surroundings, our domestic animals, our wildlife, and ourselves. Tremendous efforts worldwide have been mobilized to evaluate the nature, presence, magnitude, fate, and toxicology of the chemicals loosed upon the Earth. Among the sequelae of this broad new emphasis is an undeniable need for an articulated set of authoritative publications, where one can find the latest important world literature produced by these emerging areas of science together with documentation of pertinent ancillary legislation.

Research directors and legislative or administrative advisers do not have the time to scan the escalating number of technical publications that may contain articles important to current responsibility. Rather, these individuals need the background provided by detailed reviews and the assurance that the latest information is made available to them, all with minimal literature searching. Similarly, the scientist assigned or attracted to a new problem is required to glean all literature pertinent to the task, to publish new developments or important new experimental details quickly, to inform others of findings that might alter their own efforts, and eventually to publish all his/her supporting data and conclusions for archival purposes. In the fields of environmental contamination and toxicology, the sum of these concerns and responsibilities is decisively addressed by the uniform, encompassing, and timely publication format of the Springer triumvirate:

Reviews of Environmental Contamination and Toxicology [Vol. 1 through 97 (1962–1986) as Residue Reviews] for detailed review articles concerned with any

aspects of chemical contaminants, including pesticides, in the total environment with toxicological considerations and consequences.

Bulletin of Environmental Contamination and Toxicology (Vol. 1 in 1966) for rapid publication of short reports of significant advances and discoveries in the fields of air, soil, water, and food contamination and pollution as well as methodology and other disciplines concerned with the introduction, presence, and effects of toxicants in the total environment.

Archives of Environmental Contamination and Toxicology (Vol. 1 in 1973) for important complete articles emphasizing and describing original experimental or theoretical research work pertaining to the scientific aspects of chemical contaminants in the environment.

Manuscripts for Reviews and the Archives are in identical formats and are peer reviewed by scientists in the field for adequacy and value; manuscripts for the Bulletin are also reviewed, but are published by photo-offset from camera-ready copy to provide the latest results with minimum delay. The individual editors of these three publications comprise the joint Coordinating Board of Editors with referral within the board of manuscripts submitted to one publication but deemed by major emphasis or length more suitable for one of the others.

Coordinating Board of Editors

Preface

The role of *Reviews* is to publish detailed scientific review articles on all aspects of environmental contamination and associated toxicological consequences. Such articles facilitate the often complex task of accessing and interpreting cogent scientific data within the confines of one or more closely related research fields.

In the nearly 50 years since *Reviews of Environmental Contamination and Toxicology (formerly Residue Reviews)* was first published, the number, scope, and complexity of environmental pollution incidents have grown unabated. During this entire period, the emphasis has been on publishing articles that address the presence and toxicity of environmental contaminants. New research is published each year on a myriad of environmental pollution issues facing people worldwide. This fact, and the routine discovery and reporting of new environmental contamination cases, creates an increasingly important function for *Reviews*.

The staggering volume of scientific literature demands remedy by which data can be synthesized and made available to readers in an abridged form. Reviews addresses this need and provides detailed reviews worldwide to key scientists and science or policy administrators, whether employed by government, universities, or the private sector.

There is a panoply of environmental issues and concerns on which many scientists have focused their research in past years. The scope of this list is quite broad, encompassing environmental events globally that affect marine and terrestrial ecosystems; biotic and abiotic environments; impacts on plants, humans, and wildlife; and pollutants, both chemical and radioactive; as well as the ravages of environmental disease in virtually all environmental media (soil, water, air). New or enhanced safety and environmental concerns have emerged in the last decade to be added to incidents covered by the media, studied by scientists, and addressed by governmental and private institutions. Among these are events so striking that they are creating a paradigm shift. Two in particular are at the center of everincreasing media as well as scientific attention: bioterrorism and global warming. Unfortunately, these very worrisome issues are now superimposed on the already extensive list of ongoing environmental challenges.

The ultimate role of publishing scientific research is to enhance understanding of the environment in ways that allow the public to be better informed. The term "informed public" as used by Thomas Jefferson in the age of enlightenment conveyed the thought of soundness and good judgment. In the modern sense, being "well informed" has the narrower meaning of having access to sufficient information. Because the public still gets most of its information on science and technology from TV news and reports, the role for scientists as interpreters and brokers of scientific information to the public will grow rather than diminish. Environmentalism is the newest global political force, resulting in the emergence of multinational consortia to control pollution and the evolution of the environmental ethic. Will the new politics of the twenty-first century involve a consortium of technologists and environmentalists, or a progressive confrontation? These matters are of genuine concern to governmental agencies and legislative bodies around the world.

For those who make the decisions about how our planet is managed, there is an ongoing need for continual surveillance and intelligent controls to avoid endangering the environment, public health, and wildlife. Ensuring safety-in-use of the many chemicals involved in our highly industrialized culture is a dynamic challenge, for the old, established materials are continually being displaced by newly developed molecules more acceptable to federal and state regulatory agencies, public health officials, and environmentalists.

Reviews publishes synoptic articles designed to treat the presence, fate, and, if possible, the safety of xenobiotics in any segment of the environment. These reviews can be either general or specific, but properly lie in the domains of analytical chemistry and its methodology, biochemistry, human and animal medicine, legislation, pharmacology, physiology, toxicology, and regulation. Certain affairs in food technology concerned specifically with pesticide and other food-additive problems may also be appropriate.

Because manuscripts are published in the order in which they are received in final form, it may seem that some important aspects have been neglected at times. However, these apparent omissions are recognized, and pertinent manuscripts are likely in preparation or planned. The field is so very large and the interests in it are so varied that the editor and the editorial board earnestly solicit authors and suggestions of underrepresented topics to make this international book series yet more useful and worthwhile.

Justification for the preparation of any review for this book series is that it deals with some aspect of the many real problems arising from the presence of foreign chemicals in our surroundings. Thus, manuscripts may encompass case studies from any country. Food additives, including pesticides, or their metabolites that may persist into human food and animal feeds are within this scope. Additionally, chemical contamination in any manner of air, water, soil, or plant or animal life is within these objectives and their purview.

Manuscripts are often contributed by invitation. However, nominations for new topics or topics in areas that are rapidly advancing are welcome. Preliminary communication with the editor is recommended before volunteered review manuscripts are submitted.

Summerfield, NC David M. Whitacre

Contents

Aquatic Life Water Quality Criteria Derived via the UC Davis Method: I. Organophosphate Insecticides

Amanda J. Palumbo, Patti L. TenBrook, Tessa L. Fojut, Isabel R. Faria, and Ronald S. Tjeerdema

1 Introduction

Water quality criteria are numeric concentrations for chemicals in water bodies that, if not exceeded, should protect aquatic wildlife from toxic effects of those chemicals. These criteria, which do not consider economics or societal values, typically are derived using the existing toxicity data. Water quality criteria can be used as a basis to set legal and enforceable water quality standards or objectives in accordance with the Clean Water Act.

A new methodology for deriving freshwater pesticide water quality criteria for the protection of aquatic life was developed by the University of California Davis (TenBrook et al. 2010). The need for a new methodology was identified by a review of existing methodologies (TenBrook et al. 2009) that was commissioned by the California Central Valley Regional Water Quality Control Board (CVRWQCB). New research in the fields of aquatic toxicology and risk assessment has been incorporated into the UC Davis methodology (UCDM), whereas the United States Environmental Protection Agency (USEPA) method for derivation of aquatic life criteria has not been updated since 1985 (USEPA 1985). The fundamentals of the

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new method are similar to those of the USEPA (1985) approach, in that a species sensitivity distribution (SSD) is the preferred method of criteria calculation and an acute-to-chronic ratio (ACR) is used when chronic data are limited. Some of the major differences provided by the UCDM are a thorough and transparent study evaluation procedure; a more advanced SSD; alternate procedures if data requirements for the SSD or ACR cannot be met; and inclusion of mixtures.

The UCDM has been used to derive aquatic life criteria for several pesticides of particular concern in the Sacramento River and San Joaquin River watersheds, which are also widely used throughout the USA. This paper is the first in a series in which criteria were derived for three organophosphate (OP) insecticides (chlorpyrifos, diazinon, and malathion), five pyrethroid insecticides (bifenthrin, cyfluthrin, cypermethrin, lambda-cyhalothrin, and permethrin), and one phenyl-urea herbicide (diuron). Diazinon and chlorpyrifos were chosen as the first pesticides to be evaluated with the UCDM because there were already national and state criteria for these compounds to which the results of the UCDM could be compared; malathion was included in the analysis because it is another organophosphate pesticide that is of concern for water quality. The UCDM contains detailed procedures for criteria derivation, as well as the rationale behind the selection of specific methods (TenBrook et al. 2010). This organophosphate criteria derivation article describes the procedures used to derive criteria according to the UCDM, and provides several references to specific sections numbers of the UCDM document (TenBrook et al. 2010) so that the reader may refer to the UCDM for further details.

2 Data Collection and Evaluation

Chlorpyrifos (*O*,*O*-diethyl *O*-(3,5,6-trichloro-2-pyridinyl) phosphorothioate), diazinon (*O*,*O*-diethyl *O*-2-isopropyl-6-methylpyrimidin-4-yl phosphorothioate), and malathion (diethyl 2-dimethoxyphosphinothioylsulfanylbutanedioate) are organophosphate insecticides. The physical–chemical properties of these OPs (Table 1) indicate that some fraction remains dissolved in the water column and eventually degrades there (Table 2), some fraction partitions to the sediments, and that they are not likely to volatilize from the water column.

Original studies on the effects of chlorpyrifos (~340), diazinon (~250), and malathion (~200) on aquatic life were identified and reviewed. Studies were from both the open literature and unpublished studies submitted to the USEPA and California Department of Pesticide Regulation (CDPR) by pesticide registrants. Unpublished studies held by these agencies can be requested from the respective agencies; the full request instructions to acquire them are given in the UCDM (TenBrook et al. 2010). To determine the usefulness of these studies for criteria derivation, they were subjected to a review process, depending on the type of study; the three types were (1) single-species effects, (2) ecosystem-level studies, and (3) terrestrial wildlife studies.

Table 1 Summary of physical–chemical properties

	Chlorpyrifos	Diazinon	Malathion
Molecular weight	350.6	304.36	330.358
Density (g/mL)	1.44[c] (20°C)	1.11[j] (20°C)	1.22 (geomean, $n = 3$)[o]
Water solubility (mg/L)	1.46 (geomean, $n = 3$)[d]	46.0 (geomean, $n = 4$)[k]	146.16 (geomean, $n = 7$)[p]
Melting point (°C)	42.73 (geomean of extremes)[e]	Liquid at room temperature[c]	2.43 (geomean, $n = 4$)[q]
Vapor pressure (Pa)	2.36×10^{-3} (geomean, $n = 3$)[f]	0.014 (geomean, $n = 3$)[c,l]	1.20×10^{-3} (geomean, $n = 6$)[r]
Henry's law constant (K_H) (Pa m^3/mol)	0.640 (geomean, $n = 4$)[c,g]	0.0114 (geomean, $n = 2$)[m]	1.65×10^{-3} (geomean, $n = 4$)[s]
Log K_{oc}[a]	4.06 (geomean, $n = 2$)[h]	3.35 (geomean, $n = 8$)[n]	2.77 (geomean, $n = 8$)[t]
Log K_{ow}[b]	4.96[i]	3.81[i]	2.84 (geomean, $n = 8$)[c,u]

[a] Log K_{oc}: log-normalized organic carbon–water partition coefficient
[b] Log K_{ow}: log-normalized octanol–water partition coefficient
[c] Tomlin (2003)
[d] Hummel and Crummet (1964), Felsot and Dahm (1979), and Drummond (1986)
[e] Bowman and Sans (1983a), Brust (1964, 1966), McDonald et al. (1985), and Rigertink and Kenaga (1966)
[f] Brust (1964), McDonald et al. (1985), and Chakrabarti and Gennrich (1987)
[g] Wu et al. (2002), Fendinger and Glotfelty (1990), and Downey (1987)
[h] Racke (1993) and Spieszalski et al. (1994)
[i] Sangster Research Laboratories (2004)
[j] Worthing (1991)
[k] Martin and Worthing (1977), Jarvinen and Tanner (1982), Kanazawa (1981), and Bowman and Sans (1979, 1983b)
[l] Kim et al. (1984) and Hinckley et al. (1990)
[m] Fendinger and Glotfelty (1988) and Fendinger et al. (1989)
[n] Iglesias-Jimenez et al. (1997), Cooke et al. (2004), and Kanazawa (1989)
[o] Barton (1988), Mackay et al. (2006), and Verschueren (1996)
[p] Kidd and James (1991), Howard (1989), Cheminova (1988), Kamrin and Montgomery (2000), Kabler (1989), and Hartley and Graham-Bryce (1980)
[q] Lide (2004), Kidd and James (1991), Budavari et al. (1996), Howard (1989), and Barton (1988)
[r] Howard (1989), Hartley and Graham-Bryce (1980), Verschueren (1996), Kidd and James (1991), Tondreau (1987), Melnikov (1971), and Barton (1988)
[s] Howard (1989), Mackay et al. (2006), and Kamrin and Montgomery (2000)
[t] Mackay et al. (2006), Kamrin and Montgomery (2000), Karickhoff (1981), and Sabljic et al. (1995)
[u] Kamrin and Montgomery (2000), Howard (1989), Barton (1988), Verschueren (1996), and Mackay et al. (2006)

Table 2 Environmental fate of chlorpyrifos, diazinon, and malathion

	Chlorpyrifos	Diazinon	Malathion
Hydrolysis half-life (days)	210 (pH 4.7/15°C)[a]	0.49 (pH 3.1/20°C)[f]	40 (pH 8/0°C)[m]
	99.0 (pH 6.9/15°C)[a]	6 (pH 10.4/20°C)[f]	36 h (pH 8/27°C)[m]
	54.2 (pH 8.1/15°C)[a]	17 (pH 8.0/40°C)[g]	1 h (pH 8/40°C)[m]
	120 (pH 6.1/20°C)[b]	30 (pH 7.4–7.8/22.5°C)[h]	10.5 (pH 7.4/20°C)[n]
	53 (pH 7.4/20°C)[b]	31 (pH 5.0/20°C)[f]	1.3 (pH 7.4/37.5°C)[n]
	62.7 (pH 4.7/25°C)[a]	37.2[i]	107 (pH 5/25°C)[o]
	77 (pH 5.9/25°C)[c]	52 (pH 7.3/22°C)[j]	6.21 (pH 7, 25°C)[o]
	204 (pH 6.1/25°C)[c]	69 (pH 6.1/22°C)[j]	0.49 (pH 9, 25°C)[o]
	35.3 (pH 6.9/25°C)[a]	80 (pH 7.3/22°C)[j]	
	22.8 (pH 8.1/25°C)[a]	88 (pH 8.0/24°C)[h]	
	15 (pH 9.7/25°C)[c]	136 (pH 9.0/20°C)[f]	
	15.7 (pH 4.7/35°C)[a]	171 (pH 7.3/21°C)[k]	
	11.5 (pH 6.9/35°C)[a]	185 (pH 7.4/20°C)[f]	
	4.5 (pH 8.1/35°C)[a]		
Aqueous photolysis (days)	13.9 (pH 5.0)[d]	9–12 (25°C)[l]	156 (pH 4/25°C)[p]
	21.7(pH 6.9)[d]		94 (pH 4, 25°C)[p]
	13.1(pH 8.0)[d]		
	31(pH 7.0)[e]		
	43 (pH 7.0)[e]		
	345 (pH 7.0)[e]		

NR not reported
[a] Meikle and Youngson (1978)
[b] Freed et al. (1979a)
[c] Macalady and Wolfe (1983)
[d] Meikle et al. (1983)
[e] Dilling et al. (1984)
[f] Gomaa et al. (1969) and Faust and Gomaa (1972)
[g] Noblet et al. (1996)
[h] Jarvinen and Tanner (1982)
[i] Medina et al. (1999)
[j] Lartiges and Garrigues (1995)
[k] Mansour et al. (1999)
[l] Kamiya and Kameyama (1998)
[m] Wolfe et al. (1977)
[n] Freed et al. (1979b)
[o] Teeter (1988)
[p] Carpenter (1990)

Single-species effects studies were evaluated in a two-step numeric scoring process. First, studies were evaluated based on six main criteria: (1) use of a control; (2) freshwater species; (3) species belongs to a family in North America; (4) chemical purity >80%; (5) end point linked to survival, growth, or reproduction; and (6) a toxicity value was calculated or is calculable. Studies that met all of these parameters were rated relevant (R) while studies that did not meet one or two of the six relevance criteria were rated less relevant (L). Finally, studies that lacked more than two of these criteria were considered to be not relevant (N). The studies rated as relevant (R) or less relevant (L) were subject to a second evaluation while those that rated as not

relevant (N) were not considered further. Data summaries detailing study parameters and scoring for all studies are included as the Supporting Material (http://extras.springer.com/).

The second review of the studies rated R or L was designed to evaluate data reliability. Reliability scores were based on if test parameters were reported and the acceptability of those parameters according to standard methods; some of the scored test parameters were organism source and care, control description and response, chemical purity, concentrations tested, water quality conditions, and statistical methods. Numeric scores were translated into ratings of reliable (R), less reliable (L), or not reliable (N). Each study was given a two-letter code, with the first letter corresponding to the relevance rating and the second letter corresponding to the reliability rating. Acceptable studies, rated as relevant and reliable (RR), were used for numeric criteria derivation. Supplemental studies, rated as relevant and less reliable (RL), less relevant and reliable (LR) or less relevant and less reliable (LL), were not used directly for criteria calculation, but were used for evaluation of the criteria to check that they are protective of particularly sensitive species and threatened and endangered species, which may not be represented in the RR data sets. Data that were rated as acceptable (RR) for criteria derivation are summarized in Tables 3–8. All other toxicity data are available as the Supporting Material (http://extras.springer.com/). Studies that were rated not relevant (N) or relevant or less relevant, but not reliable (RN or LN), were not used in any aspect of criteria derivation.

Mesocosm, microcosm, and ecosystem (field and laboratory) studies were subject to a separate evaluation of reliability. Studies that were rated reliable (R) or less reliable (L) were used to evaluate the derived criteria to ensure that they are protective of ecosystems. Terrestrial wildlife toxicity studies for mallard ducks were evaluated specifically for the consideration of bioaccumulation. Mallard duck studies that were rated reliable (R) or less reliable (L) were used in estimations of bioaccumulative potential.

3 Data Reduction

Multiple toxicity values for each pesticide for the same species were combined into one species mean acute value (SMAV) or one species mean chronic value (SMCV) by calculating the geometric mean of appropriate values. To arrive at one SMAV or SMCV per species, some data rated RR were excluded from the final RR data set for the following reasons: tests that used measured concentrations are preferred over tests that used nominal concentrations; flow-through tests are preferred over static tests; a test with a more sensitive life stage of the same species was available; longer exposure durations are preferred; tests at standard conditions are preferred over those at nonstandard conditions; and tests with more sensitive end points were available. Acceptable acute and chronic data that were excluded, and the reasons for their exclusion, are shown in Tables S1–S3 (Supporting Material http://extras.springer.com/). For chlorpyrifos, the final acceptable data sets contain 17 SMAVs

Table 3 Final acute toxicity data set for chlorpyrifos

Species	Test type	Meas/Nom	Chemical grade (%)	Duration (h)	Temp (°C)	End point	Age/size	LC/EC_{50} (µg/L)	References
Ceriodaphnia dubia	S	Meas	99.0	96	25	Mortality	<24 h	0.053	Bailey et al. (1997)
C. dubia	S	Meas	99.0	96	25	Mortality	<24 h	0.055	Bailey et al. (1997)
C. dubia	SR	Meas	99.0	96	24.6	Mortality	<24 h	0.13	CDFG (1992e)
C. dubia	SR	Meas	99.0	96	24.3	Mortality	<24 h	0.08	CDFG (1992b)
C. dubia	SR	Meas	99.8	96	24.6	Survival	<24 h	0.0396	CDFG (1999)
Geometric mean								0.0654	
Chironomus tentans	S	Meas	98.0	96	21	Immobility	Third to fourth instar	0.16	Belden and Lydy (2006)
C. tentans	S	Meas	90.0	96	21	Immobility	Fourth instar	0.17	Lydy and Austin (2005)
C. tentans	S	Meas	98.0	96	20	Immobility + mortality	Fourth instar	0.39	Belden and Lydy (2000)
Geometric mean								0.220	
Daphnia ambigua	S	Meas	99.0	48	21	Immobility	Neonates	0.035	Harmon et al. (2003)
Daphnia magna	S	Meas	99.0	48	19.5	Mortality	<24 h	1.0	Kersting and Van Wijngaarden (1992)
D. magna	FT	Nom (most)	95.5	48	18–21	Mortality	<24 h	0.10	Burgess (1988)
Geometric mean								0.32	
Daphnia pulex	S	Meas	Technical	48	20	Immobility	<24 h	0.25	Van Der Hoeven and Gerritsen (1997)
Hyalella azteca	S	Meas	90.0	96	20	Mortality	14–21 days	0.0427	Anderson and Lydy (2002)
H. azteca	SR	Meas	98.1	96	19	Mortality	14–21 days	0.138	Brown et al. (1997)
Geometric mean								0.077	
Ictalurus punctatus	FT	Meas	99.9	96	17.3	Mortality	7.9 g	806	Phipps and Holcombe (1985)

Lepomis macrochirus	FT	Meas	99.9	96	17.3	Mortality	0.8 g	10	Phipps and Holcombe (1985)
L. macrochirus	FT	Meas	99.9	96	22	Mortality	2.1 g	5.8	Bowman (1988)
Geometric mean								7.6	
Neomysis mercedis	SR	Meas	99.0	96	17.4	Mortality	<5 days	0.15	CDFG (1992d)
N. mercedis	SR	Meas	99.0	96	17.2	Mortality	<5 days	0.16	CDFG (1992a)
N. mercedis	SR	Meas	99.0	96	17.1	Mortality	<5 days	0.14	CDFG (1992c)
Geometric mean								0.150	
Oncorhynchus mykiss	FT	Meas	99.9	96	12	Mortality	Juvenile	8.0	Holcombe et al. (1982)
O. mykiss	FT	Meas	95.9	96	12	Mortality	0.25 g	25.0	Bowman (1988)
Geometric mean								14	
Oncorhynchus tshawytscha	SR	Meas	99.5	96	14.8	Mortality	Juvenile	15.96	Wheelock et al. (2005)
Orconectes immunis	FT	Meas	99.9	96	17.3	Mortality	1.8 g	6	Phipps and Holcombe (1985)
Pimephales promelas	FT	Meas	99.9	96	25	Mortality	32 days	200	Geiger et al. (1988)
P. promelas	FT	Meas	99.9	96	25	Mortality	31–32 days	203	Holcombe et al. (1982)
P. promelas	FT	Meas	98.7	96	25	Mortality	Newly hatched	140	Jarvinen and Tanner (1982)
Geometric mean								178	
Procloeon sp.	SR	Meas	99	48	21.3	Mortality	0.5–1.0 cm	0.1791	Anderson et al. (2006)
Procloeon sp.	SR	Meas	99	48	21.3	Mortality	0.5–1.0 cm	0.0704	Anderson et al. (2006)
Procloeon sp.	SR	Meas	99	48	21.3	Mortality	0.5–1.0 cm	0.0798	Anderson et al. (2006)

(continued)

Table 3 (continued)

Species	Test type	Meas/Nom	Chemical grade (%)	Duration (h)	Temp (°C)	End point	Age/size	LC/EC_{50} (µg/L)	References
Geometric mean								0.100	
Pungitius pungitius	FT	Meas	99.8	96	19	Mortality	Adult	4.7	Van Wijngaarden et al. (1993)
Simulium vittatum IS-7	S	Meas	98.0	24	19	Mortality	Second and third instar	0.06	Hyder et al. (2004)
Xenopus laevis	SR	Nom	99.80	96	24.7	Mortality	<24 h	2,410	El-Merhibi et al. (2004)

All studies were rated relevant and reliable (RR) and were conducted at standard temperature (Standard temperatures are particular for each species. See standard methods referenced in Tables 9 and 10 of TenBrook et al. (2010))

S static, *SR* static renewal, *FT* flow through

Table 4 Final chronic toxicity data set for chlorpyrifos

Species	Test type	Meas/ Nom	Chemical grade (%)	Duration (days)	Temp (°C)	End point	Age/size	NOEC (µg/L)	LOEC (µg/L)	MATC (µg/L)	Reference
Ceriodaphnia dubia	SR	Meas	99.8	7	24.6	Mortality	<24 h	0.029	0.054	0.0396	CDFG (1999)
C. dubia	SR	Meas	99.8	7	24.6	Reproduction	<24 h	0.029	0.054	0.0396	CDFG (1999)
Geometric mean								0.029	0.054	0.0396	
Pimephales promelas	FT	Meas	98.7	60	24.3–25.9	Growth	<24 h	0.63	1.21	0.87	Jarvinen et al. (1983)
P. promelas	FT	Meas	98.7	32	23.5–26.0	Weight	Newly hatched	1.6	3.2	2.3	Jarvinen and Tanner (1982)
P. promelas	FT	Meas	99.7	25 and 32	25.0–25.5	F_0 and F_1 Mortality	<24 h	0.568	1.093	0.788	Mayes et al. (1993)
Geometric mean								0.83	1.62	1.16	
Neomysis mercedis	SR	Meas	99.0	96	17	Mortality	<5 days	0.001[a]			CDFG (1992a)
N. mercedis	SR	Meas	99.0	96	17	Mortality	<5 days	0.001[a]			CDFG (1992d)
Geometric mean								0.001[a]			

All studies were rated relevant and reliable (RR) and were conducted at standard temperatures for a given species

SR static renewal, *FT* flow through

[a]Chronic values for *Neomysis mercedis* were estimated from acute data

Table 5 Final acute toxicity data set for diazinon

Species	Test type	Meas/ Nom	Chemical grade (%)	Duration (h)	Temp (°C)	End point	Age/size	LC/EC_{50} (μg/L)	Reference
Ceriodaphnia dubia	SR	Meas	87.3	96	24.7	Mortality	<24 h	0.436 (0.342–0.504)	CDFG (1998a)
C. dubia	SR	Meas	88.0	96	24.4	Mortality	<24 h	0.47	CDFG (1992f)
C. dubia	SR	Meas	88.0	96	24.4	Mortality	<24 h	0.507 (0.42–0.71)	CDFG (1992g)
C. dubia	S	Meas	99.0	96	25	Mortality	<24 h	Test 1: 0.32 (0.27–0.38) Test 2: 0.35 (0.32–0.38)	Bailey et al. (1997)
C. dubia	S	Meas	99.0	48	25	Mortality	<24 h	Test 3: 0.26 (0.21–0.32) Test 4: 0.29 (0.19–0.46)	Bailey et al. (1997)
C. dubia	S	Meas	Analytical	48	25	Mortality	<24 h	0.33	Bailey et al. (2000)
C. dubia	S	Meas	99.0	48	25	Mortality	<24 h	Test 1: 0.38 Test 2: 0.33	Bailey et al. (2001)
C. dubia	S	Meas	99.8	48	25	Mortality	<24 h	0.21	Banks et al. (2005)
Geometric mean								0.34	
Chironomus dilutus (formerly *tentans*)	S	Nom	95.0	96	23	Mortality/ immobility	Third instar	10.7 (7.55–15.2)	Ankley and Collyard (1995)
Daphnia magna	FT	Meas	87.7	96	20	Mortality/ immobility	<24 h	0.52 (0.32–0.83)	Surprenant (1988)
Gammarus pseudolimnaeus	S/R	Meas	100.0	96	18	Mortality	Mature	16.82 (12.82–22.08)	Hall and Anderson (2005)
Hyalella azteca	S	Meas	98.0	96	20	Mortality	14–21 days	4.3 (3.7–5.6)	Anderson and Lydy (2002)

Jordanella floridae	FT	Meas	92.5	96	25	Mortality	6–7 weeks	Test 1: 1,500 (1,200–1,900) Test 2: 1,800 (1,600–2,000)	Allison and Hermanutz (1977)
Geometric mean								1,643	
Lepomis macrochirus	FT	Meas	92.5	96	25	Mortality	1 year	Test 1: 480 (340–670) Test 2: 440 (310–620)	Allison and Hermanutz (1977)
Geometric mean								460	
Neomysis mercedis	S/R	Meas	88.0	96	17	Mortality	<5 days	3.57 (2.99–4.36)	CDFG (1992h)
N. mercedis	S/R	Meas	88.0	96	17.5	Mortality	<5 days	4.82 (3.95–6.00)	CDFG (1992i)
Geometric mean								4.15	
Physa spp.	S/R	Meas	87.0	96	21.6	Mortality	Juvenile	4,441	CDFG (1998b)
Pimephales promelas	FT	Meas	92.5	96	25	Mortality	15–20 weeks	Test 1: 6,800 Test 2: 6,600 Test 3: 10,000	Allison and Hermanutz (1977)
P. promelas	FT	Meas	87.1	96	24.5	Mortality	31 days	9,350 (8,120–10,800)	Geiger et al. (1988)
P. promelas	FT	Meas	87.1	96	23.5–26	Mortality	Newly hatched	6,900 (6,200–7,900)	Jarvinen and Tanner (1982)
Geometric mean								7,804	
Pomacea paludosa	FT	Meas	87.0	96	26–27.4	Mortality	1 day, 7 days	Test 1: 2,950 Test 2: 3,270 Test 3: 3,390	Call (1993)

(continued)

Table 5 (continued)

Species	Test type	Meas/ Nom	Chemical grade (%)	Duration (h)	Temp (°C)	End point	Age/size	LC/EC_{50} (µg/L)	Reference
Geometric mean								3,198	
Procloeon sp.	S/R	Meas	99.0	48	22.1	Mortality	0.5–1 cm	Test 1: 1.53 Test 2: 2.11 Test 3: 1.77	Anderson et al. (2006)
Geometric mean								1.79	
Salvelinus fontinalis	FT	Meas	92.5	96	12	Mortality	1 year	Test 1: 800 (440–1,140) Test 2: 450 (320–630) Test 3: 1,050 (720–1,520)	Allison and Hermanutz (1977)
Geometric mean								723	

All studies were rated relevant and reliable (RR) and were conducted at standard temperature for a given species

S static, *SR* static renewal, *FT* flow through

Table 6 Final chronic toxicity data set for diazinon

Species	Test type	Meas/ Nom	Chemical grade (%)	Duration (days)	Temp (°C)	Endpoint	Age/size	NOEC (µg/L)	LOEC (µg/L)	MATC (µg/L)	Reference
Daphnia magna	FT	Meas	87.7	21	20	Mortality/ immobility	<24 h	0.17	0.32	0.23	Surprenant (1988)
Pimephales promelas	FT	Meas	92.5	274	25	Mortality	5 days	28	60.3	41	Allison and Hermanutz (1977)
P. promelas	FT	Meas	87.1	32	23.5–26.0	Weight	Newly hatched	50	90	67	Jarvinen and Tanner (1982)
Geometric mean										54	
Salvelinus fontinalis	FT	Meas	92.5	173	±1°C; variable acc. to date	Mortality	1 year	4.8	9.6	6.8	Allison and Hermanutz (1977)
Selenastrum capricornutum	S	Meas	87.7	7	24	Mean standing crop (cells/ mL)	6–8-day-old culture	–	–	EC_{50} 6,400	Hughes (1988)
S. capricornutum	S	Meas	87.7	7	24	Mean standing crop (cells/ mL)	6–8-day-old culture	–	–	EC_{25} 4,250	Hughes (1988)

All studies were rated relevant and reliable (RR)
S static, *S/R* static renewal, *FT* flow through

Table 7 Final acute toxicity data set for malathion

Species	Test type	Meas/ Nom	Chemical grade (%)	Duration (h)	Temp (°C)	End point	Age/size	LC_{50}/EC_{50} (μg/L)	Reference
Acroneuria pacifica	FT	Nom	95	96	12.8	Mortality	Naiads	7.7	Jensen and Gaufin (1964b)
Anisops sardeus	S	Nom	>99	48	27	Immobility/ mortality	Adult	42.2 (40.5–44.9)	Lahr et al. (2001)
Ceriodaphnia dubia	S	Nom	99.2	48	25	Mortality	≤24 h	3.35 (2.68–3.93)	Maul et al. (2006)
C. dubia	S	Nom	97	48	25	Mortality	≤24 h	1.14 (1.04–0.25)	Nelson and Roline (1998)
Geometric mean								1.95	
Chironomus tentans	S	Meas	98	96	20	Immobility/ mortality	Fourth instar	1.5 (1.2–1.9)	Belden and Lydy (2000)
C. tentans	S	Nom	99	96	20	Immobility/ mortality	Fourth instar	19.09 (11.98–30.44)	Pape-Lindstrom and Lydy (1997)
Geometric mean								5.35	
Daphnia magna	S	Nom	Analytical	48	21	Immobility/ mortality	<24 h	1.8 (1.5–2.0)	Kikuchi et al. (2000)
Elliptio icterina	S	Nom	96	96	25	Mortality	Juvenile	32,000	Keller and Ruessler (1997)
Gambusia affinis	S	Nom	>90	48	27	Mortality	5 days	3,440 (2,720–4,370)	Tietze et al. (1991)
Gila elegans	SR	Meas	93	96	22	Mortality	6 days	15,300	Beyers et al. (1994)
Jordanella floridae	FT	Meas	95	96	24.4–25.2	Mortality	33 days	349	Hermanutz (1978)
Lampsilis siliquoidea	S	Nom	96	48	25 (pH 7.5)	Mortality	Glochidia	7,000	Keller and Ruessler (1997)
Lampsilis subangulata	S	Nom	96	96	25 (pH 7.5)	Mortality	Juvenile	28,000	Keller and Ruessler (1997)
Megalonaias nervosa	S	Nom	96	24	25 (pH 7.5)	Mortality	Glochidia	22,000	Keller and Ruessler (1997)

Morone saxatilis	FT	Meas	94.2	96	15–17	Mortality	11 days	16 (13–19)	Fujimura et al. (1991)
M. saxatilis	FT	Meas	94.2	96	15–17	Mortality	45 days	25 (19–34)	Fujimura et al. (1991)
M. saxatilis	FT	Meas	94.2	96	15–17	Mortality	29 days	12 (11–14)	Fujimura et al. (1991)
M. saxatilis	FT	Meas	94.2	96	15–17	Mortality	13 days	64 (55–77)	Fujimura et al. (1991)
M. saxatilis	FT	Meas	94.2	96	15–17	Mortality	45 days	100 (87–150)	Fujimura et al. (1991)
M. saxatilis	FT	Meas	94.2	96	15–17	Mortality	45 days	66 (58–74)	Fujimura et al. (1991)
Geomean								36	
Neomysis mercedis	FT	Meas	94.2	96	17	Mortality	Neonates: ≤5 days	2.2 (2.0–2.5)	Brandt et al. (1993)
N. mercedis	FT	Meas	94.2	96	17	Mortality	Neonates: ≤5 days	1.5 (1.2–1.8)	Brandt et al. (1993)
N. mercedis	FT	Meas	94.2	96	17	Mortality	Neonates: ≤5 days	1.4 (1.3–1.5)	Brandt et al. (1993)
Geomean								1.7	
Oncorhynchus clarki	SR	Nom	95	96	13	Mortality	0.33	Test 1: 150 (133–170)	Post and Schroeder (1971)
O. clarki	SR	Nom	95	96	13	Mortality	1.25 g	Test 2: 201 (175–231)	Post and Schroeder (1971)
Geometric mean								174	
Oncorhynchus kisutch	SR	Nom	95	96	13	Mortality	1.7 g	130 (208–388)	Post and Schroeder (1971)
Oncorhynchus mykiss	SR	Nom	95	96	13	Mortality	0.41 g	122 (98–153)	Post and Schroeder (1971)
Pimephales promelas	FT	Meas	95	96	25	Mortality	29–30 days; 0.069 g; 1.7 cm	141,00 (12,300–16,100)	Geiger et al. (1984)
Pteronarcys californica	S	Nom	95	96	11.5	Mortality	Naiads, 4–6 cm	50	Jensen and Gaufin (1964a)
Ptychocheilus lucius	SR	Meas	93	96	22	Mortality	26 days	9,140	Beyers et al. (1994)

(continued)

Table 7 (continued)

Species	Test type	Meas/ Nom	Chemical grade (%)	Duration (h)	Temp (°C)	End point	Age/size	LC_{50}/EC_{50} (µg/L)	Reference
Rana palustris	S	Meas	98	48	16.5	Mortality	Tadpole, Gosner 26	17,100	Budischak et al. (2009)
Salvelinus fontinalis	SR	Nom	95	96	13	Mortality	Test 1: 1.15 g	Test 1: 130 (110–154)	Post and Schroeder (1971)
S. fontinalis	SR	Nom	95	96	13	Mortality	Test 2: 2.13 g	Test 2: 120 (96–153)	Post and Schroeder (1971)
Geometric mean								125	
Simulium vittatum	S	Meas	98	48	21	Mortality	Sixth and seventh instar	54.20 (44.70–66.43)	Overmyer et al. (2003)
Streptocephalus sudanicus	S	Nom	>99	48	27	Immobility/ mortality	Adult	67,750 (52,220–90,300)	Lahr et al. (2001)
Utterbackia imbecillis	S	Nom	96	96	25 (pH 7.5)	Mortality	Juvenile	215,000	Keller and Ruessler (1997)
Villosa lienosa	S	Nom	96	24	25 (pH 7.9)	Mortality	Glochidia	54,000	Keller and Ruessler (1997)
Villosa villosa	S	Nom	96	96	25 (pH 7.9)	Mortality	Juvenile	142,000	Keller and Ruessler (1997)

All studies were rated RR and were conducted at standard temperature
S static, *SR* static renewal, *FT* flow through

Table 8 Final chronic toxicity data set for malathion

Species	Test type	Meas/ Nom	Chemical grade (%)	Duration	Temp (°C)	Endpoint	Age/size	NOEC (µg/L)	LOEC (µg/L)	MATC (µg/L)	Reference
Clarias gariepinus	SR	Nom	98	5 days	27	Length/ weight	Eggs	630	1,250	887	Nguyen and Janssen (2002)
C. gariepinus	SR	Nom	98	5 days	27	Length	Eggs 3–5 hold	1,250	2,500	1,768	Lien et al. (1997)
Geometric mean										1,252	
Daphnia magna	FT	Meas	94	21 days	20	Mortality	First instar <24 h	0.06	0.1	0.077	Blakemore and Burgess (1990)
Gila elegans	FT	Meas	93	32 days	22	Growth	48 days	990	2,000	1,407	Beyers et al. (1994)
Jordanella floridae	FT	Meas	95	30 days	25.1–25.4	Growth	1–2 days	8.6	10.9	9.68	Hermanutz (1978)
Lepomis macrochirus	FT	Meas	95	10 months	9–29	Mortality	8 cm, 12 g, 1.5 years	7.4	14.6	10.4	Eaton (1970)
Oncorhynchus mykiss	FT	Meas	94	97 days	7.8–13.6	Mortality	Eggs 8 h post fert.	21	44	30.4	Cohle (1989)
Ptychocheilus lucius	FT	Meas	93	32 days	22	Growth	41 days	1,680	3,510	2,428	Beyers et al. (1994)
P. lucius	FT	Meas	93	32 days	22	Mortality	41 days	1,680	3,510	2,428	Beyers et al. (1994)
Geometric mean										2,428	

All studies were rated RR and were conducted at standard temperature
SR static renewal, *FT* flow through

and 3 SMCVs (Tables 3 and 4), the final diazinon data sets contain 13 SMAVs and 5 SMCVs (Tables 5 and 6), and the final malathion data sets contain 27 SMAVs and 7 SMCVs (Tables 7 and 8).

4 Acute Criterion Calculations

The final acute data sets for both chlorpyrifos and diazinon (Tables 3 and 5) include species from each of the five taxa requirements of the SSD procedure: a warm water fish, a species in the family Salmonidae, a planktonic crustacean, a benthic crustacean, and an insect (TenBrook et al. 2010). Cumulative probability plots of the SMAVs (Figs. 1 and 2) revealed bimodal distributions for both compounds, with invertebrates encompassing the lower subset and fish and amphibians in the upper subset. However, the SSDs were fit to the entire data set for both compounds because it is preferable to use all of the data, unless the goodness of fit test indicates a lack of fit to the entire data set. The Burr Type III SSD was fit to these data sets for the acute criteria calculations because more than eight acceptable acute toxicity values were available in the chlorpyrifos and diazinon acute data sets. The Burr Type III SSD consists of a family of three related distributions, among which the

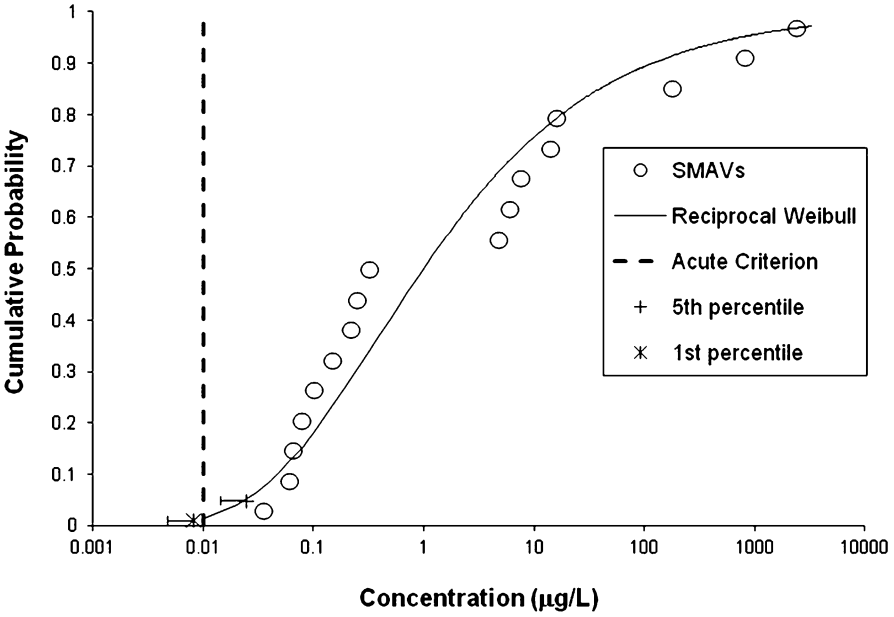

Fig. 1 Plot of species mean acute values for chlorpyrifos and fit of the Reciprocal Weibull distribution. The graph shows the median fifth and first percentiles with the lower 95% confidence limits and the acute criterion at 0.01 µg/L

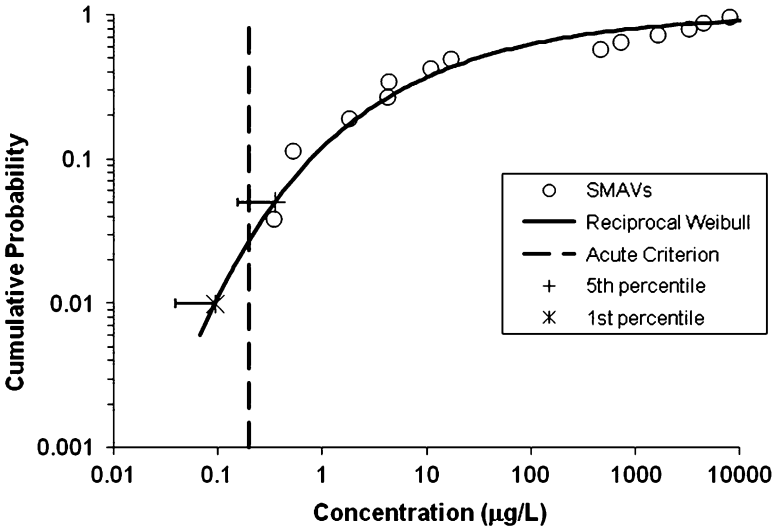

Fig. 2 Plot of species mean acute values for diazinon and fit of the Reciprocal Weibull distribution. The graph shows the median fifth and first percentiles with the lower 95% confidence limits and the acute criterion at 0.2 µg/L

BurrliOZ software (CSIRO 2001) selected the Reciprocal Weibull distribution as the best fit for both compounds based on maximum likelihood estimation.

The BurrliOZ software was used to derive fifth percentiles (median and lower 95% confidence limit), as well as first percentiles (median and lower 95% confidence limit). The median fifth percentile was used in criteria derivation because it is the most robust of the distributional estimates.

Chlorpyrifos Reciprocal Weibull Distribution

Fit parameters: $\alpha = 0.691$; $\beta = 0.394$ (likelihood = 54.083508)
Fifth percentile, 50% confidence limit: 0.0243 µg/L
Fifth percentile, 95% confidence limit: 0.0144 µg/L
First percentile, 50% confidence limit: 0.00816 µg/L
First percentile, 95% confidence limit: 0.00469 µg/L
Recommended acute value = 0.0243 µg/L (median fifth percentile)

$$\text{Acute criterion} = \frac{\text{Acute value}}{2}. \tag{1}$$

Chlorpyrifos acute criterion = 0.01 µg/L

Diazinon Reciprocal Weibull Distribution

Fit parameters: $\alpha = 2.123041$; $\beta = 0.326993$ (likelihood = 87.377508)
Fifth percentile, 50% confidence limit: 0.349 µg/L

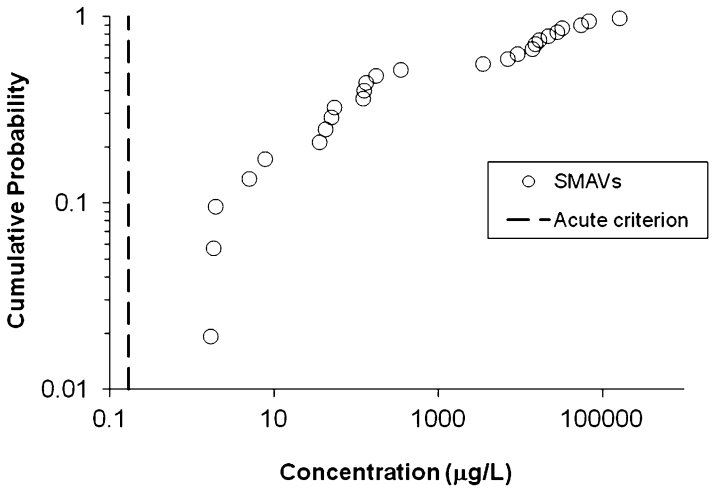

Fig. 3 Malathion species mean acute values with the acute criterion displayed at 0.17 µg/L

Fifth percentile, 95% confidence limit: 0.155 µg/L
First percentile, 50% confidence limit: 0.0937 µg/L
First percentile, 95% confidence limit: 0.0392 µg/L
Recommended acute value = 0.349 µg/L (median fifth percentile)
Diazinon acute criterion = 0.2 µg/L

No significant lack of fit to the whole data sets was found for either compound using a fit test based on cross validation and Fisher's combined test, with $X^2_{2n} = 0.1326$ for chlorpyrifos and $X^2_{2n} = 0.1561$ for diazinon (calculations shown in the Supporting Material http://extras.springer.com/). The acute data sets and corresponding Reciprocal Weibull distributions are shown in Figs. 1 and 2. The criteria are reported with one significant figure because of the variability indicated by the different confidence limit estimates.

The cumulative probability plot of the malathion SMAVs (Fig. 3) indicated that the data set is possibly bimodal, but the trend is not clearly defined. The malathion acute data set did not contain a species that fulfilled the benthic crustacean taxa requirement for use of an SSD; therefore, the malathion acute criterion could not be calculated with an SSD, and was instead calculated with an assessment factor (AF) procedure. The AF procedure estimates the median fifth percentile of the distribution by dividing the lowest SMAV in the data set by an AF, the magnitude of which was determined by the number of taxa available that fulfill the five SSD taxa requirements. An AF of 5.1 was used because the malathion data set contained four of the five taxa requirements (TenBrook et al. 2010) and the lowest SMAV in the malathion data set is 1.7 µg/L for *Neomysis mercedis*.

$$\begin{aligned}\text{Acute value} &= \frac{\text{Lowest SMAV}}{\text{Assessment factor}}, \\ &= \frac{1.7\mu g/L}{5.1} = 0.333 \ \ \mu g/L.\end{aligned} \tag{2}$$

Using Eq. 1:

$$\text{Malathion acute criterion} = \frac{0.333\mu g/L}{2} = 0.17 \ \ \mu g/L.$$

5 Chronic Criterion Calculations

Chronic data were limited for each of the three selected organophosphates and none of the chronic data sets contained enough data to meet the five taxa requirements of the SSD procedure. Thus, ACRs were used to calculate the chronic criteria (TenBrook et al. 2010). The UCDM ACR procedure follows the USEPA (1985) ACR instructions, except that the UCDM includes a default ACR that can be used when ACRs based on experimental data are lacking. For chlorpyrifos, two of the five SSD taxa requirements were satisfied: warm water fish (*Pimephales promelas*) and planktonic crustacean (*Ceriodaphnia dubia* and *N. mercedis*). To avoid excessive layers of estimation, the estimated chronic values for *N. mercedis* were not used to calculate ACRs, but the other two chronic data were used with appropriate corresponding acute data to calculate species mean ACRs (SMACRs). Since there were insufficient freshwater data to satisfy the three family requirements of the ACR procedure (viz., a fish, an invertebrate, and another sensitive species), saltwater data for the California grunion (*Leuresthes tenuis*) were used to meet the third taxa requirement. Three of the five diazinon taxa requirements were satisfied: a species in the family Salmonidae (*Salvelinus fontinalis*), a warm water fish (*P. promelas)*, and a planktonic crustacean (*Daphnia magna*). These three chronic values were each paired with appropriate corresponding acute toxicity values, which satisfied the three family requirements for the ACR procedure. Three of the malathion chronic toxicity values were paired with corresponding acute toxicity values (*Gila elegans*, *Ptychocheilus lucius*, *Jordanella floridae*). Since only fish data were available, the invertebrate taxa requirement was not satisfied. A default ACR of 12.4 was included in the malathion ACR data set to compensate for the lack of invertebrate data (TenBrook et al. 2010).

An SMACR was calculated by dividing the acute LC_{50} by the chronic maximum acceptable toxicant concentration (MATC) for a given species (Tables 9–11). The final ACR for malathion of 11.8 was calculated as the geometric mean of all the SMACRs in the data set and one default ACR (Table 11). The SMACRs varied by

Table 9 Calculation of the final acute-to-chronic ratio for chlorpyrifos

Species	LC_{50} (μg/L)	Reference	Chronic end point	MATC (μg/L)	Reference	ACR (LC_{50}/MATC)
Ceriodaphnia dubia	0.0396	CDFG (1999)	Mortality	0.040	CDFG (1999)	1.0
C. dubia	0.0396	CDFG (1999)	Reproduction	0.040	CDFG (1999)	1.0
C. dubia				Species mean ACR		1.0[a]
Pimephales promelas	140	Jarvinen and Tanner (1982)	Weight	2.3	Jarvinen and Tanner (1982)	61[b]
Leuresthes tenuis[c]	1.0	Borthwick et al. (1985)	Growth	0.2	Goodman et al. (1985)	5.0[a]
					Final ACR	2.2

[a] Values used in calculation
[b] Excluded; >10× the ACR for cladocerans whose species mean acute value is nearest the fifth percentile of 0.026 μg/L
[c] Saltwater species included in ACR calculation; study rated relevant and reliable in every other respect

Table 10 Calculation of the species mean acute-to-chronic ratios for diazinon

Species	LC_{50} (μg/L)	Chronic end point	MATC (μg/L)	Reference	ACR (LC_{50}/MATC)
Daphnia magna	0.52	21 days mortality/immobility	0.23	Surprenant (1988)	2.3[a]
Pimephales promelas	7,800	274 days mortality	41	Allison and Hermanutz (1977)	190
P. promelas	6,900	32 days weight	67	Jarvinen and Tanner (1982)	103
P. promelas				Species mean ACR	140[b]
Salvelinus fontinalis	723	173 days mortality	6.8	Allison and Hermanutz (1977)	106[b]

[a] Value used in calculation
[b] Excluded; >10× the ACR for cladocerans whose species mean acute value is nearest the fifth percentile of 0.026 μg/L

more than a factor of 10, and there was an increasing trend of SMACRs as the SMAVs increased for both chlorpyrifos and diazinon. To utilize the most relevant values for these two compounds, the final multispecies ACRs were calculated as the geometric mean of the SMACRs for species whose SMAVs were close to the acute value. For chlorpyrifos, the species with an SMAV closest to the acute median fifth percentile was *C. dubia* (SMAV = 0.0396 μg/L), with an SMACR

Table 11 Calculation of the final acute-to-chronic ratio for malathion

Species	LC_{50} (μg/L)	Reference	Chronic end point	MATC (μg/L)	Reference	ACR (LC_{50}/MATC)
Gila elegans	15,300	Beyers et al. (1994)	Growth	1,407	Beyers et al. (1994)	10.8
Jordanella floridae	349	Hermanutz (1978)	Growth	9.68	Hermanutz (1978)	36.0
Ptychocheilus lucius	9,140	Beyers et al. (1994)	Growth	2,428	Beyers et al. (1994)	3.7
Invertebrate	Default ACR					12.4
					Final ACR	11.8

All values were used in the calculation

of 1.0. The SMACR for *L. tenuis* was within a factor of 10 of this, so it was also included in the calculation, to give a final ACR of 2.2 for chlorpyrifos. The species with an SMAV closest to the acute median fifth percentile for diazinon was *D. magna* (SMAV = 0.52 μg/L), with an SMACR of 2.3. None of the other SMACRs were within a factor of 10 of this value; therefore, the final multispecies ACR was 2.3 for diazinon. To calculate the chronic criteria, the recommended acute values (median fifth percentiles) were divided by the final ACRs. The diazinon chronic criterion is adjusted downward later in this chapter based on comparisons to data for sensitive species, threatened and endangered species, and ecosystem-level effects.

Chlorpyrifos chronic criterion calculated with the acute median fifth percentile estimate:

Fifth percentile, 50% confidence limit: 0.0243 μg/L

$$\begin{aligned}\text{Chronic criterion} &= \frac{\text{Acute fifth percentile}}{\text{ACR}},\\ &= \frac{0.0243\ \mu\text{g/L}}{2.2},\\ &= 0.01\ \ \mu\text{g/L}.\end{aligned}$$

Diazinon chronic criterion calculated with the acute median fifth percentile estimate:

Fifth percentile, 50% confidence limit: 0.349 μg/L

$$\begin{aligned}\text{Chronic criterion} &= \frac{0.349\mu\text{g/L}}{2.3},\\ &= 0.2\ \ \mu\text{g/L}.\end{aligned}$$

Malathion chronic criterion calculated with the acute median fifth percentile estimate:

Fifth percentile, 50% confidence limit: 0.333 μg/L

$$\text{Chronic criterion} = \frac{0.333\mu g/L}{11.80}, \\ = 0.028 \quad \mu g/L.$$

6 Bioavailability

Chlorpyrifos, diazinon, and malathion have moderate to high octanol–water partition coefficients (log K_{ow}s of 4.96, 3.81, and 2.84, respectively), indicating that sorption to sediment or dissolved organic matter could reduce bioavailability of these compounds, but few studies were identified regarding this topic. One relevant study reported that the bioavailability of diazinon to *D. magna* was inversely proportional to the dissolved humic material concentration, presumably because diazinon was binding to the dissolved humic material (Steinberg et al. 1993). The results of a study by Phillips et al. (2003) are less clear; they found that fewer walleye survived exposure to chlorpyrifos–humic acid (HA) complexes than to either HA alone or chlorpyrifos alone, and no differences were seen in cholinesterase inhibition between chlorpyrifos–HA and aqueous chlorpyrifos exposures. The uptake of malathion from spiked sediment by freshwater snails (*Stagnicola* sp.) occurred quickly (up to 0.1 μg/g in 36 h), indicating that malathion was bioavailable in sediment (Martinez-Tabche et al. 2002). With such little and inconsistent information regarding the toxicity of the three selected organophosphates when bound or complexed, the bioavailability of these compounds is not predictable without site-specific, species-specific data. Until such data is available, it is recommended that criteria compliance should be determined based on whole water concentrations.

7 Chemical Mixtures

Mixtures of OP pesticides are common in waterways of the USA (Gilliom 2007) and several studies have demonstrated that mixtures of organophosphates exhibit additive toxicity (Bailey et al. 1997; Hunt et al. 2003; Lydy and Austin 2005; Rider and LeBlanc 2005). Because all OPs have the same mode of action, concentration addition is a valid assumption. To determine criteria compliance when a mixture of OPs is present, either the toxic unit or relative potency factor approach can be used (TenBrook et al. 2010). However, concentration addition may underestimate mixture toxicity of OPs in some cases. For example, malathion had a synergistic,

rather than additive effect on acetylcholinesterase (AChE) activities in Coho salmon (*Oncorhynchus kisutch*; Laetz et al. 2009) when combined with either chlorpyrifos or diazinon. Many fish species die after high rates of acute brain AChE inhibition (>70–90%; Fulton and Key 2001), but this study did not provide a way to quantitatively incorporate these nonadditive interactions into compliance.

Several researchers reported greater than additive toxicity of both chlorpyrifos and diazinon in combination with triazine herbicides (Anderson and Lydy 2002; Belden and Lydy 2000; Jin-Clark et al. 2002; Lydy and Austin 2005) while additive effects were reported for a mixture of atrazine and malathion (Belden and Lydy 2000). Multiple interaction coefficients (also called synergistic ratios) were available for atrazine with either chlorpyrifos or diazinon over a range of concentrations, so these values were used to derive quantitative relationships. The interaction coefficient (K) is calculated by dividing the concentration that affects 50% of the exposed population (EC_{50}) for the pesticide alone by the EC_{50} in the presence of a nontoxic concentration of the synergist. When K is greater than unity, a synergistic interaction is indicated, and when K is less than unity an antagonistic interaction is indicated. All available Ks for chlorpyrifos and diazinon are given in Tables S4 and S5 (Supporting Material http://extras.springer.com/).

Least squares regressions of the *Chironomus tentans* and *Hyalella azteca* combined diazinon data resulted in a significant relationship between atrazine concentration and K ($p<0.001$; JMP IN v.5.1.2; JMP 2004):

$$K = 0.0095\ [\text{atrazine}] + 1.05\ (r^2 = 0.87, p = 0.0007).$$

To determine compliance or to assess potential for harm, Eq. 4 may be used to establish the effective concentration of diazinon in the presence of atrazine:

$$C_a = C_m\ (K), \tag{3}$$

where C_a is the adjusted, or effective, concentration of chemical of concern (i.e., diazinon); C_m is the concentration measured for chemical of concern (i.e., diazinon); and K is the coefficient of interaction, calculated for the synergist concentration in water.

The effective concentration may be compared to diazinon criteria or may be used in one of the additivity models.

Least squares regressions of the combined *C. tentans* and *H. azteca* chlorpyrifos data also resulted in a significant relationship between atrazine concentration and Ks ($p<0.005$; JMP IN v.5.1.2; JMP 2004), but the r^2 is not very high ($r^2 = 0.52$); so the two species were considered independently. For *C. tentans*, the relationship between K and atrazine concentration was not significant ($p>0.05$), but for *H. azteca* the following relationship was determined:

$$K = 0.009\ [\text{atrazine}] + 1.12\ (r^2 = 0.94, p = 0.03).$$

This relationship should be used with caution because of the small data set ($n = 4$) and the fact that three of the four values are from the same study. The lack of a significant relationship between atrazine concentration and *K*s for *C. tentans* may be due to differences between studies (there were not enough data to evaluate the experiment effect statistically). Since *H. azteca* is among the most sensitive species in the data set, it is worthwhile to use Eq. 4 to estimate *K*s for various levels of atrazine co-occurring with chlorpyrifos. To assess potential for harm, Eq. 4 may be used to estimate the effective concentration of chlorpyrifos in the presence of atrazine, which may be compared to chlorpyrifos criteria or may be used in one of the additivity models.

The toxicity of mixtures of chlorpyrifos, diazinon, and/or malathion has been documented to occur with many other chemicals (Ankley and Collyard 1995; Bailey et al. 2001; Banks et al. 2003, Belden and Lydy 2006; Denton et al. 2003; Hermanutz et al. 1985; Macek 1975; Mahar and Watzin 2005; Overmyer et al. 2003; Rawash et al. 1975; Solomon and Weis 1979; Van Der Geest et al. 2000; Venturino et al. 1992), but multispecies synergistic ratios are not available; so these interactions cannot be incorporated into criteria compliance.

8 Water Quality Effects

Several studies have shown increased toxicity of chlorpyrifos and diazinon with increased temperature (Humphrey and Klumpp 2003; Johnson and Finley 1980; Landrum et al. 1999; Lydy et al. 1999; Macek et al. 1969; Mayer and Ellersieck 1986; Patra et al. 2007). Conversely, one toxicity study on malathion demonstrated decreased toxicity with increasing temperature due to increased degradation of malathion (Keller and Ruessler 1997). However, none of these studies were rated RR, so they were not used to quantify effects of temperature on toxicity in criteria compliance. In addition, two studies showed no effect of pH on toxicity (Keller and Ruessler 1997; Landrum et al. 1999).

9 Sensitive Species

The criteria derived using the acute median fifth percentiles were compared to toxicity values for the most sensitive species in both the acceptable (RR) and supplemental (RL, LR, LL) data sets (Tables S6–S8, Supporting Material http://extras.springer.com/) to ensure that all species are adequately protected in an ecosystem. The malathion criteria are below all available toxicity data, so there is no indication of underprotection of sensitive species in the data set. There is one measured chlorpyrifos chronic value that is just under the derived chronic criterion, which is an MATC of 0.0068 μg/L for *Mysidopsis bahia* (Sved et al. 1993); however, this is a saltwater species and there were significant effects observed in the solvent control.

The estimated chronic value of 1 ng/L for *N. mercedis* (CDFG 1992a, d) is below the calculated criterion, but the chronic criterion should not be adjusted unless the estimated value is supported by measured data.

The lowest value in the acute diazinon RR data set is a value for *C. dubia* of 0.21 μg/L (Table 5), which is almost identical to the calculated criterion of 0.2 μg/L. This value for *C. dubia* is the lowest compared to ten others used for criteria derivation (0.26, 0.29, 0.32, 0.33, 0.33, 0.35, 0.38, 0.436, 0.47, 0.507, SMAV is 0.34 μg/L). There is also a similar value in the supplemental data set of 0.25 μg/L (Table S7, Supporting Material http://extras.springer.com/). In this case, downward adjustment of the acute criterion is not recommended because the *C. dubia* SMAV of 0.34 μg/L indicates that the acute criterion of 0.2 μg/L is protective of this species.

The lowest measured SMCV in the diazinon data set rated RR is 0.23 μg/L for *D. magna* (Surprenant 1988), which is just above the chronic criterion (0.2 μg/L). This is the only highly rated value for *D. magna* or any cladoceran species. The supplemental data set (Table S7, Supporting Material http://extras.springer.com/) contains 6 MATCs for *D. magna* that are approximately equivalent to the criterion (0.16, 0.16, 0.22, 0.24, 0.24, and 0.24 μg/L; Dortland 1980; Fernández-Casalderrey et al. 1995; Sánchez et al. 1998) and 12 MATCs for *D. magna* of 0.07 μg/L that are below the chronic criterion (Sánchez et al. 1998, 2000). These studies did not rate highly because test parameters were not well-documented, but had no obvious flaws in study design or execution. Sánchez et al. (2000) reported the concentrations incorrectly in their original report as ng/L instead of μg/L, which was confirmed via correspondence with the authors. This was a multigenerational test, which would be expected to be more sensitive than the test rated RR that only monitored reproduction in one generation (Surprenant 1988). The only other chronic value for a cladoceran is 0.34 μg/L for a *C. dubia* 7-day test (Norberg-King 1987) in the supplemental data set. *C. dubia* is the most sensitive species in the acute distribution; thus, this gap in the RR chronic data set may lead to an underprotective criterion. The supplemental data set also contains a toxicity value of 0.13 μg/L for *H. aztec*a, which is below the chronic criterion, but the end point in this study does not have an established connection to survival, growth, or reproduction.

Based on this evidence, the diazinon chronic criterion, as calculated, may be underprotective of cladocerans; therefore, the next lowest distributional estimate was used to calculate the chronic criterion. Using the lower 95% confidence limit of the fifth percentile to calculate the chronic criterion yielded a recommended chronic criterion of 0.07 μg/L for diazinon.

Diazinon chronic criterion calculated with the lower 95% confidence interval of the acute fifth percentile estimate:

Fifth percentile, lower 95% confidence limit: 0.155 μg/L

$$\begin{aligned}\text{Chronic criterion} &= \frac{0.155\mu g/L}{2.3},\\ &= 0.07 \ \ \mu g/L.\end{aligned}$$

10 Ecosystem-Level Studies

Multispecies studies may provide more realistic exposure conditions than single-species laboratory studies; therefore, the results of these studies were compared to the derived chronic criteria to ensure that the criteria are protective of ecosystems. Twenty-one chlorpyrifos studies, four diazinon studies, and two malathion studies on the effects on microcosms, mesocosms, and model ecosystems were rated acceptable (R or L reliability rating, Table S9, Supporting Material http://extras.springer.com/). In the two acceptable malathion studies, the authors applied concentrations well above the chronic criterion and did not calculate ecosystem-level NOECs (Kennedy and Walsh 1970; Relyea 2005); thus, no information was reported by these authors that indicates that the chronic malathion criterion is underprotective of organisms in ecosystems.

Many of the chlorpyrifos studies involved one-time application at levels well above the calculated criteria (Brock et al. 1992a, b, 1993; Cuppen et al. 1995; Kersting and Van Wijngaarden 1992; Rawn et al. 1978; Van Breukelen and Brock 1993; Van Donk et al. 1995; Van Wijngaarden and Leeuwangh 1989). The authors of several other chlorpyrifos studies reported effects with exposures ranging from 0.1 to 2 μg/L, which are 1–2 orders of magnitude higher than the derived criteria (Eaton et al. 1985; Giddings et al. 1997; Macek et al. 1972; Pusey et al. 1994; Van Den Brink et al. 1995; Van Wijngaarden 1993; Ward et al. 1995). Four studies provided community NOECs for chlorpyrifos, which are the most relevant values to compare to the derived chronic criterion (0.01 μg/L). Van Wijngaarden et al. (1996) reported 7-day mesocosm EC_{50}s ranging from 0.1 μg/L for *Mystacides* spp. to 2.8 μg/L for *Ablabesmyia* spp. In the same study, 7-day EC_{10}s were reported, which are sometimes equated to MATCs, and the EC_{10}s values ranged from 0.01 μg/L for *Mystacides* spp. to 2.7 μg/L for *Ablabesmyia* spp. indicating that the chronic criterion would likely be protective of *Mystacides* spp. Van Wijngaarden et al. (2005) and Van Den Brink et al. (1996) both reported community NOECs of 0.1 μg/L in laboratory microcosms and outdoor experimental ditches. In various measures of ecosystem metabolism, Kersting and Van Den Brink (1997) reported ecosystem NOECs ranging from <0.1 to 6 μg/L chlorpyrifos based on system oxygen concentration, system pH, gross production (mg O_2/L-d), and respiration (mg O_2/L-d). The authors acknowledged that the latter two significant findings may be due to a Type II error.

Werner et al. (2000) performed laboratory toxicity tests and toxicity identification evaluations on samples collected from the Sacramento-San Joaquin River Delta. Six filtered samples exhibiting significant mortality in ≤4 days had chlorpyrifos concentrations ranging from 0.09 to 0.52 μg/L (with no other pesticides detected). Two filtered samples exhibiting chronic toxicity (significant mortality in >4 days) had chlorpyrifos concentrations ranging from 0.058 to 0.068 μg/L (with no other pesticides detected). Hundreds of other samples did not exhibit toxicity, implying that they had chlorpyrifos levels below those found in the samples that induced toxicity. In a treated pond study by Siefert (1984), the first two applications of a

granular formula resulted in variable measured chlorpyrifos concentrations ranging from nondetects to 0.30 µg/L and reduction or elimination of seven species of cladocerans and benthic invertebrates. Unfortunately, there is no way to determine the no-effect concentration in this study. However, one of the most sensitive species in the study was *H. azteca*, which was included in the criteria derivation. Given the results of these studies, it appears that acute and chronic criteria of 0.01 µg/L are protective of organisms in ecosystems.

The four acceptable diazinon ecosystem studies did not indicate that the derived criteria are underprotective of any tested species. Giddings et al. (1996) applied a range of diazinon concentrations (2.0–500 µg/L) to aquatic microcosms and reported a community-level LOEC of 9.2 µg/L and a community-level NOEC of 4.3 µg/L (70-day averages). Arthur et al. (1983) used three outdoor experimental channels to assess the effect of a 12-week exposure to diazinon using a low treatment of 0.3 µg/L and high treatment of 6 µg/L (nominal concentrations), followed by 4 week at higher concentrations (12 and 30 µg/L, respectively). Effects on amphipods and insects were seen in the lowest treatment with lower numbers of mayflies and damselflies emerging from treated channels. Moore et al. (2007) reported that survival of *H. azteca* was affected after exposure to leaf litter contaminated with diazinon (measured residues of ≥60 µg/kg). The concentrations tested in these ecosystem studies are all well above the diazinon criteria, except the study by Arthur et al. (1983) that documented effects at 0.3 µg/L, which is only slightly above the chronic criterion derived using the acute median fifth percentile (0.2 µg/L). This study adds support for use of a lower chronic criterion of 0.07 µg/L (derived using the lower 95% confidence interval of the acute fifth percentile).

11 Threatened and Endangered Species

The derived criteria were compared to measured and predicted toxicity values for threatened and endangered species (TES), ensuring that they are protective of these species. TES were those plants and animals listed by the US Fish and Wildlife Service (USFWS 2010) and the California Department of Fish and Game (CDFG 2010a, b).

Two listed salmonid species, *Oncorhynchus mykiss* and *Oncorhynchus tshawytscha*, were included in the acute chlorpyrifos criterion calculation and their SMAVs were well above the final criterion. None of the listed animals or plants are represented in the acceptable acute or chronic diazinon data sets. There are six threatened or endangered species in the acute malathion data set: *G. elegans*, *Lampsilis subangulata*, *Oncorhynchus clarki*, *O. kisutch*, *O. mykiss*, and *P. lucius*. Three of these species are also included in the chronic malathion data set: *G. elegans*, *O. mykiss*, and *P. lucius*. The toxicity values for all of these species are at least two orders of magnitude larger than the derived malathion acute and chronic criteria, indicating that the criteria should be protective of these species.

The supplemental data sets (Tables S6–S8, Supporting Material http://extras.springer.com/) also contain toxicity values for several TES. The chlorpyrifos supplemental data set contains toxicity values for additional listed fish, *O. clarki*, *Notropis mekistocholas*, and *Gasterosteus aculeatus*, which has a listed subspecies (*G. aculeatus williamsoni*). The diazinon supplemental data set contains toxicity values for *N. mekistocholas* and two additional salmonids, *O. clarki* and *O. tshawytscha*, that are all much higher than the derived criteria. Although not as reliable, these data support that the derived criteria are protective of these endangered fish.

Toxicity data for species in the same genus or family as TES were used as surrogates to predict TES toxicity values with the USEPA interspecies correlation estimation software (Web-ICE v. 3.1; Raimondo et al. 2010). *P. promelas* was used as a surrogate to predict toxicity values for 26 TES in the Cyprinidae family and *O. mykiss* and *O. tshawytscha* were used to predict toxicity values for 11 salmonids for chlorpyrifos (Table S10, Supporting Material http://extras.springer.com/). *Gammarus pseudolimnaeus*, *S. fontinalis*, and *P. promelas* were used to predict toxicity values for a total of 41 TES for diazinon (Table S11, Supporting Material http://extras.springer.com/). For malathion, *G. elegans*, *P. promelas*, *P. lucius*, *O. clarki*, *O. kisutch*, *O. mykiss*, and *S. fontinalis* were all used as surrogates (Table S12, Supporting Material http://extras.springer.com/). Based on the available data and estimated values for animals, there is no evidence that the calculated acute and chronic criteria for chlorpyrifos, diazinon, or malathion are underprotective of TES. However, a caveat is that no data were found for effects on federally endangered cladocerans or insects, or acceptable surrogates (i.e., in the same family), which are the most sensitive species in the data sets.

There was one algal study (the only plant value) that rated RR for diazinon, but no algae species are on the federal endangered, threatened, or rare species lists. For chlorpyrifos and malathion, none of the plant studies identified rated RR, and none of the studies were for plants on the state or federal endangered, threatened, or rare species lists. Plants are relatively insensitive to OPs, so the calculated criteria should be protective of this taxon.

12 Bioaccumulation

Bioaccumulation is defined as accumulation of chemicals in an organism from all possible exposure routes, e.g., partitioning from the water and/or intake via food. A bioaccumulation factor (BAF) is a measure of the total accumulation by all possible exposure routes and is defined here as the ratio of the concentration in an organism and the concentration in surrounding media ($BAF = C_{organism}/C_{media}$). When the chemical accumulates up the food chain from prey to predator, the phenomenon is called biomagnification. The potential for bioaccumulation was assessed to ensure that if concentrations of the selected OPs are at or below the derived water quality criteria, they will not lead to toxicity in terrestrial wildlife via bioaccumulation.

Chlorpyrifos and diazinon have similar physical–chemical characteristics, including molecular weights <1,000 and log-normalized octanol–water partition coefficients (log K_{ow}) >3.0 L/kg, which indicates that both compounds have the potential to bioaccumulate. Malathion has a lower log K_{ow} of 2.84 L/kg and it does not appear to bioaccumulate from the available studies, so bioaccumulative potential was not assessed for malathion. Assessment for bioaccumulation in humans was not done because there is low potential and there are no tolerances or US Food and Drug Administration (USFDA) action levels for any of the three compounds in fish tissue (USFDA 2000).

Uptake of chlorpyrifos and diazinon from water has been measured in a number of studies and bioconcentration factors (BCFs) vary widely among different species (Table S13, Supporting Material http://extras.springer.com/). Most studies disclosed that diazinon is relatively quickly eliminated from tissues after placing organisms in clean water (3–8 days), and that a steady state is reached within a few days (Deneer et al. 1999; El Arab et al. 1990; Kanazawa 1978; Keizer et al. 1991; Palacio et al. 2002; Sancho et al. 1993; Tsuda et al. 1990, 1995, 1997). Varó et al. (2002) reported biomagnification factors (BMFs), which are a measure of uptake from food items or prey, of 0.7–0.3 (decreasing with increasing time of exposure) for chlorpyrifos in a two-level food chain experiment with *Artemia* spp., and the fish *Aphanus iberius*. BMFs of less than 1.0, and the fact that the BMFs decrease over time, indicate that chlorpyrifos does not biomagnify. Varó et al. (2002) suggest that this is due to the ability of fish to biotransform chlorpyrifos and to the moderate log K_{ow} of chlorpyrifos. Data suggests only slight bioaccumulation of malathion (Forbis and Leak 1994; Kanazawa 1975; Olvera-Hernandez et al. 2004; Tsuda et al. 1989, 1990). For the freshwater snail (*Stagnicola* sp.), uptake of malathion occurred quickly (up to 0.1 μg/g in 36 h); however, the short elimination half-life ($t_{1/2\_e}$ = 46.79 h) led to the conclusion that this compound was not being stored in snails (Martinez-Tabche et al. 2002).

Since chlorpyrifos and diazinon have properties indicating bioaccumulative potential, the aqueous concentrations of these compounds required to cause toxicity due to bioaccumulation in mallard ducks (Table S14, Supporting Material http://extras.springer.com/) was estimated, and then compared to the derived criteria. For diazinon, no BAFs or BMFs were identified in the literature. A BAF can be calculated as the product of a BCF and a BMF (BAF = BCF × BMF). For diazinon, a BCF of 188 L/kg for *Poecilia reticulata* (Keizer et al. 1993) and a default BMF of 2, based on the log K_{ow} of diazinon (TenBrook et al. 2010), were used to estimate a BAF. A conservative aqueous NOEC was calculated by dividing the lowest dietary NOEC for mallard duck (8.3 mg/kg feed; USEPA 2004a) by the estimated BAF.

$$\mathrm{NOEC}_{\mathrm{water}} = \frac{\mathrm{NOEC}_{\mathrm{oral\_predator}}}{\mathrm{BCF}_{\mathrm{food\_item}} \times \mathrm{BMF}_{\mathrm{food\_item}}}. \quad (4)$$

The resulting $NOEC_{water}$ for diazinon is 22.1 μg/L, which is well above the chronic criterion of 0.07 μg/L, which indicates that diazinon at concentrations equal to or below the chronic criterion will not likely cause harm via bioaccumulation.

A similar calculation was performed with chlorpyrifos data. The highest nonlipid-based BCF (1,700 L/kg; Jarvinen et al. 1983), the highest reported BMF for chlorpyrifos of 0.7 (Varó et al. 2002), and the lowest dietary NOEC for a mallard of 25 mg/kg (USEPA 2002) were used in this analysis to assess a worst-case bioaccumulation scenario. The $NOEC_{water}$ estimated for chlorpyrifos using this data was 21 μg/L. This value is well above both the acute and chronic criteria of 0.01 μg/L; therefore, the criteria are likely to be protective of terrestrial animals feeding on aquatic organisms.

13 Harmonization with Air or Sediment Criteria

The maximum allowable concentration of these compounds in water may impact life in other environmental compartments through partitioning. Chlorpyrifos, diazinon, and malathion have all been observed in the atmosphere and shown to be transported via rain and fog (Charizopoulos and Papadopoulou-Mourkidou 1999; Glotfelty et al. 1990; McConnell et al. 1998; Scharf et al. 1992; Zabik and Seiber 1993). However, there are no federal or California state air quality standards for any of the compounds (CARB 2010; USEPA 2009b), so no estimates of the partitioning from water to the atmosphere were made. There are sediment guidelines available for diazinon and malathion that were estimated based on equilibrium partitioning from water using the USEPA water quality criteria (USEPA 2004b); these values are not useful for estimating back to a water concentration because that would simply undo the original partitioning estimate. No other federal or California state sediment quality standards were identified for these compounds (CDWR 1995; Ingersoll et al. 2000; NOAA 1999; USEPA 2009a); thus, partitioning between water and sediment was not predicted for the water quality criteria.

14 Assumptions, Limitations, and Uncertainties

The assumptions, limitations, and uncertainties involved in criteria generation are included to inform environmental managers of the accuracy and confidence in criteria. The UCDM discusses these points for each section as different procedures were chosen and includes a review of all of the assumptions inherent in the methodology (TenBrook et al. 2010). Additionally, the different calculations of distributional estimates for chlorpyrifos and diazinon included in Sect. 4 of this article may be used to consider the uncertainty in the resulting acute criteria.

For all three compounds, a major limitation was lack of chronic data, especially for the most sensitive species, cladocerans and other invertebrates. For malathion,

there were inadequate invertebrate data for the ACR, so a default value was included. For diazinon, the chronic criterion calculated with the ACR and acute median fifth percentile estimate was not clearly protective of sensitive invertebrates, so the next lowest distributional estimate was used to adjust the criterion downward. Another major limitation was that the malathion acute data set was lacking the benthic crustacean taxa requirement, which precluded the use of an SSD. Instead, the final acute criterion was derived using an assessment factor. When additional highly rated data is available, particularly chronic data for invertebrates, or data regarding temperature effects or mixtures, the criteria should be recalculated to incorporate new research.

15 Comparison to Existing Criteria

There are existing state and federal water quality criteria or objectives for both chlorpyrifos and diazinon to which the criteria derived in this article can be compared. The USEPA and the CDFG have both derived water quality criteria for chlorpyrifos and diazinon using the USEPA (1985) method. The agencies derived criteria at different times, and therefore used different data sets; so the results are not identical. The USEPA (1985) criteria derivation method has been the standard used in the USA, and produces robust and reliable criteria, partly because of the large amount of data required to derive criteria following this method. One goal of creating the UCDM was to create a methodology for use in the future that had less data requirements and more flexible statistical methods than those used by the USEPA method, but which still produced criteria that are as robust and reliable as those produced by the USEPA (1985) methodology.

The final UCDM acute and chronic chlorpyrifos criteria (both 0.01 μg/L) are lower than those derived by the USEPA (1986a) of 0.084 and 0.041 μg/L, respectively, but are closer to those derived by the CDFG of 0.025 and 0.015 μg/L, respectively (Siepmann and Finlayson 2000). These three acute and chronic criteria all differ by less than a factor of 10, but there are four SMAVs in the UCDM acute data set that are below the USEPA acute criterion, and one SMCV below the USEPA chronic criterion, indicating that these species would not be protected by the USEPA criteria. After a detailed comparison of the data sets and calculation methodologies used by the different agencies (Appendix A, Supporting Material http://extras.springer.com/), it was concluded that the primary cause of differing results was the inclusion of studies performed at later dates, as described above.

The final UCDM diazinon acute criterion of 0.2 μg/L is slightly higher than the USEPA diazinon acute criterion of 0.17 μg/L (USEPA 2005) while the final UCDM diazinon chronic criterion of 0.07 μg/L is lower than the USEPA chronic criterion of 0.17 μg/L (USEPA 2005). The CDFG acute and chronic water quality criteria (0.16 and 0.10 μg/L, respectively) are also very similar to those calculated using

the UCDM (Siepmann and Finlayson 2000). The acute criteria from the USEPA, the CDFG, and the UCDM all differ by less than a factor of 2, and part of the difference is because only one significant figure was reported by the UCDM while two are reported by the USEPA and the CDFG. Based on the UCDM data sets, the diazinon criteria from the various agencies all appear to be protective of aquatic ecosystems. Criteria calculated using the UCDM and the EPA method are likely similar because the criteria calculation procedures for chemicals that have larger data sets are similar in the two methods. Many of the novel aspects to the UCDM were added to enable criteria generation for compounds with more limited data sets or to incorporate other factors that affect toxicity.

In the USA, the only existing aquatic life water quality criterion identified for malathion was not derived using the USEPA (1985) methodology. Instead, a chronic criterion of 100 ng/L was calculated for malathion by applying an application factor of 0.1 to the 96-h LC_{50} data for the most sensitive species (*Gammarus lacustris*, *Gammarus fasciatus*, and *Daphnia pulex*), which were approximated as 1,000 ng/L (USEPA 1986b). This EPA chronic criterion is approximately a factor of 3.6 greater than the UCDM chronic criterion of 28 ng/L. The EPA chronic criterion would not be protective of the most sensitive species in the current UCDM data set, *D. magna* (MATC = 77 ng/L).

The UCDM criteria were also compared to criteria, or analogous values, derived by other countries. Maximum permissible concentrations (MPCs) of 0.0028, 0.037, and 0.013 μg/L for chlorpyrifos, diazinon, and malathion, respectively, were derived in the Netherlands using a statistical extrapolation method (Crommentuijn et al. 2000). MPCs are analogous to chronic criteria, and these MPCs are all lower than the UCDM chronic criteria for these compounds, which may, in part, be because the Dutch method uses NOECs instead of MATCs in their distribution. There are short-term (acute) and long-term (chronic) Canadian water quality guidelines for the protection of aquatic life for chlorpyrifos of 0.02 and 0.002 μg/L, respectively (CCME 2008). The short-term guideline was derived using an SSD while the long-term guideline was derived by applying a safety factor of 20 to the lowest acute toxicity value (0.04 μg/L for *H. azteca*). This safety factor may be overprotective because paired acute and chronic data indicate that acute and chronic toxicity occur at similar concentrations. The UK has existing environmental quality standards for diazinon, and also newly proposed values (UKTAG 2008). The existing short-term (acute) and long-term (chronic) environmental quality standards are 0.1 and 0.03 μg/L, respectively, while the proposed values are 0.02 and 0.01 μg/L, respectively. The proposed short-term value was derived by applying a safety factor of 10 to the lowest LC_{50} of 0.2 μg/L for *G. fasciatus* and the proposed long-term value was derived by applying an assessment factor of 10 to the NOEC of 0.1 μg/L for Atlantic salmon. Both the existing and proposed environmental quality standards are lower than those derived via the UCDM, but it appears that they used data not included in the UCDM data sets.

16 Comparison to the USEPA 1985 Method

The main cause for differences between criteria derived by different agencies is that different data sets were used, primarily because more studies are undertaken and completed as time passes. To compare only the SSD calculation methods, example criteria were generated for chlorpyrifos, diazinon, and malathion using the USEPA (1985) criteria derivation methodology with the data set gathered for this article. The USEPA acute methods have three additional taxa requirements beyond the five required by the SSD procedure of the UCDM. They are:

1. A third family in the phylum Chordata (e.g., fish, amphibian)
2. A family in a phylum other than Arthropoda or Chordata (e.g., Rotifera, Annelida, Mollusca)
3. A family in any order of insect or any phylum not already represented

These three additional requirements were all met for diazinon and example criteria are calculated below. The chlorpyrifos data set does not contain a family in a phylum other than Arthropoda or Chordata. However, the CDFG has calculated criteria for compounds with incomplete data sets if the missing taxa requirements are known to be relatively insensitive to the compound of interest. Data in the supplemental data set shows that mollusks are relatively insensitive to chlorpyrifos exposure (LC_{50}s>94 μg/L), so example criteria were calculated. The three additional taxa requirements were met for malathion, but the malathion data set does not contain a benthic invertebrate; so it is still deficient. Data in the supplemental data set shows that benthic crustaceans have moderate to high sensitivity to malathion exposure (LC_{50}s range from 0.5 to 290 μg/L for seven benthic species), and without a high-quality study for this important missing datum EPA criteria were not generated for malathion.

Using the log-triangular calculation (following the USEPA 1985 guidelines) and the acute chlorpyrifos and diazinon data sets, the following acute criteria were calculated. (Note: USEPA methodology uses *genus* mean acute values while *species* mean acute values are used in the UCDM. Since there is only one species from each genus in Tables 3 and 5, the final data sets would be the same in both schemes.)

	Example acute criterion = Final acute value/2
Chlorpyrifos:	Example final acute value (fifth percentile) = 0.052 μg/L
	Example acute criterion = 0.026 μg/L
Diazinon :	Example final acute value (fifth percentile) = 0.1662 μg/L
	Example acute criterion = 0.083 μg/L

According to the USEPA (1985) method, the criteria were rounded to two significant digits. The chlorpyrifos example acute criterion is higher than the acute criterion calculated by the UCDM (0.01 μg/L) by a factor of 2.6. The diazinon example acute criterion is lower than the acute criterion calculated using the Burr Type III distribution of the UCDM (0.2 μg/L) by approximately a factor of 2.

For the chronic criterion, there are only chlorpyrifos data for three species and the diazinon data set only has four species, which are not enough for the use of an SSD according to either method. The USEPA (1985) methodology contains a similar ACR procedure as the UCDM, to be used when three acceptable ACRs are available. The same three ACRs calculated for the UCDM (Tables 9 and 10) were calculated according to the USEPA (1985) methodology to give a final chlorpyrifos ACR of 2.2 and a final diazinon ACR of 2.3. Chronic criteria are calculated by dividing the final acute value by the final ACR:

Example chronic criterion = Final acute value/Final ACR
Chlorpyrifos example chronic criterion = 0.024 μg/L
Diazinon example chronic criterion = 0.072 μg/L

The chlorpyrifos example chronic criterion is a factor of 2.4 higher than the one recommended by the UCDM. The diazinon example chronic criterion is very similar to the one recommended by the UCDM.

It is anticipated that criteria from the UCDM will be fairly similar to those derived by the USEPA method for chemicals that have larger data sets, since the criteria calculation procedures are similar for such compounds. Many of the novel aspects of the UCDM were added to enable criteria generation for compounds with limited data sets or to incorporate other factors that affect toxicity, such as how to account for mixtures in criteria compliance, which other criteria methodologies do not include.

17 Final Criteria Statements

- Chlorpyrifos: Aquatic life should not be affected unacceptably if the 4-day average concentration of chlorpyrifos does not exceed 0.01 μg/L (10 ng/L) more than once every 3 years on the average and if the 1-h average concentration does not exceed 0.01 μg/L (10 ng/L) more than once every 3 years on the average. Mixtures of chlorpyrifos and other OPs should be considered in an additive manner (see Sect. 7).
- Diazinon: Aquatic life should not be affected unacceptably if the 4-day average concentration of diazinon does not exceed 0.07 μg/L (70 ng/L) more than once every 3 years on the average and if the 1-h average concentration does not exceed 0.2 μg/L (200 ng/L) more than once every 3 years on the average. Mixtures of diazinon and other OPs should be considered in an additive manner (see Sect. 7).
- Malathion: Aquatic life should not be affected unacceptably if the 4-day average concentration of malathion does not exceed 0.028 μg/L more than once every 3 years on the average and if the 1-h average concentration does not exceed 0.17 μg/L more than once every 3 years on average. Mixtures of malathion and other OPs should be considered in an additive manner (see Sect. 7).

18 Summary

A new methodology for deriving freshwater aquatic life water quality criteria, developed by the University of California Davis, was used to derive criteria for three organophosphate insecticides. The UC Davis methodology resulted in similar criteria to other accepted methods, and incorporated new approaches that enable criteria generation in cases where the existing USEPA guidance cannot be used. Acute and chronic water quality criteria were derived for chlorpyrifos (10 and 10 ng/L, respectively), diazinon (200 and 70 ng/L, respectively), and malathion (170 and 28 ng/L, respectively). For acute criteria derivation, Burr Type III SSDs were fitted to the chlorpyrifos and diazinon acute toxicity data sets while an alternative assessment factor procedure was used for malathion because that acute data set did not contain adequate species diversity to use a distribution. ACRs were used to calculate chronic criteria because there was a dearth of chronic data in all cases, especially for malathion, for which there was a lack of paired acute and chronic invertebrate data. Another alternate procedure enabled calculation of the malathion chronic criterion by combining a default ratio with the experimentally derived ratios. A review of the diazinon chronic criterion found it to be underprotective of cladoceran species, so a more protective criterion was calculated using a lower distributional estimate. The acute and chronic data sets were assembled using a transparent and consistent system for judging the relevance and reliability of studies, and the individual study review notes are included. The resulting criteria are unique in that they were reviewed to ensure particular protection of sensitive and threatened and endangered species, and mixture toxicity is incorporated into criteria compliance for all three compounds.

For chlorpyrifos and diazinon, the UCDM generated criteria similar to the long-standing USEPA (1985) method, with less taxa requirements, a more statistically robust distribution, and the incorporation of new advances in risk assessment and ecotoxicology. According to the USEPA (1985) method, the data set gathered for malathion would not be sufficient to calculate criteria because it did not contain data for a benthic crustacean. Benthic crustacean data is also required to use a distributional calculation method by the UCDM, but when data is lacking the UCDM provides an alternate calculation method. The resulting criteria are associated with higher, unquantifiable uncertainty, but they are likely more accurate than values generated using static safety factors, which are currently common in risk assessment.

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Aquatic Life Water Quality Criteria Derived via the UC Davis Method: II. Pyrethroid Insecticides

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1 Introduction

Pyrethroid insecticides are broad spectrum agents that have been widely detected in sediments and surface waters in the USA (Amweg et al. 2006; Budd et al. 2007; Gan et al. 2005; Hladik and Kuivila 2009; Weston et al. 2004). They are hydrophobic compounds that primarily partition to sediments and solid materials in the water column, and exposure to pyrethroid-contaminated sediments has been demonstrated to produce toxicity in the environment (Anderson et al. 2006; Holmes et al. 2008; Phillips et al. 2010; Weston et al. 2004; Weston et al. 2005). Only very low concentrations are found freely dissolved in the aqueous phase, but these pesticides are still of concern to water quality managers because they exhibit toxicity to aquatic organisms at very low concentrations (<1 μg/L). Water quality regulators in the USA are required, under the Clean Water Act (section 303(c)(2)(B)), to provide numeric water quality criteria for priority pollutants that could reasonably be expected to interfere with the designated uses of a state's waters. Numeric water quality criteria are chemical concentrations in water bodies that should protect aquatic wildlife from the toxic effects of those chemicals, if these concentrations are not exceeded. Numeric criteria are derived using existing toxicity data; consequently, criteria calculation is dependent on the availability of these data. In the USA, there are currently no numeric criteria available for the pyrethroids, and many of the available pyrethroid data sets do not meet the requirements of the 1985 US Environmental Protection Agency (USEPA) criteria derivation methodology (USEPA 1985). One of the goals of developing the UC Davis methodology (UCDM) was to be able to derive criteria for compounds that do not meet all of the USEPA (1985) data requirements, such as the pyrethroids.

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The UCDM is an updated water quality criteria derivation methodology that was designed to be more flexible than the USEPA (1985) methodology, and to incorporate the results from new research in environmental toxicology and risk assessment. Like the USEPA (1985) method, the UCDM continues to recommend the use of a species sensitivity distribution (SSD) for criteria calculation, and an acute-to-chronic ratio (ACR) when chronic data are limited. The main procedures of the UCDM that differ from those of the USEPA method are that the UCDM provides for a thorough and transparent study evaluation procedure, a more advanced SSD, alternate procedures if data requirements for the SSD or ACR cannot be met, and a consideration for the toxicity of chemical mixtures. Previous publications have described why there was a need for a new methodology (TenBrook et al. 2009), the rationale behind the development of this new methodology, and detailed instructions for UCDM criteria derivation (TenBrook et al. 2010).

This paper is the second in a series in which water quality criteria were derived for nine pesticides: chlorpyrifos, diazinon, malathion, bifenthrin, cyfluthrin, cypermethrin, λ-cyhalothrin, permethrin, and diuron. In this article, we describe the derivation of water quality criteria for five pyrethroid insecticides (bifenthrin, cyfluthrin, cypermethrin, λ-cyhalothrin, and permethrin) according to the UCDM; we have also extended this review to render it wide ranging and useful as a review of the current knowledge regarding the risk to aqueous ecosystems of the pyrethroids' toxicity.

2 Data Collection and Evaluation

Bifenthrin ((2-methyl[1,1′-biphenyl]-3-yl)methyl (1*R*,3*R*)-rel-3-[(1*Z*)-2-chloro-3,3,3-trifluoro-1-propenyl]-2,2-dimethylcyclopropanecarboxylate), cyfluthrin (cyano(4-fluoro-3-phenoxyphenyl)methyl 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate (unstated stereochemistry)), cypermethrin (cyano(3-phenoxyphenyl) methyl 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate), λ-cyhalothrin ([1α(*S**), 3α (*Z*)]-(±)-cyano-(3-phenoxyphenyl)methyl 3-(2-chloro-3,3,3-trifluoro-1-propenyl)-2,2-dimethylcyclopropanecarboxylate), and permethrin ((3-phenoxyphenyl) methyl 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate) are widely applied pyrethroid insecticides. Bifenthrin and permethrin are type I pyrethroids while cyfluthrin, cypermethrin, and λ-cyhalothrin are type II pyrethroids (containing an α-cyano moiety); the two types are distinguished by slightly different toxicological mechanisms (Breckenridge et al. 2009). These pyrethroids are hydrophobic organic compounds that are moderately persistent (see Tables S1 and S2 of the Supporting Material http://extras.springer.com/). Based on their physical–chemical properties (Table 1), they are likely to partition to sediments from the aqueous phase, and are not likely to volatilize.

Aquatic toxicity effects studies were identified in the peer-reviewed open literature and from unpublished studies submitted to the USEPA and California Department of Pesticide Regulation (CDPR) for bifenthrin (~40), cyfluthrin (~53),

Table 1 Physical–chemical properties of five selected pyrethroids

	Bifenthrin	Cyfluthrin	Cypermethrin	λ-Cyhalothrin	Permethrin
Molecular weight	422.87	434.3	416.3	449.850	391.288
Density (g/mL)	1.21 (geomean, $n = 2$)	1.28[d] (20°C)	1.24[d] (20°C)	1.33 (25°C[d,f])	1.23 (geomean, $n = 2$)
Water solubility (mg/L)	0.001 (geomean, $n = 2$)	0.0023[e] (20°C)	0.004 (geomean, $n = 2$)	0.0047 (geomean, $n = 4$)	0.0057 (geomean, $n = 2$)
Melting point (°C)	69.3 (geomean, $n = 2$)	60[d]	71.2 (geomean of extremes)	48.3 (geomean of extremes)	36.4 (geomean of extremes)
Vapor pressure (Pa)	2.41×10^{-5} (geomean, $n = 2$)	2×10^{-6}[e]	2.87×10^{-7} (geomean, $n = 2$)	2.0×10^{-7} (20°C) (geomean, $n = 3$)	3.74×10^{-6} (geomean, $n = 4$)
Henry's law constant (K_H) (Pa m^3 mol^{-1})	0.24 (geomean, $n = 2$)	0.37[e]	0.0238 (geomean, $n = 3$)	1.96×10^{-2} (geomean, $n = 2$)	0.12 (geomean, $n = 2$)
Log K_{oc}[a]	5.29 (geomean, $n = 7$)	5.09[e] (mean, $n = 4$)	5.49[e] (mean, $n = 3$)	5.52 (geomean, $n = 2$)	5.12 (geomean, $n = 2$)
Log K_{ow}[b]	6.00[c]	5.97[e] (mean, $n = 4$)	6.57 (geomean, $n = 2$)	7.0[d,e,f]	6.3 (geomean, $n = 2$)

[a] Log-normalized organic carbon–water partition coefficient
[b] Log-normalized octanol–water partition coefficient
[c] Sangster Research Laboratories (2010)
[d] Tomlin (2003)
[e] Laskowski (2002)
[f] Mackay et al. (2006)

cypermethrin (~108), λ-cyhalothrin (~65), and permethrin (~155). Each study was reviewed according to the UCDM paradigm to determine the usefulness of these studies for criteria derivation. Studies were divided into three categories to be rated: (1) single-species effects, (2) ecosystem-level studies, and (3) terrestrial wildlife studies.

The UCDM provides a detailed numeric rating scheme for single-species effects studies that assigns (1) a relevance score and (2) a reliability score, which is summarized in the first chapter of this volume (Palumbo et al. (2012)). The possible relevance scores were relevant (R), less relevant (L), or not relevant (N). The studies rated N were deemed irrelevant for criteria derivation, and only the relevant (R) and less relevant (L) studies were evaluated for reliability. For all studies, study details and scoring were summarized in data summary sheets (Supporting Material http://extras.springer.com/). The reliability evaluation assigned possible scores of reliable (R), less reliable (L), or not reliable (N) so that each single-species study is described by a two-letter code, corresponding to the relevance and reliability ratings. The only studies used directly in criteria

calculation were those rated as relevant and reliable (RR), which are summarized in Table 11. Studies that were rated as relevant and less reliable (RL), less relevant and reliable (LR), or less relevant and less reliable (LL) were used to evaluate the derived criteria against data for any particularly sensitive, threatened, or endangered species found in these data sets. Studies that were rated N for either relevance or reliability were not considered in any aspect of criteria derivation.

Multispecies studies conducted in mesocosms, microcosms, and other field and laboratory ecosystems were rated for reliability. The results of the studies that were rated reliable (R) or less reliable (L) were compared to the derived criteria to ensure that they are protective of ecosystems. Studies of the effects of pyrethroids on mallard ducks were rated for reliability using the terrestrial wildlife evaluation. Mallard studies rated as reliable (R) or less reliable (L) were used to consider bioaccumulation of pyrethroids.

3 Data Reduction

As described in Palumbo et al. (2012), multiple toxicity values for a given species in the acceptable data set were combined into one species mean acute value (SMAV) or one species mean chronic value (SMCV). Some data that were rated RR were excluded from the final data set for one or more of the following reasons: flow-through tests are preferred over static tests, a test with a more sensitive life stage of the same species was available, more appropriate exposure durations were available, and tests with more sensitive end points were available (Tables S3–S6, Supporting Material http://extras.springer.com/). For bifenthrin, the final acceptable data sets contain 8 SMAVs and 2 SMCVs (Tables 2 and 3), the final cyfluthrin data sets contain 8 SMAVs and 3 SMCVs (Tables 4 and 5), the final cypermethrin data sets contain 14 SMAVs and 1 SMCV (Tables 6 and 7), the final λ-cyhalothrin data sets contain 20 SMAVs and 2 SMCVs (Tables 8 and 9), and the final permethrin data sets contain 19 SMAVs and 3 SMCVs (Tables 10 and 11).

4 Acute Criterion Calculations

An acute data set must have species representing five taxa to use a SSD to calculate the acute criterion; the five taxa are a warm water fish, a species in the family Salmonidae, a planktonic crustacean, a benthic crustacean, and an insect. The final acute data sets for each of the five pyrethroids (Tables 2, 4, 6, 8, and 10) met the five taxa requirement. Log-logistic distributions were fit to the bifenthrin and cyfluthrin acute data sets using the ETX 1.3 software (Aldenberg 1993) because there were between five and eight SMAVs in each of these data sets. The Burr Type III distribution was fit to the acute λ-cyhalothrin and permethrin data sets because there were more than eight SMAVs in these data sets. Of the three related distributions in the Burr Type III SSD, the Burr III

Table 2 Final acute toxicity data set for bifenthrin

Species	Test type	Meas/ Nom	Chemical grade (%)	Duration (h)	Temp (°C)	End point	Age/size	LC/ EC_{50} (µg/L)	Reference
Ceriodaphnia dubia	SR	Est	97.8	96	24.0–24.7	Mortality	<24 h	0.078	Guy (2000a)
C. dubia	S	Nom	97.0	48	25	Mortality	<24 h	0.142	Wheelock et al. (2004)
Geometric mean								0.105	
Chironomus dilutes	FT	Nom	100	96	23 ± 1	Mortality	Third instar	2.615	Anderson et al. (2006)
Daphnia magna	FT	Nom	88.4	48	20–21	Mortality	<24 h	1.6	Surprenant (1983)
Hyalella azteca	S	Nom	100.0	96	23 ± 1	Mortality	7–14 days	0.0093	Anderson et al. (2006)
H. azteca	SR	Est	98	96	23 ± 1	Mortality	7–14 days	0.0027	Weston and Jackson (2009)
H. azteca	SR	Est	98	96	23 ± 1	Mortality	7–14 days	0.0073	Weston and Jackson (2009)
H. azteca	SR	Est	98	96	23 ± 1	Mortality	7–14 days	0.0080	Weston and Jackson (2009)
H. azteca	SR	Est	98	96	23 ± 1	Mortality	7–14 days	0.0082	Weston and Jackson (2009)
Geometric mean								0.0065	
Lepomis macrochirus	FT	Nom	88.4	96	21–22	Mortality	2.5 g, 8 mm	0.35	Hoberg (1983a)
Oncorhynchus mykiss	FT	Nom	88.4	96	11–12	Mortality	1.0 g, 46 mm	0.15	Hoberg (1983b)
Pimephales promelas	S	Meas	96.2	96	25 ± 1	Mortality	40 days, 0.059 g	0.21	McAllister (1988)
P. promelas	SR	Est	97.8	96	24.0–24.5	Mortality	8 days, 0.0039–0.0052 g	0.78	Guy (2000b)
Geometric mean								0.405	
Procloeon sp.	S	Nom	100.0	48	23 ± 1	Mortality	0.5–1.0 cm	0.0843	Anderson et al. (2006)

All studies were rated relevant and reliable (RR)

Est Toxicity values were calculated based on estimated concentrations (calculated from the recovery of some concentrations), *S* static, *SR* static renewal, *FT* flow through

Table 3 Final chronic toxicity data set for bifenthrin

Species	Test type	Meas/Nom	Chemical grade (%)	Duration (days)	Temp (°C)	End point	Age/size	NOEC (µg/L)	LOEC (µg/L)	MATC (µg/L)	Reference
Daphnia magna	FT	Meas	97.0	21	19–22	Reproduction	<24 h	0.0013	0.0029	0.0019	Burgess (1989)
Pimephales promelas	FT	Meas	96.2	92	25	Mortality	<48 h	0.040	0.090	0.060	McAllister (1988)

All studies were rated relevant and reliable (RR)
FT flow through

Table 4 Final acute toxicity data set for cyfluthrin

Species	Test type	Meas/ Nom	Chemical grade (%)	Duration (h)	Temp (°C)	End point	Age/size	LC/EC_{50} (μg/L) (95% CI)	Reference
Aedes aegypti Rockefellar	S	Nom	93.0	24	25	Mortality	Early fourth instar	1 (1–2)	Rodriguez et al. (2007)
A. aegypti Nicaragua	S	Nom	93.0	24	25	Mortality	Early fourth instar	0.5 (0.5–0.6)	Rodriguez et al. (2007)
A. aegypti Peru	S	Nom	93.0	24	25	Mortality	Early fourth instar	0.3 (0.1–0.4)	Rodriguez et al. (2007)
A. aegypti Geometric mean								0.5	
Ceriodaphnia dubia	S	Nom	97.0	48	25	Mortality	<24 h	0.344 ± 0.041	Wheelock et al. (2004)
C. dubia	S	Nom	99.0	96	21	Mortality	<24 h	0.093 (0.050–0.146)	Yang et al. (2007)
C. dubia	S	Nom	99.0	96	21	Mortality	<24 h	0.136 (0.103–0.185)	Yang et al. (2007)
C. dubia	S	Nom	99.0	96	21	Mortality	<24 h	0.189 (0.112–0.292)	Yang et al. (2007)
C. dubia	S	Nom	99.0	96	21	Mortality	<24 h	0.134 (0.097–0.194)	Yang et al. (2007)
C. dubia	S	Nom	99.0	96	21	Mortality	<24 h	0.170 (0.121–0.229)	Yang et al. (2007)
C. dubia	S	Nom	99.0	96	21	Mortality	<24 h	0.145 (0.105–0.185)	Yang et al. (2007)
C. dubia	S	Nom	99.0	96	21	Mortality	<24 h	0.102 (0.027–0.395)	Yang et al. (2007)
C. dubia	S	Nom	99.0	96	21	Mortality	<24 h	0.159 (0.105–0.234)	Yang et al. (2007)
C. dubia	S	Nom	99.0	96	21	Mortality	<24 h	0.180 (0.127–0.280)	Yang et al. (2007)
Geometric mean								0.155	
Daphnia magna	FT	Meas	98.6	48	19	Mortality	<24 h (first instar)	0.16 (0.14–0.18)	Burgess (1990)
Hyalella azteca	SR	Est	98.0	96	23	Mortality	7–14 days	0.0017 (0.0011–0.0023)	Weston and Jackson (2009)
H. azteca	SR	Est	98.0	96	23	Mortality	7–14 days	0.0023 (0.0009–0.0028)	Weston and Jackson (2009)

(continued)

Table 4 (continued)

Species	Test type	Meas/ Nom	Chemical grade (%)	Duration (h)	Temp (°C)	End point	Age/size	LC/EC_{50} (μg/L) (95% CI)	Reference
H. azteca	SR	Est	98.0	96	23	Mortality	7–14 days	0.0031 (0.0021–0.0046)	Weston and Jackson (2009)
Geometric mean								0.0023	
Lepomis macrochirus	FT	Meas	97.6	96	22	Mortality	0.82 g, 31.8 mm	0.998	Gagliano (1994)
Oncorhynchus mykiss	FT	Meas	97.6	96	11	Mortality	0.92 g, 39 mm	0.209	Gagliano and Bowers (1994)
O. mykiss	FT	Meas	97.6	96	12	Mortality	1.4 g, 43.3 mm	0.302 (0.240–0.432)	Bowers (1994)
Geometric mean								0.2512	
Pimephales promelas	FT	Meas	99.0	96	25	Mortality	30-day old	2.49	Rhodes et al. (1990)
Procambarus clarkii	FT	Meas	97.0	96	20	Mortality	0.59 g, 29 mm	0.062	Surprenant (1990)

All studies were rated relevant and reliable (RR). *Est* Toxicity values were calculated based on estimated concentrations (calculated from the recovery of some concentrations)

S static, *SR* static renewal, *FT* flow through, *95% CI* 95% confidence interval

Table 5 Final chronic toxicity data set for cyfluthrin

Species	Test type	Meas/ Nom	Chemical (%)	Duration (days)	Temp (°C)	End point	Age/ size	NOEC (µg/L)	LOEC (µg/L)	MATC (µg/L)	Reference
Daphnia magna	FT	Meas	94.7	21	20	Reproduction (young/ female/day)	<24 h	0.020	0.041	0.02864	Forbis et al. (1984)
D. magna	FT	Meas	94.7	21	20	Length	<24 h	0.020	0.041	0.02864	Forbis et al. (1984)
Geometric mean										0.02864	
Oncorhynchus mykiss	FT	Meas	96.0	58	9.4	Biomass/chamber	Eggs	0.01	0.0177	0.0133	Carlisle (1985)
O. mykiss	FT	Meas	96.0	58	9.4	Mean weight/fish	Eggs	0.01	0.0177	0.0133	Carlisle (1985)
Geometric mean										0.0133	
Pimephales promelas	FT	Meas	99.0	7–61	25	F_0 survival	Eggs	0.14	0.29	0.20	Rhodes et al. (1990)
P. promelas	FT	Meas	99.0	61–120	25	F_0 survival	Eggs	0.14	0.29	0.20	Rhodes et al. (1990)
P. promelas	FT	Meas	99.0	90	25	F_1 % hatch	Eggs	0.14	0.29	0.20	Rhodes et al. (1990)
P. promelas	FT	Meas	99.0	60	25	F_1 survival	Eggs	0.14	0.29	0.20	Rhodes et al. (1990)
Geometric mean										0.20	

All studies were rated relevant and reliable (RR)
S static, *SR* static renewal, *FT* flow through

Table 6 Final acute toxicity data set for cypermethin

Species	Test type	Meas/ Nom	Chemical grade (%)	Duration (h)	Temp (°C)	End point	Age/size	LC/EC_{50} (μg/L) (95% CI)	Reference
Aedes aegypti	S	Nom	>85	24	18	Mortality	Larvae	1 (0.4–4)	Stephenson (1982)
Asellus aquaticus	S	Nom	>85	24	15	Mortality	3–8 mm	0.2 (0.1–0.4)	Stephenson (1982)
Ceriodaphnia dubia	SR	Nom	>90	48	25	Mortality	<24 h	0.683 ± 0.072	Wheelock et al. (2004)
Chaoborus crystallinus	S	Nom	>85	24	15	Mortality	Larvae	0.2 (0.03–0.4)	Stephenson (1982)
Chironomus thummi	S	Nom	>85	24	15	Immobility	Larvae	0.2 (0.1–0.3)	Stephenson (1982)
Cloeon dipterum	S	Nom	>85	24	15	Mortality	Larvae	0.6 (0.3–1)	Stephenson (1982)
Corixa punctata	S	Nom	>85	24	15	Immobility	Adults	0.7 (0.4–2)	Stephenson (1982)
Daphnia magna	SR	Meas	92.3	48	20	Mortality	<24-h old	0.134 (0.114–0.157)	Ward and Boeri (1991)
D. magna	FT	Nom	95.7	48	20	Mortality	<24-h old	0.1615 (0.1344–0.1917)	Wheat and Evans (1994)
Geometric mean								0.147	
Gammarus pulex	S	Nom	>85	24	15	Mortality	3–8 mm	0.1 (0.08–0.2)	Stephenson (1982)

Gyrinus natator	S	Nom	>85	24	15	Immobility	Adults	0.07 (0.04–0.2)	Stephenson (1982)
Hyalella azteca	SR	Meas	>98	96	23	Mortality	7–14 days	0.0021 (0.0017–0.0025)	Weston and Jackson (2009)
H. azteca	SR	Meas	>98	96	23	Mortality	7–14 days	0.0023 (0.0013–0.0035)	Weston and Jackson (2009)
H. azteca	SR	Meas	>98	96	23	Mortality	7–14 days	0.0031 (0.0020–0.0044)	Weston and Jackson (2009)
H. azteca	SR	Nom	97.0	96	23	Mortality	Adults	0.0036 (0.002–0.0049)	Hamer (1997)
Geometric mean								0.0027	
Oncorhynchus mykiss	FT	Meas	91.5	96	12	Mortality	83-day-old juvenile	0.90 (0.72–1.35)	Vaishnav and Yurk (1990)
Oreochromis niloticus	FT	Meas	98.4	96	25	Mortality	0.6–3.0 g	2	Stephenson et al. (1984)
Piona carnea	S	Nom	>85	24	15	Mortality	Adults	0.05 (0.03–0.08)	Stephenson (1982)

All studies were rated relevant and reliable (RR)

S static, *SR* static renewal, *FT* flow through, *95% CI* 95% confidence interval

Table 7 Final chronic toxicity data set for cypermethrin

Species	Test type	Meas/ Nom	Chemical grade (%)	Duration (days)	Temp (°C)	End point	Age/size	NOEC (µg/L)	LOEC (µg/L)	MATC (µg/L)	Reference
Pimephales promelas	FT	Meas	93.1	60	25	Mortality	<48 h	0.077	0.15	0.11	Tapp et al. (1988)

All studies were rated relevant and reliable (RR)

S static, *SR* static renewal, *FT* flow through, *NR* not reported

Table 8 Final acute toxicity data set for λ-cyhalothrin

Species	Test type	Meas/ Nom	Chemical grade (%)	Duration (h)	Temp (°C)	End point	Age/size	LC_{50}/EC_{50} (μg/L) (95% CI)	Reference
Asellus aquaticus	S	Nom	88.0	48	20	Immobility	NR	0.026 (0.018–0.036)	Hamer et al. (1998)
Brachydanio rerio	FT	Meas	88.7	96	25	Mortality	0.70 g, 36 mm	0.64 (0.48–0.90)	Kent and Shillabeer (1997c)
Ceriodaphnia dubia	S	Nom	97.0	48	25	Mortality	<24	0.200 ± 0.090	Wheelock et al. (2004)
Chaoborus sp.	S	Nom	88.0	48	20	Maintenance of body shape/ equilibrium	Larvae	0.0028 (0.0018–0.0041)	Hamer et al. (1998)
Cloeon dipterum	S	Nom	88.0	48	20	Immobility	Nymph	0.038 (0.023–0.093)	Hamer et al. (1998)
Corixa sp.	S	Nom	88.0	48	20	Immobility	NR	0.030 (0.021–0.042)	Hamer et al. (1998)
Cyclops sp.	S	Nom	88.0	48	20	Immobility	NR	0.300 (0.200–0.460)	Hamer et al. (1998)
Daphnia magna	FT	Meas	94.3	72	20	Mortality	<24 h	0.013 (0.010–0.017)	Farrelly and Hamer (1989)
Gammarus pulex	FT	Meas	99.2	96	15	Immobility	5 mm, >3 weeks	0.0059	Hamer et al. (1985a)
Gasterosteus aculeatus	FT	Meas	87.7	96	12	Mortality	0.41 g, 34 mm	0.40 (0.33–0.50)	Long and Shillabeer (1997a)
Hyalella azteca	S	Nom	88.0	48	20	Immobility	NR	0.0023 (0.0010–0.0078)	Hamer et al. (1998)
Hydracarina (Class)	S	Nom	88.0	48	20	Immobility	NR	0.047 (0.033–0.062)	Hamer et al. (1998)
Ictalurus punctatus	FT	Meas	87.7	96	17	Mortality	1.57 g, 48 mm	0.16 (0.13–0.20)	Long and Shillabeer (1997b)

(continued)

Table 8 (continued)

Species	Test type	Meas/ Nom	Chemical grade (%)	Duration (h)	Temp (°C)	End point	Age/size	LC_{50}/EC_{50} (μg/L) (95% CI)	Reference
Lepomis macrochirus Rafinesque	FT	Meas	99.0	96	21.9	Mortality	Juvenile	0.106 (0.0855–0.140)	Marino and Rick (2001)
L. macrochirus	FT	Meas	98.0	96	22	Mortality	1.51 g, 38.2 mm	0.21 (0.18–0.25)	Hill (1984b)
Geometric mean								0.15	
Leuciscus idus	FT	Meas	88.7	96	12	Mortality	2.15 g, 53 mm	0.078 (0.056–0.11)	Kent and Shillabeer (1997a)
Oncorhynchus mykiss	FT	Meas	99.0	96	12	Mortality	39 mm, 0.52 g	0.19 (0.16–0.20)	Machado (2001)
O. mykiss	FT	Meas	81.5	96	12	Mortality	43 mm, 1.12 g	0.44 (0.38–0.51)	Tapp et al. (1989)
O. mykiss	FT	Meas	98.0	96	12	Mortality	38.3 mm, 0.83 g	0.24 (0.08–0.70)	Hill (1984a)
Geometric mean								0.27	
Ostracoda (class)	S	Nom	88.0	48	20	Immobility	NR	3.300 (2.100–6.600)	Hamer et al. (1998)
Pimephales promelas	FT	Meas	97.0	96	25	Mortality	Larvae	0.360 (0.252–0.765)	Tapp et al. (1990)
P. promelas	FT	Meas	88.7	96	25	Mortality	0.37 g, 28 mm	0.70 (0.38–1.3)	Kent and Shillabeer (1997d)
Geometric mean								0.50	
Poecilia reticulata	FT	Meas	88.7	96	25	Mortality	0.62 g, 33 mm	2.3 (1.8–3.1)	Kent and Shillabeer (1997b)
Procambarus clarkii	SR	Nom	99.1	96	21.7	Mortality	3-month old	0.16 (0.06–0.27)	Barbee and Stout (2009)

All studies were rated relevant and reliable (RR)
S static, *SR* static renewal, *FT* flow through

Table 9 Final chronic toxicity data set for λ-cyhalothrin

Species	Test type	Meas/ Nom	Chemical grade (%)	Duration (days)	Temp (°C)	End point	Age/size	NOEC (μg/L)	LOEC (μg/L)	MATC (μg/L)	Reference
Daphnia magna	FT	Meas	94.3	21	20	Reproduction (young/ female/ day)	<24 h	0.00198	0.00350	0.00263	Farrelly and Hamer (1989)
D. magna	SR	Meas	94.3	21	20	Reproduction (young/ female/ day)	<24 h	0.00375	0.00490	0.00429	Hamer et al. (1985b)
Geometric mean										0.00336	
Pimephales promelas	FT	Meas	97.0	56	25	F_1 survival	F_1 larvae	0.031	0.062	0.044	Tapp et al. (1990)

All studies were rated relevant and reliable (RR)
SR static renewal, *FT* flow through

Table 10 Final acute toxicity data set for permethrin

Species	Test type	Meas/ Nom	Chemical grade (%)	Duration (h)	Temp (°C)	End point	Age/size	LC/EC_{50} (μg/L) (95% CI)	Reference
Ceriodaphnia dubia	S	Nom	99.0	48	25	Mortality	<24 h	0.250 (±119)	Wheelock et al. (2004)
C. dubia	S	Nom	99.3	96	21	Mortality	<24 h	0.652 (0.484–0.856)	Yang et al. (2007)
C. dubia	S	Nom	99.3	96	21	Mortality	<24 h	0.788 (0.545–1.040)	Yang et al. (2007)
C. dubia	S	Nom	99.3	96	21	Mortality	<24 h	0.622 (0.427–0.824)	Yang et al. (2007)
C. dubia	S	Nom	99.3	96	21	Mortality	<24 h	0.772 (0.574–1.013)	Yang et al. (2007)
C. dubia	S	Nom	99.3	96	21	Mortality	<24 h	0.745 (0.568–0.957)	Yang et al. (2007)
C. dubia	S	Nom	99.3	96	21	Mortality	<24 h	0.858 (0.591–1.138)	Yang et al. (2007)
C. dubia	S	Nom	99.3	96	21	Mortality	<24 h	0.571 (0.427–0.740)	Yang et al. (2007)
C. dubia	S	Nom	99.3	96	21	Mortality	<24 h	0.580 (0.407–0.718)	Yang et al. (2007)
C. dubia	S	Nom	99.3	96	21	Mortality	<24 h	0.609 (0.486–0.747)	Yang et al. (2007)
C. dubia	S	Nom	99.3	96	21	Mortality	<24 h	0.570 (0.459–0.689)	Yang et al. (2007)
C. dubia	S	Nom	99.3	96	21	Mortality	<24 h	0.827 (0.669–1.012)	Yang et al. (2007)
C. dubia	S	Nom	99.3	96	21	Mortality	<24 h	0.585 (0.677–0.793)	Yang et al. (2007)
C. dubia	S	Nom	99.3	96	21	Mortality	<24 h	0.849 (0.655–1.085)	Yang et al. (2007)
C. dubia	S	Nom	99.3	96	21	Mortality	<24 h	0.889 (0.666–1.120)	Yang et al. (2007)
C. dubia	S	Nom	99.3	96	21	Mortality	<24 h	0.865 (0.672–1.098)	Yang et al. (2007)
Geometric mean						Mortality		0.664	
Chironomus dilutus	S	Meas	>96	96	23	Mortality	Fourth instar	0.189 (0.131–0.295)	Harwood et al. (2009)
Danio rerio	SR	Nom	90.0	96	23	Mortality	3.0 cm, 0.3 g	2.5 (1.7–3.2)	Zhang et al. (2010)
Daphnia magna	S	Nom	Technical	48	22	Immobility	<24 h	0.32 (0.24–0.44)	LeBlanc (1976)
Erimonax monachus	S	Nom	95.2	96	17	Mortality	NR	1.7	Dwyer et al. (2005)
Etheostoma fonticola	S	Nom	95.2	96	22	Mortality	62 mg, 20.2 mm	3.34 (2.75–4.16)	Dwyer et al. (1999, 2005)
Etheostoma lepidum	S	Nom	95.2	96	22	Mortality	NR	2.71 (2.36–3.13)	Dwyer et al. (1999, 2005)
Hyalella azteca	S	Nom	100.0	96	23	Mortality	Third instar	0.0211	Anderson et al. (2006)

Ictalurus punctatus	S	Nom	92.4	96	21	Mortality	1.2 g, 35 mm	5.4 (3.9–7.4)	Buccafusco (1976a)
Notropis mekistocholas	S	Nom	95.2	96	17	Mortality	NR	4.16	Dwyer et al. (2005)
Oncorhynchus apache	S	Nom	95.2	96	12	Mortality	0.615 g	1.71 (1.3–2.2)	Dwyer et al. (1995, 2005), Sappington et al. (2001)
Oncorhynchus clarki henshawi	S	Nom	95.2	96	12	Mortality	0.46 g	1.58 (1.1–2.2)	Dwyer et al. (1995, 2005), Sappington et al. (2001)
Oncorhynchus mykiss	FT	Meas	91.9	96	15.6	Mortality	Juvenile	7.0	Holcombe et al. (1982)
Orconectes immunis	S	Nom	92.0	96	16.5	Mortality	Juvenile 2 g	0.21 (0.17–0.25)	Paul and Simonin (2006)
Pimephales promelas	S	Nom	95.2	96	22	Mortality	0.41 g	9.38 (6.7–16)	Dwyer et al. (1995, 2005), Sappington et al. (2001)
Procambarus blandingi	FT	Nom	89.1	96	22	Mortality	24 g, 48 mm	0.21 (0.13–0.33)	Buccafusco (1977)
Procloeon sp.	S	Nom	100.0	48	23	Mortality	0.5–1 cm	0.0896	Anderson et al. (2006)
Salmo salar	S	Nom	92.4	96	12	Mortality	1 g, 35 mm	1.5 (1.1–2.0)	Buccafusco (1976b)
Xyrauchen texanus	S	Nom	95.2	96	22	Mortality	0.32 g	5.95 (4.6–7.7)	Dwyer et al. (1995, 2005), Sappington et al. (2001)

All studies were rated relevant and reliable (RR)
S static, *SR* static renewal, *FT* flow through

Table 11 Final chronic toxicity data set for permethrin

Species	Test type	Meas/ Nom	Chemical grade (%)	Duration (days)	Temp (°C)	End point	Age/size	NOEC (μg/L)	LOEC (μg/L)	MATC (μg/L)	Reference
Brachycentrus americanus	FT	Meas	Technical	21	15	Mortality	Larvae	–	–	LC_{50}: 0.17 (0.09–0.34)	Anderson (1982)
Daphnia magna	FT	Meas	98.6	21	20	Reproduction	<24 h	0.039	0.084	0.057	Kent et al. (1995a)
D. magna	FT	Meas	98.6	21	20	Length	<24 h	0.039	0.084	0.057	Kent et al. (1995a)
D. magna										0.057	
Pimephales promelas	FT	Meas	92.0	32	25	Mortality	4–5-day-old larvae	0.66	1.4	0.96	Spehar et al. (1983)

All studies were rated relevant and reliable (RR)
S static, *SR* static renewal, *FT* flow through, *NR* not reported

distribution was selected as the best fit for both λ-cyhalothrin and permethrin based on maximum likelihood estimation using the BurrliOZ software (CSIRO 2001). Fit tests based on cross validation and Fisher's combined test found no significant lack of fit for bifenthrin, cyfluthrin, λ-cyhalothrin, or permethrin, with $X^2_{2n} > 0.199$ for these four compounds (calculations shown in the Supporting Material http://extras.springer.com/). The Burr III distribution was initially selected as the best fit for the cypermethrin data set, but this distribution did not provide a satisfactory fit based on the fit test ($\chi^2_{2n} = 0.000014$; calculations shown in the Supporting Material http://extras.springer.com/); so a log-logistic distribution, which is less likely to overfit the data, was fit to the cypermethrin data set instead.

Acute values were derived from the distributions, including fifth percentiles (median and lower 95% confidence limit), as well as first percentiles (median and lower 95% confidence limit). The median fifth percentile is the most robust of the four distributional estimates, and is therefore the estimate recommended for criteria calculation.

Bifenthrin Log-Logistic Distribution

HC5 fitting parameters: $\alpha = -0.661$; β (median) = 0.4872, β (lower 95% CI) = 0.9328

Fifth percentile, 50% confidence limit: 0.00803 μg/L
Fifth percentile, 95% confidence limit: 0.000391 μg/L
First percentile, 50% confidence limit: 0.00126 μg/L
First percentile, 95% confidence limit: 0.0000113 μg/L
Recommended acute value: 0.00803 μg/L (median fifth percentile)

$$\text{Acute criterion} = \frac{\text{Acute value}}{2}. \quad (1)$$

Bifenthrin acute criterion = 0.004 μg/L

Cyfluthrin Log-Logistic Distribution

HC5 fitting parameters: $\alpha = -0.7446$; β (median) = 0.5478; β (lower 95% CI) = 1.04898

Fifth percentile, 50% confidence limit: 0.00439 μg/L
Fifth percentile, 95% confidence limit: 0.000147 μg/L
First percentile, 50% confidence limit: 0.000547 μg/L
First percentile, 95% confidence limit: 0.0000027 μg/L
Recommended acute value: 0.00439 μg/L (median fifth percentile)
Cyfluthrin acute criterion = 0.002 μg/L

Cypermethrin Log-Logistic Distribution

HC_5 fitting parameters: $\alpha = -0.6601$, β(median) = 0.4199, β(lower 95% CI) = 0.6768

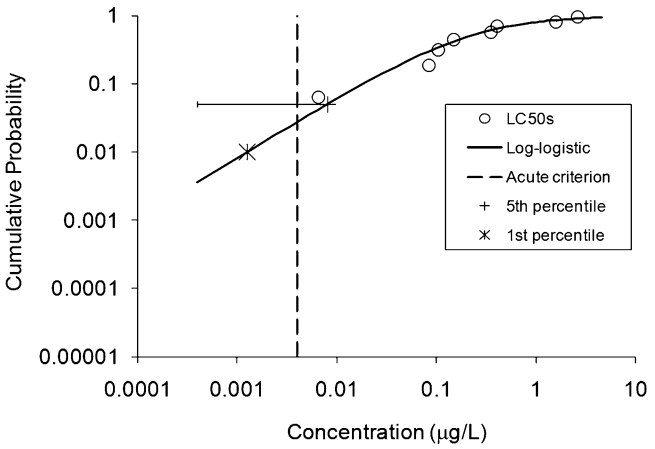

Fig. 1 Plot of bifenthrin species mean acute values and fit of the log-logistic distribution. The graph shows the median fifth and first percentiles with the lower 95% confidence limit on the fifth percentile and the acute criterion at 0.004 µg/L

Fifth percentile, 50% confidence limit: 0.0127 µg/L
Fifth percentile, 95% confidence limit: 0.00222 µg/L
First percentile, 50% confidence limit: 0.00257 µg/L
First percentile, 95% confidence limit: 0.000170 µg/L
Recommended acute value: 0.0127 µg/L (median fifth percentile)
Cypermethrin acute criterion = 0.006 µg/L

λ-Cyhalothrin Burr III Distribution

Fit parameters: $b = 0.232356$; $c = 1.100750$; $k = 0.596085$ (likelihood = −4.987264)

Fifth percentile, 50% confidence limit: 0.00243 µg/L
Fifth percentile, 95% confidence limit: 0.000501 µg/L
First percentile, 50% confidence limit: 0.000208 µg/L
Recommended acute value: 0.002432 µg/L (median fifth percentile)
λ-Cyhalothrin acute criterion = 0.001 µg/L

Permethrin Burr III Distribution

Fit parameters: $b = 7.80465$; $c = 6.599725$; $k = 0.07608$ (likelihood = 35.742158)

Fifth percentile, 50% confidence limit: 0.020008 µg/L
First percentile, 50% confidence limit: 0.000811 µg/L
Recommended acute value: 0.020008 µg/L (median fifth percentile)
Permethrin acute criterion = 0.01 µg/L

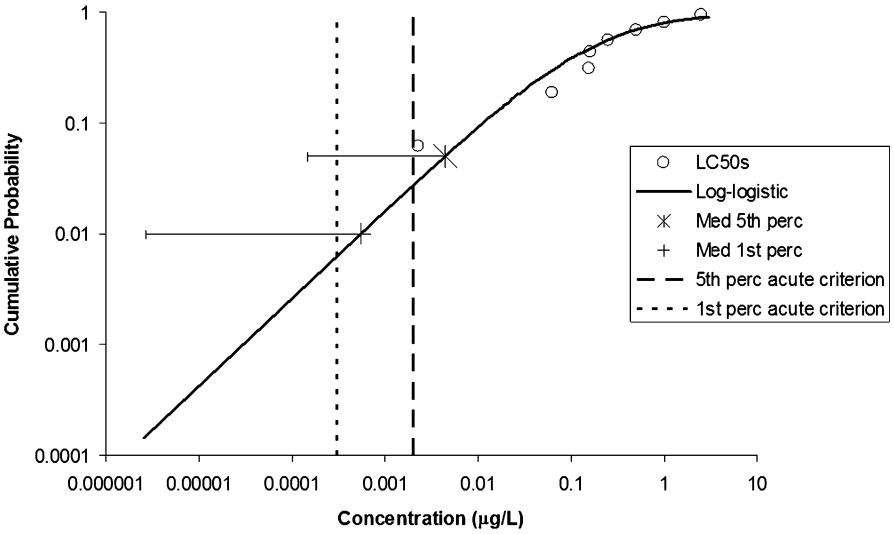

Fig. 2 Plot of cyfluthrin species mean acute values and fit of the log-logistic distribution. The graph shows the median fifth and first percentile values with the lower 95% confidence limits and the acute criteria calculated using both the median fifth percentile value and the median first percentile value

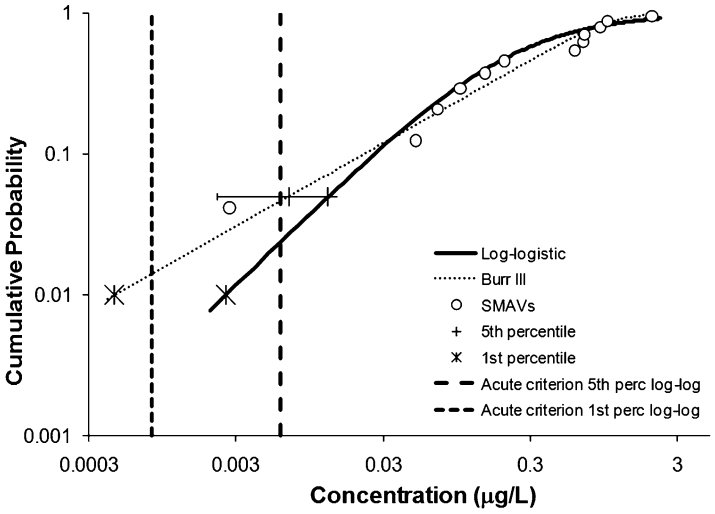

Fig. 3 Plot of species mean acute values for cypermethrin and fit of the log-logistic and Burr Type III distributions. The graph shows the median fifth and first percentiles for both distributions with the lower 95% confidence limit for the median fifth percentile on the log-logistic, and the acute criteria calculated using both the median fifth and first percentiles of the log-logistic distribution

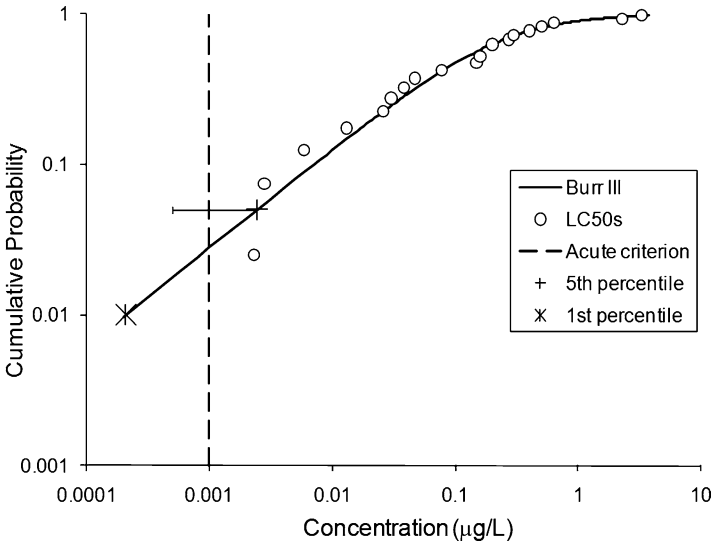

Fig. 4 Plot of species mean acute values for λ-cyhalothrin and fit of the Burr III distribution. The graph shows the median fifth and first percentile values with the lower 95% confidence limit of the fifth percentile and the acute criterion at 0.001 μg/L

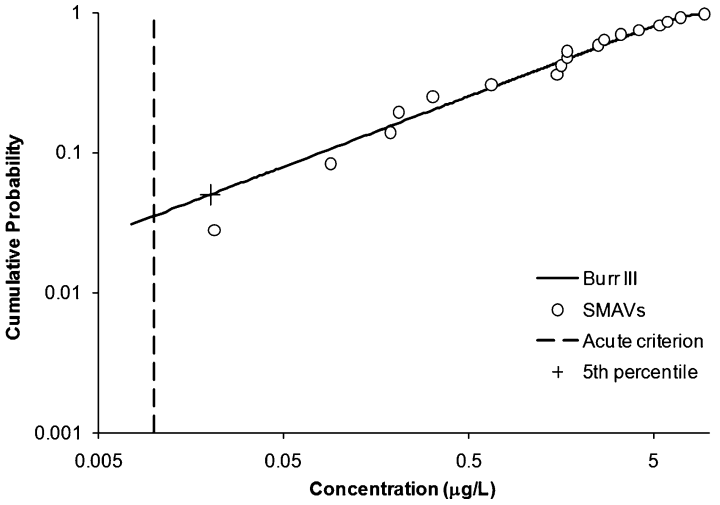

Fig. 5 Plot of species mean acute values for permethrin and fit of the Burr III distribution. The graph shows the median fifth percentile and the acute criterion at 0.01 μg/L

The fits of the distributions to the acute data sets are shown in Figs. 1–5, in cumulative probability plots. Because there is variability between the first significant digits of the median and lower 95% confidence limit estimates, the final criteria are reported with one significant figure. Although a lower 95% confidence limit could not be calculated for the permethrin distribution for comparison, the permethrin acute criterion is also reported with one significant digit because there was variability in the first digit of the fifth percentiles generated in the fit test. Later in this chapter, the acute criteria for cyfluthrin and cypermethrin are recalculated using lower percentile estimates because the criteria for these compounds calculated with the median fifth percentile acute values were not protective when compared to data for sensitive species, threatened and endangered species, and multispecies ecosystem-level studies.

5 Chronic Criterion Calculations

The chronic data sets of all five pyrethroids were limited and did not include data that met the five taxa requirements of the SSD procedure. Instead, the ACR procedure (TenBrook et al. 2010) was used for chronic criteria calculation, which is based on the ACR procedure in the USEPA (1985) method, but also includes a default ACR, when ACR data is also limited. For bifenthrin and cypermethrin, only one or two of the five SSD taxa requirements were satisfied (Tables 3 and 7), and none of these values could be paired with an appropriate corresponding acute toxicity value to calculate ACRs. There were also no appropriate saltwater data to use for ACR calculation; thus, these chronic criteria were calculated with the default ACR of 12.4 (TenBrook et al. 2010). Three of the five cyfluthrin taxa requirements were satisfied: a species in the family Salmonidae (*Oncorhynchus mykiss*), a warm water fish (*Pimephales promelas*), and a planktonic crustacean (*Daphnia magna*). Each of these three chronic values were paired with appropriate corresponding acute toxicity values, which satisfied the three family requirements (a fish, an invertebrate, and another sensitive species) for the ACR procedure with measured toxicity data. There were two λ-cyhalothrin chronic toxicity values, satisfying two of the five taxa requirements: a warm water fish (*P. promelas*) and a planktonic crustacean (*D. magna*). Both freshwater chronic values were paired with corresponding acute toxicity values to calculate ACRs, and paired data for the saltwater species *Cyprinodon variegatus* was used to complete the third family requirement for the ACR procedure. While two chronic values were available for permethrin, neither could be paired with appropriate acute data, but paired data for the saltwater species *Americamysis bahia* was available. This ACR was combined with two default ACRs to complete the three ACR requirements, allowing for the calculation of a final ACR for permethrin.

To calculate species mean ACRs (SMACRs) for each species, the acute LC_{50} was divided by the chronic maximum acceptable toxicant concentration (MATC)

Table 12 Calculation of the final acute-to-chronic ratio for cyfluthrin

Species	LC_{50} (μg/L)	Acute reference	Chronic end point	MATC (μg/L)	Chronic reference	ACR (LC_{50}/MATC)
Daphnia magna	0.160	Burgess (1990)	Reproduction/length	0.02864	Forbis et al. (1984)	5.58659
Oncorhynchus mykiss	0.2512	Bowers (1994), Gagliano and Bowers (1994)	Biomass/weight	0.0133	Carlisle (1985)	18.88970
Pimephales promelas	2.49	Rhodes et al. (1990)	Various	0.20149	Rhodes et al. (1990)	12.35793
Multispecies ACR = geomean (individual ACRs)						10.27

Table 13 Calculation of the species mean acute-to-chronic ratios for λ-cyhalothrin

Species	LC_{50} (μg/L)	Chronic end point	MATC (μg/L)	Reference	ACR (LC_{50}/MATC)
Cyprinodon variegatus	0.81	Weight	0.31	Hill et al. (1985)	2.6129
Daphnia magna	0.013	Reproduction (young/female/day)	0.00263	Farrelly and Hamer (1989)	4.9430
Pimephales promelas	0.36	FI survival	0.044	Tapp et al. (1990)	8.1818
Multispecies ACR = geomean (individual ACRs)					4.73

Table 14 Acute-to-chronic ratios used for derivation of the permethrin chronic criterion

Species	LC_{50} (μg/L)	Acute reference	Chronic end point	MATC (μg/L)	Chronic reference	SMACR (LC_{50}/MATC)
Americamysis bahia	0.075	Thompson (1986)	Mortality	0.016	Thompson et al. (1989)	4.6875
Default						12.4[a]
Default						12.4[a]
Multispecies ACR = geomean (individual ACRs)						8.96592

[a] The derivation and source data of the default ACR are described in the UCDM (TenBrook et al. 2010)

for a given species. The final ACRs for cyfluthrin (10.27) and λ-cyhalothrin (4.73) were calculated as the geometric mean of all of the SMACRs in each ACR data set and the final ACR for permethrin (8.96592) was calculated with one SMACR and two default ACRs (Tables 12–14) while the default ACR of 12.4 was used for bifenthrin and cypermethrin. Chronic criteria were calculated by dividing the recommended acute value (median fifth percentile) by the final ACR. Later in this chapter, the cyfluthrin and cypermethrin are adjusted downward to be protective based on comparisons to data for sensitive, threatened, and endangered species and ecosystem-level studies.

Bifenthrin chronic criterion calculated with the acute median fifth percentile estimate:

Fifth percentile, 50% confidence limit: 0.00803 μg/L

$$\begin{aligned}\text{Chronic criterion} &= \frac{\text{Recommended acute value}}{\text{ACR}}, \\ &= \frac{0.0243\ \mu g/L}{12.4}, \\ &= 0.0006\ \ \mu g/L, \\ &= 0.6\ ng/L.\end{aligned} \tag{2}$$

Cyfluthrin chronic criterion calculated with the acute median fifth percentile estimate:

Fifth percentile, 50% confidence limit: 0.00439 μg/L

$$\begin{aligned}\text{Chronic criterion} &= \frac{0.00439\ \mu g/L}{10.27}, \\ &= 0.0004\ \ \mu g/L, \\ &= 0.4\ ng/L.\end{aligned}$$

Cypermethrin chronic criterion calculated with the acute median fifth percentile estimate:

Fifth percentile, 50% confidence limit: 0.0126904 μg/L

$$\begin{aligned}\text{Chronic criterion} &= \frac{0.0126904\ \mu g/L}{12.4}, \\ &= 0.001\ \ \mu g/L, \\ &= 1\ ng/L.\end{aligned}$$

λ-Cyhalothrin chronic criterion calculated with the acute median fifth percentile estimate:

Fifth percentile, 50% confidence limit: 0.00243 μg/L

$$\begin{aligned}\text{Chronic criterion} &= \frac{0.00243\ \mu g/L}{4.73}, \\ &= 0.0005\ \ \mu g/L, \\ &= 0.5\ ng/L.\end{aligned}$$

Permethrin chronic criterion calculated with the acute median fifth percentile estimate:

Fifth percentile, 50% confidence limit: 0.020008 μg/L

$$\begin{aligned}\text{Chronic criterion} &= \frac{0.020008\ \mu g/L}{8.96592}, \\ &= 0.002\ \ \mu g/L, \\ &= 2\ ng/L.\end{aligned}$$

6 Bioavailability

Although pyrethroids are not very soluble in water, aquatic organisms are very sensitive to the pyrethroids and toxicity does occur. Pyrethroids have been found as the cause of toxicity in surface waters in the California Central Valley (Phillips et al. 2007; Weston et al. 2009a; Weston and Lydy 2010). This toxicity is believed to occur primarily from the fraction of the compound that is dissolved in the water, not from the compound that is associated with particulate phases. For example, Surprenant (1988) demonstrated that bifenthrin from spiked soil samples was available at concentrations sufficient to cause toxicity to *D. magna* that were housed in a separate container from the sediment, but shared the same recirculating water (however, dissolved particles could have been involved in this exposure).

Numerous studies demonstrate that the uptake and toxicity of pyrethroids are greatly reduced when solids or dissolved organic matter (DOM) are present (Day 1991; DeLorenzo et al. 2006; Lajmanovich et al. 2003; Muir et al. 1985, 1994; Smith and Lizotte 2007; Yang et al. 2006a, b, c, 2007). These studies indicate that bound pyrethroids are unavailable, and thus nontoxic to aquatic organisms. It has been presumed that the pyrethroids primarily sorb to the organic carbon phase of solids or DOM, and Hunter et al. (2008) demonstrated that sediment OC-normalized concentrations of permethrin were highly correlated with the uptake of permethrin by *Chironomus dilutus* (formerly *C. tentans*), which supports this assumption. Yet Yang et al. (2007) did not find a direct correlation between dissolved organic carbon (DOC) content and uptake or toxicity of pyrethroids, indicating that partitioning is not solely dependent on the quantity of DOC, but is also dependent on the quality of the DOC. Consequently, to accurately estimate pyrethroid sorption to DOC and particulate OC in whole water, site-specific partition coefficients would be preferred.

Alternately, the bioavailable fraction of pyrethroids can be estimated by measuring only the freely dissolved concentration using solid-phase microextraction (SPME). Yang et al. (2006a, 2007) reported that organism uptake was closely mimicked by SPME results and that the aqueous concentration of pyrethroids measured by SPME correlated well with the variations in uptake and toxicity with various DOM. Xu et al. (2007) clearly demonstrated that it is the freely dissolved aqueous concentration of pyrethroid that is bioavailable when they tested bifenthrin and cyfluthrin toxicity to *C. tentans* in 10-day sediment exposures with three types of sediment. The researchers reported LC_{50}s for five phases: bulk sediment, OC-normalized sediment, bulk pore water, DOC-normalized pore water, and freely dissolved pyrethroid. The LC_{50}s calculated for each of the five phases varied greatly, and varied between sediments for all phases tested except the freely dissolved, indicating that toxicity of the freely dissolved phase is independent of site-specific characteristics. The LC_{50}s based on the freely dissolved concentrations were at least an order of magnitude lower than those based on bulk pore water concentrations that included DOC, indicating that toxicity may be greatly underestimated if bioavailability is not taken into account. Based on these myriad studies, it can be concluded that the freely dissolved concentration is the most accurate predictor of toxicity and that bound pyrethroids were unavailable to the studied organisms.

However, bound pyrethroids can continue to desorb into the water column for long periods of time because pyrethroids have long equilibration times (~30 days; Bondarenko et al. 2006) and environmental systems are usually not at true equilibrium. The fraction of chemical that is potentially available to an organism is known as the bioaccessible fraction, and it has been linked to biological effects (Semple et al. 2004; You et al. 2011). Benthic organisms, such as *Hyalella azteca*, may be at greater risk because of their exposure to pore water and close proximity to sediments, where dissolved concentrations may persist.

Additionally, the role of dietary exposure on bioavailability of pyrethroids has not been considered. In the tests performed by Yang et al. (2006a, b) with *Ceriodaphnia dubia* and *D. magna*, organisms were not fed during the test. Organisms living in contaminated waters may also be ingesting food with sorbed hydrophobic compounds that can be desorbed by digestive juices (Mayer et al. 2001). The effects of dietary exposure may also be species specific, depending on typical food sources; some species may have greater interaction with particles, increasing their exposure. Palmquist et al. (2008) examined the effects due to dietary exposure of the pyrethroid esfenvalerate on three aqueous insects with different feeding functions: a grazing scraper (*Cinygmula reticulata* McDunnough), an omnivore filter feeder (*Brachycentrus americanus* Banks), and a predator (*Hesperoperla pacifica* Banks). The researchers observed adverse effects in *C. reticulata* and *B. americanus* after feeding on esfenvalerate-laced food sources and that none of the three insects avoided the contaminated food. The effects included reduced growth and egg production of *C. reticulata* and abandonment and mortality in *B. americanus*. Stratton and Corke (1981) tested toxicity of permethrin to *D. magna* with and without feeding of algae, and found that mortality at 24 h was significantly increased when daphnids were fed, although mortality at 48 h was not affected. The authors proposed that permethrin may have been ingested by the daphnids if it was sorbed on the algal cells, and caused increased toxicity, although the same effect was not seen when bacteria were provided as a food source. These limited studies indicate that ingestion may be an exposure route, but it is not currently possible to incorporate this exposure route into criteria compliance assessment.

The studies above suggest that the freely dissolved fraction of pyrethroids is the primary bioavailable fraction and that this concentration is the best indicator of toxicity; thus, it is recommended that the freely dissolved fraction is directly measured or calculated based on site-specific information for compliance assessment. The most direct way to determine compliance would be to measure the pyrethroid concentration in the dissolved phase to determine the total bioavailable concentration. SPME has shown to be a good predictor of pyrethroid toxicity in many studies (Bondarenko et al. 2007; Bondarenko and Gan 2009; Hunter et al. 2008; Xu et al. 2007; Yang et al. 2006a, b, c, 2007). Bondarenko and Gan (2009) reported method detection limits of 1.0 ng/L for bifenthrin, 2.0 ng/L for cyfluthrin, 2.0 ng/L for cypermethrin, 2.4 ng/L for λ-cyhalothrin, 2.0 ng/L for cis-permethrin, and 3.0 for trans-permethrin, and Li et al. (2009) reported method detection limits of 0.2 ng/L for bifenthrin, 0.2 for cyhalothrin, 0.9 ng/L for cyfluthrin, 1.0 ng/L for cypermethrin,

and 1.2 ng/L for permethrin using SPME. Analytical detection limits may create a problem for criteria compliance because most of these reported detection limits are above the derived criteria, meaning it is possible that one of these pyrethroids could be present in toxic amounts, yet below the detection limit so that an excursion is not identified. Filtration of suspended solids is not recommended for determining criteria compliance because pyrethroids have been demonstrated to adsorb to glass fiber filters by Gomez-Gutierrez et al. (2007). They found that on average 58% of a 50 ng/L solution of permethrin was lost on the filter; this magnitude of loss may be critical for determining compliance at environmental concentrations.

If the freely dissolved concentration is not directly measured, the following equation can be used to translate total pyrethroid concentrations measured in whole water to the associated dissolved pyrethroid concentrations:

$$C_{\text{dissolved}} = \frac{C_{\text{total}}}{1 + ((K_{\text{OC}} \times [\text{SS}])/f_{\text{oc}}) + (K_{\text{DOC}} \times [\text{DOC}])}, \tag{3}$$

where $C_{\text{dissolved}}$ is the concentration of chemical in dissolved phase (μg/L), C_{total} is the total concentration of chemical in water (μg/L), K_{OC} is the OC–water partition coefficient (L/kg), [SS] is the concentration of suspended solids in water (kg/L), f_{oc} is the fraction of OC in suspended sediment in water, [DOC] is the concentration of dissolved organic carbon in water (kg/L), and K_{DOC} is the OC–water partition coefficient (L/kg) for DOC.

To determine compliance by this calculation, site-specific data are necessary, including K_{OC}, K_{DOC}, concentration of suspended solids, concentration of DOC, and fraction of OC in the suspended solids. If all of these site-specific data, including the partition coefficients, are not available, then this equation should not be used for compliance determination. Site-specific data are required because the sorption of pyrethroid to suspended solids and DOM depends on the physical and chemical properties of the suspended solids resulting in a range of K_{OC} and K_{DOC} values, as discussed earlier in this section.

The freely dissolved pyrethroid concentration is recommended for determination of criteria compliance because the literature suggests that the freely dissolved concentrations are the most accurate predictor of toxicity. Environmental managers may choose an appropriate method for determining the concentration of freely dissolved pyrethroid. If environmental managers choose to measure whole water concentrations for criteria compliance assessment, the bioavailable fraction will likely be overestimated.

7 Chemical Mixtures

Pyrethroids often co-occur in the environment (Trimble et al. 2009; Werner and Moran 2008), and various other chemical mixtures are ubiquitous in surface waters. Because the presence of other chemicals can add to or alter the toxicity of another

given chemical, it is important to examine the effects of chemical mixtures on individual pyrethroid toxicity. Although chemical interactions are rarely straightforward, the concentration addition model is recommended for chemicals with the same toxicological mode of action. All pyrethroids have a similar mode of action in that they bind to and prolong the opening of voltage-dependent ion channels, causing convulsions, paralysis, and death (Brander et al. 2009). The three studies that tested toxicity of pyrethroid mixtures found that the effects were generally well-predicted by the concentration addition model (Barata et al. 2006; Brander et al. 2009; Trimble et al. 2009). Overall, the concentration addition model should be used by following either the toxic unit or relative potency factor approach to determine criteria compliance when multiple pyrethroids are present.

Barata et al. (2006) observed slight antagonism for *D. magna* survival for λ-cyhalothrin—deltamethrin mixtures, but the deviation from additivity was attributed to a few unexpected extreme values for joint survival effects, as most observed effects were within a factor of 2 of the effects predicted by the concentration addition model. Brander et al. (2009) tested mixture toxicity of cyfluthrin and permethrin, and found slight antagonism for the binary mixture, but additivity was demonstrated when piperonyl butoxide (PBO) was added. Brander et al. (2009) offered several explanations for the observed antagonism between the two pyrethroids. Permethrin is a type I pyrethroid and cyfluthrin is a type II pyrethroid, and type II pyrethroids may be able to outcompete type I pyrethroids for binding sites, which is known as competitive agonism; or binding sites may be saturated so that complete additivity is not observed. They also note that cyfluthrin is metabolized more slowly than permethrin, so cyfluthrin can bind longer. PBO may remove this effect because the rate of metabolism of both pyrethroids is reduced in its presence. To examine if pyrethroid mixture toxicity is additive with a more comprehensive study design, Trimble et al. (2009) performed sediment toxicity tests with *H. azteca* in three binary combinations: type I–type I (permethrin–bifenthrin), type II–type II (cypermethrin–λ-cyhalothrin), and type I–type II (bifenthrin–cypermethrin). The toxicity of these combinations was predicted with the concentration addition model, with model deviations within a factor of 2, indicating that in general pyrethroid mixture toxicity is additive.

PBO is commonly added to pyrethroid insecticide treatments because it is known to increase the toxic effects of pyrethroids (Weston et al. 2006). Many studies have demonstrated that the addition of PBO at a concentration that would be nonlethal on its own increases the toxicity of pyrethroids (Brander et al. 2009; Brausch and Smith 2009; Hardstone et al. 2007, 2008; Kasai et al. 1998; Paul and Simonin 2006; Paul et al. 2005, 2006; Rodriguez et al. 2005; Singh and Agarwal 1986; Xu et al. 2005). Several of these studies report single-species interaction coefficients (K; also called synergistic ratios) for pyrethroids and PBO ranging from 1.35 (*D. magna*; Brausch and Smith 2009) to 60 (snails; Singh and Agarwal 1986). While many studies report interaction coefficients for synergism of PBO, none of them reported interaction coefficients for multiple PBO concentrations; so a relationship between PBO concentration and K cannot be determined for any given species. In addition, no multispecies interaction coefficients are available; thus, there is no accurate way to account for synergism with PBO in compliance determination.

Mixture effects with pyrethroids and various other chemicals have also been studied and are summarized here, but there are currently no multispecies interaction coefficients available for these combinations. Binary mixtures of λ-cyhalothrin with deltamethrin and cadmium demonstrated additivity (Barata et al. 2006, 2007). Mixtures with various fungicides have been investigated and some synergism has been demonstrated. Norgaard and Cedergreen (2010) reported synergism with equitoxic mixtures of the fungicides and α-cypermethrin, yielding interaction coefficients ranging from 1.4 to 27, while other ratios tested resulted in interaction coefficients ranging from 0.41 to 37. Adam et al. (2009) also reported synergism for mixtures of fungicides and cypermethrin, which are often found in combination in wood preservatives. Permethrin in combination with propoxur, a carbamate, demonstrated synergism, which the authors propose is due to the complementary modes of action acting on different parts of the nervous system (Corbel et al. 2003). The thiocarbamate pesticide cartap appears to be antagonistic when combined with cypermethrin as no toxicity was observed in tests with *D. magna* and *Oryzias latipes*, when the concentrations of each chemical tested in combination were higher than the reported EC/LC_{50} values for the single chemicals (Kim et al. 2008). Gartenstein et al. (2006) reported synergism for cypermethrin in binary combinations with diflubenzuron and diazinon, but the combination of all three compounds produced an antagonistic effect. Zhang et al. (2010) tested mixtures of permethrin with the organophosphates dichlorvos or phoxim and reported that the toxicity of binary combinations was additive.

No studies on aquatic organisms were found in the literature that could provide a quantitative means to consider mixtures of pyrethroids with other classes of pesticides. Although there are examples of nonadditive toxicity, multispecies interaction coefficients are not available for any pyrethroid, and therefore the concentrations of nonadditive chemicals cannot be used for criteria compliance.

8 Water Quality Effects

Temperature has been reported to be inversely proportional to the aquatic toxicity and bioavailability of pyrethroids (Miller and Salgado 1985; Werner and Moran 2008). In fact, the increase of toxicity of pyrethroids with decreasing temperature has been used to implicate pyrethroids as the source of toxicity in environmental samples (Phillips et al. 2004; Weston et al. 2009b). The inverse relationship between temperature and pyrethroid toxicity is likely due to the increased sensitivity of an organism's sodium channels at lower temperatures (Narahashi et al. 1998).

Enhanced toxicity of cyfluthrin to larval fathead minnows (*P. promelas*) at lower temperatures was demonstrated by Heath et al. (1994). Sublethal cyfluthrin concentrations reduced the ability of fish to tolerate temperatures both higher and lower than standard conditions. The toxicities of six aqueous pyrethroids were 1.33- to 3.63-fold greater at 20°C compared to 30°C for mosquito larvae (Cutkomp and Subramanyam 1986). Harwood et al. (2009) tested permethrin toxicity to *C. dilutus* in an aqueous exposure at 13 and 23°C, and reported a

3.2-fold decrease of the 96-h LC_{50} at the lower temperature. Kumaraguru and Beamish (1981) reported that for small trout the toxicity of permethrin increased by a factor of 10 with a decrease in temperature from 20 to 5°C, but showed little change from 10 to 5°C. These studies indicate that the enhanced toxic effects of pyrethroids at lower temperature may not be as accurately represented by the results of typical laboratory toxicity tests, which tend to be run at warmer temperatures, 20–23°C (USEPA 1996a, b, 2000) than those of the habitats of coldwater fishes, about 15°C or lower (Sullivan et al. 2000).

The toxicity of sediments contaminated with pyrethroids was more than twice as toxic when tested at 18°C compared to 23°C (Weston et al. 2008). Weston et al. (2008) used a toxicity identification evaluation (TIE) procedure to determine the effect of temperature reduction (18 vs. 23°C) on toxicity of a particular environmental sediment sample to *H. azteca*. These results are not directly applicable for use in water quality criteria compliance because they were sediment exposures and used environmental samples, instead of an exposure to a pure compound.

Unfortunately, there are limited data in which aquatic exposures with relevant species were used, making it unfeasible to quantify the relationship between the toxicity of these five pyrethroids and temperature for water quality criteria at this time. Information regarding the effects of pH or other water quality parameters on pyrethroid toxicity was not identified, but based on the physical–chemical properties of these compounds they are not expected to be affected by these parameters.

9 Sensitive Species

Data for particularly sensitive species found in the acceptable (RR) and supplemental (RL, LR, LL) data sets (Tables S8–S12, Supporting Material http://extras.springer.com/) were compared to the criteria. There are some species represented in the supplemental data set that are not represented in the acceptable data set, and it is possible that data at the extreme sensitive end of the data set could be below the criteria derived using the median fifth percentiles. The bifenthrin acute criterion of 4 ng/L is below the lowest freshwater SMAV in the bifenthrin data sets (6.5 ng/L for *H. azteca*), and the chronic criterion of 0.6 ng/L is below the lowest freshwater SMCV in the data sets (1.9 ng/L for *D. magna*), so these criteria appear to be protective based on the available data. For λ-cyhalothrin, the acute and chronic criteria calculated with the acute median fifth percentile (1 and 0.5 ng/L, respectively) are both below all of the freshwater toxicity values in the respective acute and chronic data sets. The lowest LC_{50} is 2.3 ng/L for *H. azteca* while the lowest freshwater MATC is 2.63 ng/L for *D. magna*. For bifenthrin and λ-cyhalothrin, there are toxicity values equal to or below the derived criteria for the saltwater species *A. bahia*, but the criteria were not adjusted because they are only intended to protect freshwater species. The permethrin acute criterion (10 ng/L) is below the lowest acute value in the acute data sets (21.1 ng/L for *H. azteca*; Anderson et al. 2006). The permethrin

chronic criterion (2 ng/L) is below all of the chronic values in the available data sets (16 ng/L for *A. bahia*; Thompson et al. 1989).

The lowest SMAV in the cyfluthrin RR data set (Table 4) was 2.3 ng/L for *H. azteca*, which is approximately equal to the derived acute criterion of 2 ng/L. Based on the available data, the criterion derived using the median fifth percentile acute value is not protective of *H. azteca*; therefore, the next lowest acute value was used to calculate the cyfluthrin criteria. The acute and chronic cyfluthrin criteria calculations using the median first percentile acute value are as follows:

Recommended acute value: 0.000547 μg/L (median first percentile)

$$\begin{aligned}\text{Cyfluthrin acute criterion} &= \frac{0.000547\ \mu\text{g/L}}{2},\\ &= 0.0003\ \mu\text{g/L}\ (0.3\ \text{ng/L}).\\ \text{Cyfluthrin chronic criterion} &= \frac{0.000547\ \mu\text{g/L}}{10.27},\\ &= 0.00005\ \mu\text{g/L}\ (0.05\ \text{ng/L}).\end{aligned}$$

The cyfluthrin chronic criterion calculated with the median first percentile (0.05 ng/L) is below the lowest MATC in the data sets of 0.27 ng/L for *A. bahia*.

The derived cypermethrin acute criterion (0.006 μg/L) is higher than one SMAV in the RR acute data set, 0.0027 μg/L for *H. azteca* (Table 6). The *H. azteca* SMAV is the geometric mean of four values, three from a study in which concentrations were measured (Weston and Jackson 2009), all of which are lower than the acute criterion of 0.006 μg/L. Thus, the next lowest estimate from the log-logistic distribution (median first percentile) was used to derive the cypermethrin acute and chronic criteria as follows:

Recommended acute value: 0.0025723 μg/L (median first percentile)

$$\begin{aligned}\text{Cypermethrin acute criterion} &= \frac{0.0025723\ \mu\text{g/L}}{2},\\ &= 0.001\ \mu\text{g/L}\ (1\ \text{ng/L}).\\ \text{Cypermethrin chronic criterion} &= \frac{0.0025723\ \mu\text{g/L}}{12.4},\\ &= 0.0002\ \mu\text{g/L}\ (0.2\ \text{ng/L}).\end{aligned}$$

There is one supplemental datum (96-h EC_{50} = 0.6 ng/L for *D. magna*) that is below the adjusted cypermethrin acute criterion, but this toxicity value was not based on measured concentrations, and this species is represented in the RR data set with an SMAV that indicates that it is protected by the acute criterion. There are two supplemental MATCs that are below the adjusted chronic criterion of 0.2 ng/L (MATCs of 0.00063 and 0.063 ng/L for *D. magna*; Kim et al. 2008), but they are based on nominal concentrations, and it is recommended that criteria should only be adjusted based on toxicity values calculated with measured concentrations.

10 Ecosystem-Level Studies

Toxicity data from multispecies studies that more closely mimic ecosystems can yield different results than single-species effect studies, so community-level study data were compared to the criteria derived from single-species studies to ensure that the criteria are protective of ecosystems. A total of 28 studies addressing effects on microcosms, mesocosms, and model ecosystems were rated acceptable (R or L reliability rating) for the five selected pyrethroids (ratings listed in Table S13, Supporting Material http://extras.springer.com/). None of the bifenthrin, cyfluthrin, or permethrin studies reported ecosystem-level NOECs or no-effect concentrations (NECs) to which the chronic criteria could be directly compared.

Data in three of the bifenthrin studies (Drenner et al. 1993; Hoagland et al. 1993; Surprenant 1988) included toxic effects at concentrations ranging from 20 to 3,150 ng/L, which are well above the derived chronic criterion (0.6 ng/L). Sherman (1989) reported toxic effects for several invertebrates and fish in a pond receiving runoff contaminated with bifenthrin, but the effects did not correlate well with aqueous bifenthrin concentrations. Average pond concentrations fluctuated from slightly above 1 to 10 ng/L, but could not be linked to the occurrence of toxicity.

Authors of all the cyfluthrin studies reported toxic effects at applied or measured concentrations that were far above the chronic criterion (Gunther and Herrmann 1986; Johnson 1992; Johnson et al. 1994; Kennedy et al. 1990; Morris 1991; Morris et al. 1994). Toxic effects were observed in all of the studies, especially on aquatic macroinvertebrates, but it is not possible to assess if effects would have occurred if lower concentrations were tested, closer to the chronic criterion of 0.05 ng/L.

Several studies consisted of single concentrations of cypermethrin (0.01–24,000 μg/L) that were well above the chronic criterion in pond or marine mesocosms, followed by measurement of the recovery of the invertebrate communities. Toxic effects were observed particularly for insects and crustaceans, and some populations did not recover during the posttreatment observation periods (Crossland 1982; Farmer et al. 1995; Maund et al. 2009; Medina et al. 2004). The study by Maund et al. (2009) simulated natural reinvasion in some microcosms by adding invertebrates to the enclosures post treatment; in these microcosms, there was a general recovery of invertebrate populations in approximately 100 days. In contrast, the microcosms that received no additional organisms showed only limited recovery after 16 weeks of observation. These results indicate that small, isolated, or heavily impacted waterbodies will likely recover more slowly than waterbodies that are only partially impacted or are near other unimpacted waterbodies from which organisms can immigrate.

Friberg-Jensen et al. (2003) calculated cypermethrin NECs for crustaceans, copepods, and cladocerans ranging from 0.02 to 0.07 μg/L in enclosures set in a lake. These NECs are all significantly higher than the chronic criterion of 0.0004 μg/L. They also reported that rotifers, protozoans, bacteria, periphyton plankton, and periphytic algae all proliferated after treatment with cypermethrin, in response to the decreased populations of grazers. A sister paper, describing

effects for the same experiment, reported an NEC of 0.01 μg/L for copepod nauplii (Wendt-Rasch et al. 2003). This paper also reported significant changes to species composition of the aforementioned communities at nominal concentrations greater than 0.13 μg/L.

Several λ-cyhalothrin studies reported community NOECs to which the calculated criteria may be compared. Van Wijngaarden et al. (2006) and Roessink et al. (2005) reported various community-level NOECs that were season- and trophic-system-dependent, the lowest being <10 μg/L, and Schroer et al. (2004) reported a community-level NOEC of 10 ng/L. Schroer et al. (2004) also calculated a community-level criterion of 4.1 ng/L while the criterion calculated based on laboratory single-species data was 2.7 ng/L. The UCDM chronic criterion (0.5 ng/L) is below the reported NOECs for this set of studies by at least a factor of 20.

Hill et al. (1994) investigated the effects of λ-cyhalothrin on artificial pond mesocosms containing microbes, algae, macrophytes, zooplankton, macroinvertebrates, and fish. λ-cyhalothrin was applied at three rates as a spray and as a soil–water slurry to simulate runoff. Few effects were observed for most taxa, but macroinvertebrates and zooplankton were adversely affected at the highest rate; macroinvertebrates experienced some effects at the middle rate as well. Measured aqueous concentrations of λ-cyhalothrin ranged from 3 to 98 ng/L, in the mesocosms treated at the highest rate, and 2 to 10 ng/L in those treated at the middle rate. λ-cyhalothrin was not detected in the ponds treated at the lowest rate. The method detection limit reported in this study ranges from 2 to 3 ng/L, so it is possible that λ-cyhalothrin was present at lower concentrations when reported as nondetects. This study indicates that the derived chronic criterion of 0.5 ng/L should be protective of macroinvertebrates and zooplankton because it is likely similar to the actual concentrations in the ponds treated at the lowest rate.

Several study authors reported significant macroinvertebrate mortality and drift due to exposure to λ-cyhalothrin (Farmer et al. 1995; Lauridsen and Friberg 2005; Rasmussen et al. 2008; Wendt-Rasch et al. 2004), particularly for *Gammarus* species. Farmer et al. (1995) sprayed pond mesocosms with λ-cyhalothrin (measured at 2 ng/L, 1 h post treatment for the lower rate) and reported that *Gammarus* spp. abundance was significantly reduced compared to controls. Rasmussen et al. (2008) demonstrated that *Gammarus pulex* exposed to 10.65 ng/L λ-cyhalothrin (nominal) for 90 min and then transferred to clean water drifted significantly more than controls ($p<0.0001$). Phytoplankton and algae productivity increased in response to λ-cyhalothrin exposure (Farmer et al. 1995; Rasmussen et al. 2008; Wendt-Rasch et al. 2004) likely due to the decrease in macroinvertebrate populations, as macroinvertebrates are known to graze on algae. Lauridsen and Friberg (2005) examined macroinvertebrate drift in outdoor experimental channels with two insect species and *G. pulex*. Catastrophic drift was observed for all three species during the 1-h pulse exposure and 2–3-h post exposure. Drift of *G. pulex* was significantly affected at 1 ng/L (nominal), and it should be noted that the measured concentrations may have been even lower. While several studies indicate that *Gammarus* species experience lethal and sublethal effects due to λ-cyhalothrin exposures at concentrations near the chronic criterion, none of them reported toxicity values

(e.g., NOEC, EC_x) or measured concentrations at or below the derived chronic criterion; thus, the chronic criterion is not adjusted downward at this time.

In all permethrin studies, adverse effects were reported on aquatic organisms, but they all used formulations and test concentrations (0.02–100 μg/L) that were significantly higher than the chronic criterion of 0.002 μg/L. In two studies, increased drifting in model riverine systems was reported after exposure to permethrin for some invertebrate species (Poirier and Surgeoner 1988; Werner and Hilgert 1992), and another model riverine study reported that snails and water thyme (*Elodea*) were both adversely affected at permethrin concentrations of 4 and 20 μg/L (Lutnicka et al. 1999). Several pond exposures also demonstrated adverse effects on various aquatic invertebrates, including some populations that did not recover during the posttreatment observation period (Conrad et al. 1999; Coulon 1982; Yasuno et al. 1988). Conrad et al. (1999) dosed small artificial ponds with permethrin (1–100 μg/L nominal Picket® formulation) and conducted bioassays with chironomids, which were compared to laboratory sediment toxicity tests with *Chironomus riparius*. The chironomid responses of reduced larval density and adult emergence were not predicted by bulk sediment chemistry, sediment toxicity tests, or laboratory bioassay results—all three measurements underestimated the acute effects. Toxicity to *C. riparius* in the field was best predicted by acute water-only toxicity test data, indicating that the primary exposure route is via the water column. This study supports measurement of the truly dissolved fraction for criteria compliance and indicates the relevance of water quality criteria for protection of aquatic life.

11 Threatened and Endangered Species

Data for species listed as threatened or endangered were examined to ensure that the criteria are protective of these species. Both the US Fish and Wildlife Service federal list of threatened and endangered plant and animal species (USFWS 2010) and the California state list of threatened and endangered plant and animal species (the California Department of Fish and Game (CDFG) 2010a, 2010b) were consulted for this evaluation.

There are ten evolutionarily significant units of *O. mykiss* listed as federally threatened or endangered, and this species is represented in the data sets of all five pyrethroids that were examined. There are SMAVs for this species in all five acute data sets ranging from 0.119 to 7 μg/L, which are well above the derived acute criteria for these compounds. The λ-cyhalothrin acute data set also includes *Gasterosteus aculeatus*, of which a subspecies (*G.a. williamsoni*) is endangered. The acute permethrin data set includes seven additional listed species: *Oncorhynchus clarki henshawi*, *Etheostoma fonticola*, *Erimonax monachus*, *Notropis mekistocholas*, *Oncorhynchus apache*, *Salmo salar*, and *Xyrauchen texanus*. All of these acute toxicity values were used in criteria calculation and are well above the derived criteria; hence, there is no evidence that the criteria are underprotective of these

species. The only chronic toxicity value for a listed species was an MATC for *O. mykiss* in the cyfluthrin data set of 0.0133 μg/L, which is much higher than the chronic criterion of 0.00005 μg/L, indicating that the chronic criterion is protective of this species.

All of the acute data sets include species that are not listed but are in the same family or genus as some of those that are. These species were used as surrogates to estimate toxicity values for related TES with the USEPA interspecies correlation estimation software (Web-ICE v. 3.1; Raimondo et al. 2010). Unfortunately, the available bifenthrin and cyfluthrin SMAVs were below the model minimum input values, so toxicity values could not be predicted for bifenthrin or cyfluthrin. *O. mykiss* was used to predict λ-cyahlothrin, cypermethrin, and permethrin acute toxicity values for up to 13 species in the Salmonidae family (Tables S14–S16, Supporting Material http://extras.springer.com/). The predicted acute toxicity values ranged from 0.262 to 0.576 μg/L for cyfluthrin, 0.860 to 1.31 μg/L for cypermethrin, and 3.48 to 11.88 μg/L for permethrin, which are all more than one order of magnitude above their respective acute criteria.

One caveat of this evaluation is that the only TES in the measured or predicted data sets for these pyrethroids were fish, which are relatively insensitive compared to aquatic amphipods and insects. There were no data for TES in these more sensitive taxa, so it is not clear if the derived criteria are protective of these species. No single-species plant studies were found in the literature for use in criteria derivation for any of these pyrethroids, so no estimation could be made for plants on the state or federal endangered, threatened, or rare species lists. Phytoplanktons were unaffected by bifenthrin in a pond study (Sherman 1989); however, bifenthrin seemed to be beneficial in some instances and harmful in others, as reported in a mesocosm study that monitored primary productivity, green algae, chlorophyll, and other end points for photosynthetic organisms (Hoagland et al. 1993). Based on the mode of action, plants should be relatively insensitive to pyrethroids and the calculated criteria should be protective of aquatic plants.

12 Bioaccumulation

Chemicals in surface waters can accumulate in organisms from both the water and food items, which is called bioaccumulation, and eventually the chemicals can move up the food chain from prey to predator. Potential bioaccumulation was assessed to ensure that the derived criteria are set at concentrations that are not likely to cause toxicity due to bioaccumulation. Bifenthrin, cyfluthrin, cypermethrin, λ-cyhalothrin, and permethrin have similar physical–chemical characteristics (Table 1), including molecular weight $<$1,000 and log-normalized octanol–water partition coefficients (log K_{ow}) $>$3.0 L/kg, which indicate that all five compounds have the potential to bioaccumulate.

Low-to-moderate bioaccumulation of pyrethroids has been documented in the literature. For example, wild-caught brown trout (*Salmo trutta*), captured in a

British stream, was found to have accumulated an average 25.4 μg/kg of cyfluthrin and as high as 109 μg/kg in tissues, even though no cyfluthrin could be detected in the water column (Bonwick et al. 1996). Additionally, Surprenant (1986) reported that elimination of bifenthrin from bluegill tissues was very slow, i.e., after 42 days of depuration, fish tissue concentrations of bifenthrin were reduced by about half.

Because the pyrethroids have the potential to bioaccumulate, available data were used to estimate aqueous concentrations not expected to lead to harmful bioaccumulation. Analogous calculations were not done for human consumption of aquatic organisms because there are no tolerance or USFDA action levels for fish tissue (USFDA 2000) for any of these compounds. To calculate an aqueous NOEC, the dietary NOEC of an oral predator (mallard duck; studies listed in Table S17, Supporting Material http://extras.springer.com/) is divided by the bioaccumulation factor (BAF) for a fish. If a BAF is not available for a fish, it can be calculated as the product of the bioconcentration factor (BCF) and a biomagnification factor (BMF) such that BAF = BCF × BMF. BCFs are a measure of the uptake of a chemical by an organism from water alone while BMFs are a measure of the uptake of a chemical by an organism from food sources. BCFs for the pyrethroids of interest varied widely among different species, and were dependent on what portion of an organism was analyzed, with BCFs ranging from 2.6 to 3,280,000 (Table S18, Supporting Material http://extras.springer.com/).

For bifenthrin, one dietary NOEC was available for reproductive effects on mallard duck of 75 mg/kg (Roberts et al. 1986). No BAFs or BMFs were identified for fish, so the BCF of 28,000 L/kg bifenthrin for whole *P. promelas* (McAllister 1988) and a default BMF of 10, based on the log K_{ow} (TenBrook et al. 2010), were used to estimate a BAF as follows:

$$\mathrm{NOEC_{water}} = \frac{\mathrm{NOEC_{oral\_predator}}}{\mathrm{BCF_{food\_item}} \times \mathrm{BMF_{food\_item}}}. \tag{4}$$

The resulting $\mathrm{NOEC_{water}}$ for bifenthrin is 267 ng/L, which is well above the chronic criterion of 0.6 ng/L, indicating that bifenthrin at concentrations equal to or below the chronic criterion will not likely cause harm via bioaccumulation.

This calculation was also performed for the other four pyrethroids. For cyfluthrin, the highest BCF of 854 L/kg for *Lepomis macrochirus* (Carlisle and Roney 1984), a default BMF of 10, and the lowest dietary NOEC for a mallard of 250 mg/kg (Carlisle 1984) were used for a conservative estimation. The $\mathrm{NOEC_{water}}$ estimated for cyfluthrin using this data was 29 μg/L, which is above the aqueous solubility of cyfluthrin (2.3 μg/L; Laskowski 2002). For cypermethrin, the values used in Eq. 4 were the highest fish BCF of 821 L/kg for *O. mykiss*, a default BMF of 10, and a dietary toxicity value for mallard duck of 50 mg/kg, although this dietary NOEC was reported as greater than (>) 50 mg/kg (USEPA 2008). These values resulted in an $\mathrm{NOEC_{water}}$ for mallard of 6.09 μg/L, which is above the aqueous solubility of cypermethrin (4 μg/L; Laskowski 2002). An $\mathrm{NOEC_{water}}$ of 1.34 μg/L was calculated for λ-cyhalothrin with the highest reported BCF of 2,240 L/kg for whole fish *Cyprinus carpio* (Yamauchi et al. 1984), a default BMF of 10, and an oral predator

dietary NOEC of 30 mg/kg for mallard duck (Beavers et al. 1990). This $NOEC_{water}$ is significantly larger than the λ-cyhalothrin chronic criterion of 0.0005 μg/L. Finally, this calculation was completed for permethrin using the highest fish BCF of 2,800 L/kg for *P. promelas*, a default BMF of 10, and the dietary NOEC for mallard duck of 125 mg/kg, giving an $NOEC_{water}$ of 4.46 μg/L, which is nearing the aqueous solubility of 5.7 μg/L. Based on these conservative calculations, these pyrethroids are not likely to cause adverse effects on terrestrial wildlife due to bioaccumulation if their concentrations do not exceed the derived chronic criteria.

13 Assumptions, Limitations, and Uncertainties

Data limitations and important assumptions are reviewed here so that environmental decision makers have information about the accuracy and confidence in the criteria. Assumptions and limitations inherent in the methodology are summarized in the UCDM (TenBrook et al. 2010). The principal limitation for these five pyrethroids was a dearth of chronic data, particularly for the most sensitive species, amphipods and other invertebrates. There were no appropriate paired acute and chronic data for bifenthrin or cypermethrin to calculate ACRs, so the default ACR was used, while measured ACRs were available for cyfluthrin, λ-cyhalothrin, and permethrin. The acute criterion for cyfluthrin calculated with the median fifth percentile was almost identical to the lowest SMAV in the RR data set while the acute criterion for cypermethrin calculated with the median fifth percentile was higher than the lowest SMAV in the RR data set, so these criteria were adjusted downward to be more protective using less robust acute values. There are inherent assumptions in the use of an SSD (TenBrook et al. 2010), and the various distributional estimates can be used to assess uncertainty in the derived criteria for each compound. Of the data that were available for these compounds, not all were from flow-through tests that reported measured concentrations, which can cause overestimation of toxicity values, because pyrethroids are highly sorptive.

Other conspicuous data gaps were regarding temperature effects and mixture toxicity, especially with PBO; additional data on these topics should lead to quantifiable correlations, and these considerations should be added to criteria compliance when available. Also, pyrethroids are known to partition to sediments, and if federal or state sediment quality standards become available for these compounds, partitioning should be predicted based on the derived water quality criteria to ensure that these aqueous concentrations are not leading to potentially harmful sediment concentrations.

14 Comparison to Existing Criteria

To date, the USEPA has not calculated water quality criteria for bifenthrin, cyfluthrin, cypermethrin, λ-cyhalothrin, or permethrin. The CDFG composed a risk assessment report for several pyrethroids, including bifenthrin, cypermethrin,

and permethrin (Siepmann and Holm 2000). CDFG concluded that there were insufficient data to calculate criteria for bifenthrin using the USEPA (1985) method, and instead they reported the lowest acute and chronic toxicity values for guidance. The lowest genus mean acute value (GMAV) for bifenthrin was 3.97 ng/L for *A. bahia*, which is only slightly below the UCDM acute criterion of 4 ng/L; it can be noted that *A. bahia* is a saltwater species, which may be more sensitive than freshwater species. The lowest bifenthrin MATC in the CDFG report was 60 ng/L for *P. promelas*, which would not be protective of *D. magna* with an MATC of 1.9 ng/L (Table 3). The CDFG risk assessment reported interim acute criteria of 2 ng/L for cypermethrin and 30 ng/L for permethrin, which are both higher than the acute criteria calculated using the UCDM by factors of 2 and 3, respectively. Chronic criteria were not calculated for cypermethrin or permethrin because there was insufficient data.

The Netherlands has done generic risk assessment for several pyrethroids and maximum permissible concentrations (MPCs) have been calculated using the Dutch criteria derivation methodology. An MPC is defined as the concentration in the environment above which the risk of adverse effects is considered unacceptable to ecosystems and they are harmonized across media (Crommentuijn et al. 2000). MPCs are analogous to chronic water quality criteria and are used as the basis for setting environmental quality standards in the Netherlands. The Dutch MPCs for bifenthrin, cypermethrin, and permethrin are 1.1, 0.09, and 0.2 ng/L, respectively (Crommentuijn et al. 2000). These values were calculated with a modified EPA method in which an assessment factor ranging from 10 to 1,000 is applied to the lowest available toxicity value. The bifenthrin MPC of 1.1 ng/L is larger than the chronic criterion derived via the UCDM of 0.6 ng/L by a factor of 1.8, but there are no data to indicate that the MPC would be underprotective. The cypermethrin and permethrin MPCs are smaller than the UCDM criteria by a factor of 2.2 and 10, respectively.

In Canada, an interim freshwater quality guideline was derived for permethrin by applying a safety factor of 0.1 to the most sensitive LOEC, which was for *Pteronarcys dorsata* (Anderson 1982). The interim aquatic life guideline for permethrin was derived as 4 ng/L, which is larger than the UCDM chronic criterion of 2 ng/L, but there are no data to indicate that 4 ng/L would be underprotective (CCME 2006). Quebec has also derived its own interim acute criterion for permethrin of 44 ng/L and an interim chronic criterion of 13 ng/L (Guay et al. 2000); the interim acute criterion is larger than the lowest SMAV in the UCD data set and would not be protective of *H. azteca*. In the UK, short-term and long-term predicted NECs (PNECs), analogous to acute and chronic criteria, were recently derived for permethrin using assessment factors (Lepper et al. 2007). The short-term PNEC of 10 ng/L was derived by applying an assessment factor of 10 to the LC_{50} for the mayfly *Hexagenia bilineata*, and the long-term PNEC of 1.5 ng/L was derived by applying an assessment factor of 20 to an LOEC for the caddisfly *B. americanus* (Lepper et al. 2007). The currently adopted long-term (chronic) environmental quality standard (EQS) in the UK for permethrin is 10 ng/L. There are also proposed long-term and short-term EQSs for cypermethrin of 0.1 and 0.4 ng/L, respectively, which are lower than the existing EQSs of 0.2 and 2.0 ng/L, respectively (UKTAG 2008).

15 Comparison to the USEPA (1985) Method

More pyrethroid toxicity data are available now than when CDFG derived criteria for bifenthrin, cypermethrin, and permethrin (Siepmann and Holm 2000) using the USEPA (1985) method. To compare the UCDM criteria to those generated using the USEPA (1985) method, the data sets gathered for this article were used to generate example USEPA criteria for these compounds. The five acute taxa requirements of the SSD procedure in the UCDM were fulfilled for each of these five pyrethroids. There are three additional taxa requirements in the USEPA acute method, as follows:

1. A third family in the phylum Chordata (e.g., fish, amphibian)
2. A family in a phylum other than Arthropoda or Chordata (e.g., Rotifera, Annelida, Mollusca)
3. A family in any order of insect or any phylum not already represented

These three additional requirements were not met for any of these compounds. The bifenthrin, λ-cyhalothrin, and permethrin data sets do not contain any species in a phylum other than Arthropoda or Chordata, but met all of the other taxa requirements. The CDFG has calculated criteria for compounds with incomplete data sets if the missing taxa requirements are known to be relatively insensitive to the compound of interest. The only data available for organisms not in the phyla Arthropoda or Chordata were for saltwater mollusks (*Crassostrea virginica* and *Crassostrea gigas*), which were very insensitive to bifenthrin and λ-cyhalothrin—EC_{50}s could not be calculated for these species because of solubility limits or no responses were observed at the highest concentrations tested (Thompson 1985; Ward 1986a, 1986b, 1987)—so example criteria were calculated for bifenthrin, λ-cyhalothrin, and permethrin. The cyfluthrin and cypermethrin acute data sets were missing two of the additional requirements, so example criteria were not calculated for these compounds.

Acute criteria were calculated by fitting the log-triangular distribution to the acute bifenthrin, λ-cyhalothrin, and permethrin data sets (Tables 2, 8, and 10) and are reported with two significant figures, according to the USEPA (1985) method. The USEPA (1985) method fits the SSD to *genus* mean acute values while the UCDM uses *species* mean acute values, so the UCDM data sets were altered when necessary to calculate genus mean acute values.

Example acute criterion = Final acute value/2

Bifenthrin : Example final acute value (fifth percentile) = 0.0009543 μg/L
Example acute criterion = 0.00048 μg/L

λ-Cyhalothrin: Example final acute value (fifth percentile) = 0.001845 μg/L
Example acute criterion = 0.00092 μg/L

Permethrin : Example final acute value (fifth percentile) = 0.039001 μg/L
Example acute criterion = 0.010 μg/L

The bifenthrin example acute criterion (0.48 ng/L) is almost one order of magnitude lower than the acute criterion calculated by the UCDM (4 ng/L). The λ-cyhalothrin example acute criterion (0.92 ng/L) is almost identical to the acute criterion calculated using the Burr Type III distribution of the UCDM (1 ng/L), and the permethrin example acute criterion (10 ng/L) is identical to the UCDM acute criterion (10 ng/L).

To calculate chronic criteria according to the USEPA (1985) method for compounds with limited chronic data such as the pyrethroids, an ACR procedure is used, which is very similar to the ACR procedure in the UCDM. The ACR procedure cannot be used for cyfluthrin and cypermethrin because acute criteria were not calculated for these compounds. The EPA ACR procedure requires data for three ACRs, which were not available for bifenthrin or permethrin. For λ-cyhalothrin, the same three SMACRs calculated for the UCDM (Table 13) were calculated according to the USEPA (1985) methodology to give a final λ-cyhalothrin ACR of 4.73. The λ-cyhalothrin chronic criterion was calculated by dividing the final acute value by the final ACR:

Example chronic criterion = Final acute value/Final ACR
λ-cyhalothrin example chronic criterion = 0.00039 μg/L

The λ-cyhalothrin example chronic criterion (0.39 ng/L) differs by less than a factor of 2 from the one recommended by the UCDM (0.5 ng/L).

This comparison of criteria calculated using the UCDM and USEPA (1985) method highlights the limitations of the USEPA method. According to the USEPA method, acute criteria could not be calculated for cyfluthrin or cypermethrin, and acute criteria were only calculated for bifenthrin, λ-cyhalothrin, and permethrin by making exceptions for the taxa requirements, and chronic criteria could not be calculated for bifenthrin, cyfluthrin, or cypermethrin. The λ-cyhalothrin acute data set was large and the criteria calculated by the two methods were very similar (1 ng/L vs. 0.92 ng/L). When large data sets are available, criteria calculated using the two methods have been similar, e.g., chlorpyrifos and diazinon (Palumbo et al. (2012)), because the calculation methods in these cases are very similar. When large data sets are not available or data sets are missing a USEPA taxa requirement, the UCDM is able to generate criteria, where the USEPA method gives no results, e.g., malathion (Palumbo et al. (2012)) and cyfluthrin.

16 Final Criteria Statements

The inputs for the final criteria statement are listed in Table 15.

Aquatic life should not be affected unacceptably if the 4-day average concentration of [1] does not exceed [2] μg/L ([3] ng/L) more than once every 3 years on the average and if the 1-h average concentration does not exceed [4] μg/L ([5] ng/L) more than once every 3 years on the average. Mixtures of [1] and other pyrethroids should be considered in an additive manner (see Sect. 7).

Table 15 Final numeric criteria for the five pyrethroids

1 Compound	2 Chronic riterion (μg/L)	3 Chronic criterion (ng/L)	4 Acute criterion (μg/L)	5 Acute criterion (ng/L)
Bifenthrin	0.004	4	0.0006	0.6
Cyfluthrin	0.00005	0.05	0.0003	0.3
Cypermethrin	0.0002	0.2	0.001	1
λ-Cyhalothrin	0.0005	0.5	0.001	1
Permethrin	0.002	2	0.01	10

It is recommended that the freely dissolved pyrethroid concentration is measured for criteria compliance because this appears to be the best predictor of the bioavailable fraction.

17 Summary

Aquatic life water quality criteria were derived for five pyrethroids using a new methodology developed by the University of California, Davis (TenBrook et al. 2010). This methodology was developed to provide an updated, flexible, and robust water quality criteria derivation methodology specifically for pesticides. To derive the acute criteria, log-logistic SSDs were fitted to the medium-sized bifenthrin, cyfluthrin, and cypermethrin acute toxicity data sets while the λ-cyhalothrin and permethrin acute data sets were larger, and Burr Type III SSDs could be fitted to these data sets. A review of the cyfluthrin acute criterion revealed that it was not protective of the most sensitive species in the data set, *H. azteca*, so the acute value was adjusted downward to calculate a more protective criterion. Similarly, the cypermethrin criteria were adjusted downward to be protective of *H. azteca*. Criteria for bifenthrin, λ-cyhalothrin, and permethrin were calculated using the median fifth percentile acute values while the cyfluthrin and cypermethrin criteria were calculated with the next lowest acute value (median first percentile). Chronic data sets were limited in all cases, so ACRs were used for chronic criteria calculations, instead of statistical distributions. Sufficient corresponding acute and chronic data were not available for bifenthrin, cypermethrin, or permethrin, so a default ACR was used to calculate these chronic criteria while measured ACRs were used for cyfluthrin and λ-cyhalothrin. A numeric scoring system was used to sort the acute and chronic data, based on relevance and reliability, and the individual study scores are included in the Supporting Information.

According to the USEPA (1985) method, the data sets gathered for these five pyrethroids would not be sufficient to calculate criteria because they were each missing at least one of the eight taxa required by that method. The USEPA (1985) method generates robust and reliable criteria, and the goal of creating the UCDM was to create a method that also yields statistically robust criteria, but with more

flexible calculation methods to accommodate pesticide data sets of varied sizes and diversities. Using the UCDM, acute and chronic water quality criteria were derived for bifenthrin (4 and 0.6 ng/L, respectively), cyfluthrin (0.3 and 0.05 ng/L, respectively), cypermethrin (1 and 0.2 ng/L, respectively), λ-cyhalothrin (1 and 0.5 ng/L, respectively), and permethrin (10 and 2 ng/L, respectively). Water quality criteria for these five pyrethroids can be used by environmental managers to control the increasing problem of surface water contamination by pesticides.

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Aquatic Life Water Quality Criteria Derived via the UC Davis Method: III. Diuron

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1 Introduction

Diuron is a phenylurea herbicide that has been frequently detected in surface waters (the US Environmental Protection Agency, USEPA 2003), including periods when relatively low amounts were used, because it is moderately persistent in the water column (Ensminger et al. 2008). Diuron poses a risk to aquatic life because it, and other herbicides, can cause adverse effects on algae and vascular plants, which are the foundation of the aquatic food chain. Water quality standards are used to regulate pesticides in surface waters, and these standards are typically based on water quality criteria for the protection of aquatic life. When pesticide concentrations do not exceed water quality criteria, no adverse effects on aquatic life are expected. The derivation of acute and chronic water quality criteria for diuron using a new methodology developed by the University of California, Davis (TenBrook et al. 2010), is described in this chapter. The UC Davis methodology (UCDM) was designed to be more flexible than the USEPA method (1985) for deriving water quality criteria, although many aspects of the methods are similar.

2 Data Collection and Evaluation

Diuron (*N′*-(3,4-dichlorophenyl)-*N*, *N*-dimethylurea) is a phenylurea herbicide that is moderately soluble in water. Based on its physical–chemical properties, the herbicide is not likely to partition to sediments or to volatilize (Table 1), and it is considered to be moderately persistent because it is stable to hydrolysis (Table 2).

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Table 1 Physical–chemical properties of diuron

Molecular weight	233.10
Density	1.4 g/mL (IUPAC 2008)
Water solubility	38 mg/L (geomean, $n = 2$; Tomlin 2003; IUPAC 2008)
Melting point	158°C (Lide 2003)
Vapor pressure	1.15×10^{-3} mPa (IUPAC 2008)
Henry's constant (K_H)	173,205 Pa m^3 mol^{-1} (geomean, $n = 2$; Mackay et al. 2006; IUPAC 2008)
Log K_{oc} [a]	2.61 (geomean, $n = 20$; Mackay et al. 2006)
Log K_{ow} [b]	2.78 (geomean, $n = 3$; Hansch et al. 1995; Sangster Research Laboratories 2008; IUPAC 2008)

[a] Log-normalized organic carbon–water partition coefficient
[b] Log-normalized octanol–water partition coefficient

Table 2 Environmental fate of diuron

	Half-life	Water	Temp (°C)	pH	Reference
Hydrolysis	>4 months	Phosphate buffer	20	5–9	Mackay et al. (2006)
	Stable	Sterile buffer	25	5, 7, 9	USEPA (2003)
Aqueous photolysis	2.25 h	Distilled	NR	NR	Mackay et al. (2006)
	43 days	NR	NR	NR	USEPA (2003)
Biodegradation (aerobic)	~20 days	Filtered sewage water	20	NR	Mackay et al. (2006)

NR not reported

Approximately 86 original studies on the effects of diuron on aquatic life were identified and reviewed. These studies are available in the open literature or may be requested from the USEPA or the California Department of Pesticide Regulation (CDPR). Studies that fell into three categories were evaluated according to the UCDM: (1) single-species effects, (2) ecosystem-level studies, and (3) terrestrial wildlife studies.

According to the UCDM scheme, single-species effect studies were rated for relevance and reliability, in a manner which was summarized by Palumbo et al. (2012). Studies that were rated as relevant (R) or less relevant (L) were also rated for reliability, whereas those that were rated as not relevant (N) were not further rated. There were three categories of study reliability: reliable (R), less reliable (L), or not reliable (N). The reliability ratings were determined by how many test parameters (e.g., nominal concentrations, source of dilution water, etc.) were reported, and if they were acceptable according to standard methods. Studies were then assigned a two-letter code in which their degree of relevance and reliability were rated. Studies that were rated not relevant (N) or not reliable (RN or LN) were not used for criteria derivation. All data rated as acceptable (RR) or supplemental (RL, LR, LL) for criteria derivation are summarized in Tables 3–7. Acceptable data rated as relevant and reliable (RR) were used for numeric criteria derivation. Supplemental data that were rated as less relevant and/or less reliable (RL, LR, or LL) for particularly sensitive, threatened, or endangered species were compared to the criteria to ensure protection of these species. Data summary records

Table 3 Final acute toxicity data set for diuron

Species	Test type	Meas/ Nom	Chemical grade (%)	Duration (h)	Temp (°C)	End point	Age/size	LC/EC_{50} (μg/L) (95% CI)	Reference
Daphnia magna	S	Nom	80.0	48	19.9	Mortality/ immobility	<24 h	12,000 (10,000–13,000)	Baer (1991)
Daphnia pulex	SR	Meas	99.8	96	22	Mortality	5 days	17,900 (14,200–22,600)	Nebeker and Schuytema (1998)
Hyalella azteca	SR	Meas	99.8	96	22	Mortality	<11 days	19,400 (17,700–21,300)	Nebeker and Schuytema (1998)

All studies were rated RR (data rated as acceptable)
S Static, *SR* static renewal, *FT* flow through

Table 4 Final chronic plant toxicity data set for diuron

Species	Test type	Meas/ Nom	Chemical grade (%)	Duration	Temp (°C)	End point	Age/size	NOEC[a] (μg/L)	LOEC[b] (μg/L)	MATC[c] (μg/L)	EC_{50} (μg/L) (95% CI)	Reference
Lemna gibba G3	S	Meas	99.1	7 days	24.7	Growth inhibition (biomass yield), relative growth rate (biomass)	Plant with 4 fronds	2.47	8.11	**4.48**	14.4 (9.26–19.6)[d]	Ferrell (2006)
Navicula pelliculosa	S	Nom	99.1	72 h	22–24	Growth inhibition (biomass)	Cells	11	33	19.1	22 (9–56)	Dengler (2006b)
N. pelliculosa	S	Nom	99.1	72 h	22–24	Growth inhibition (growth rate)	Cells	11	33	19.1	65 (33–160)	Dengler (2006b)
N. pelliculosa						Growth inhibition				**19.1**		Geomean
Pseudokirchneriella subcapitata (formerly *Selenastrum capricornutum* Printz)	S	Meas	96.8	120 h	24	Growth inhibition	2-day-old algal cells	1.3	2.5	**1.8**	2.9 (2.5–3.5)	Blasberg et al. (1991)
Scenedesmus obliquus	S	Nom	Technical	24 h	21	Growth inhibition	Algal cells	NR	NR	NR	10	Geoffroy et al. (2002)
Synechococcus leopoliensis	S	Nom	99.1	72 h	22–25	Growth inhibition (biomass)	Algal cells	3.7	11	**6.4**	26 (4–100)	Dengler (2006a)

All studies were rated RR

S Static, *SR* static renewal, *FT* flow through, *NR* not reported, *n/a* not applicable

Species mean chronic value is in bold

[a] No-observed effect concentration

[b] Lowest-observed effect concentration

[c] Maximum acceptable toxicant concentration

[d] EC_{50} based on biomass yield end point

Table 5 Final chronic animal toxicity data set for diuron

Species	Test type	Meas/ Nom	Chemical grade (%)	Duration (days)	Temp (°C)	End point	Age/size	NOEC (µg/L)	LOEC (µg/L)	MATC (µg/L)	Reference
Chironomus tentans	SR	Meas	99.8	10	24	Mortality	2 days, first instar	1,900	3,400	2,540	Nebeker and Schuytema (1998)
Daphnia pulex	S	Meas	99.8	7	NR	Reduced number of young/mortality	5 days	4,000.0	7,700	5,550	Nebeker and Schuytema (1998)
Hyalella azteca	SR	Meas	99.8	10	22	Mortality/reduced weight	<11 days	7,900	15,700	11,140	Nebeker and Schuytema (1998)
Lumbriculus variegatus	SR	Meas	99.8	10	23	Reduced weight	Small, short adults	1,800	3,500	2,510	Nebeker and Schuytema (1998)
Physa gyrina	SR	Meas	99.8	10	24	Reduced weight	2 days, first instar	13,400	22,800	17,480	Nebeker and Schuytema (1998)
Pimephales promelas	FT	Meas	98.6	64	25	Deformity, mortality	Eggs <24 h, hatched fry	33.4	78	51	Call et al. (1983, 1987)
Pseudacris regilla	SR	Meas	99.8	14	20		Tadpole	14,500	21,100	17,490	

(continued)

Table 5 (continued)

Species	Test type	Meas/ Nom	Chemical grade (%)	Duration (days)	Temp (°C)	End point	Age/size	NOEC (µg/L)	LOEC (µg/L)	MATC (µg/L)	Reference
						Growth inhibition (length)					Schuytema and Nebeker (1998)
Rana aurora	SR	Meas	99.8	7	20	Growth inhibition (wet weight)	Tadpole	7,600	14,500	10,500	Schuytema and Nebeker (1998)
Rana catesbeiana	SR	Meas	99.8	21	24	Growth inhibition (dry weight)	Tadpole	11,690[a]	16,430[a]	12,450[a]	Schuytema and Nebeker (1998)
Xenopus laevis	SR	Meas	99.8	4 days	24	Growth inhibition (length)	Embryo	10,490[b]	20,540[b]	14,680[b]	Schuytema and Nebeker (1998)

All studies were rated RR

S static, *SR* static renewal, *FT* flow through, *NR* not reported

[a] SMCV calculated from three values

[b] SMCV calculated from two values

Table 6 Acceptable excluded data rated RR with given reason for exclusion

Species	Test type	Meas/ Nom	Chemical grade (%)	Duration	Temp (°C)	End point	Age/size	LC/EC_{50} (μg/L) (95% CI)	MATC (μg/L)	Reference	Reason for exclusion
Chironomus tentans	SR	Meas	99.8	10 days	24	Reduced weight	2 days, first instar	–	4,910	Nebeker and Schuytema (1998)	A
Daphnia magna	S	Nom	80.0	24 h	19.9	Mortality/ immobility	<24 h	68,000 (55,000–86,000)	–	Baer (1991)	D
Lemna gibba G3	S	Meas	99.1	7 days	24.7	Growth inhibition (biomass)	Plant with 4 fronds	15.7 (10.06–20.8)	4.48	Ferrell (2006)	A
L. gibba G3	S	Meas	99.1	7 days	24.7	Growth inhibition (frond count)	Plant with 4 fronds	19.1 (13.4–24.8)	14.47	Ferrell (2006)	A
L. gibba G3	S	Meas	99.1	7 days	24.7	Growth inhibition (frond count yield)	Plant with 4 fronds	17.5 (11.8–23.2)	14.47	Ferrell (2006)	A
L. gibba G3	S	Meas	99.1	7 days	24.7	Relative growth rate (frond count)	Plant with 4 fronds	–	14.5	Ferrell (2006)	A
P. promelas	SR	Meas	99.8	7 days	25	Reduced weight	2.5 days embryo	–	5,900	Nebeker and Schuytema (1998)	C
P. promelas	SR	Meas	99.8	10 days	24	Mortality	1.5 months juvenile	–	23,280	Nebeker and Schuytema (1998)	B
Pseudacris regilla	SR	Meas	99.8	10 days	20	Increased deformity	Embryo	–	20,540	Schuytema and Nebeker (1998)	A

(continued)

Table 6 (continued)

Species	Test type	Meas/ Nom	Chemical grade (%)	Duration	Temp (°C)	End point	Age/size	LC/EC$_{50}$ (µg/L) (95% CI)	MATC (µg/L)	Reference	Reason for exclusion
P. regilla	SR	Meas	99.8	14 days	20	Growth inhibition (wet weight)	Tadpole	–	24,720	Schuytema and Nebeker (1998)	A
P. regilla	SR	Meas	99.8	14 days	20	Growth inhibition (dry weight)	Tadpole	–	24,750[a]	Schuytema and Nebeker (1998)	A
Rana catesbeiana	SR	Meas	99.8	21 days	24	Growth inhibition (length)	Tadpole	–	18,950[a]	Schuytema and Nebeker (1998)	A
R. catesbeiana	SR	Meas	99.8	21 days	24	Growth inhibition (wet weight)	Tadpole	–	22,560[a]	Schuytema and Nebeker (1998)	A
Synechococcus leopoliensis	S	Nom	99.1	72 h	22–25	Growth inhibition (growth rate)	Algal cells	–	19.1	Dengler (2006a)	A
Xenopus laevis	SR	Meas	99.8	4 days	24	Deformity	Embryo	–	22,560	Schuytema and Nebeker (1998)	A

Reasons for exclusion
A. Less-sensitive end point
B. Less-sensitive life stage
C. Test type not preferred (static vs. flow through)
D. Not the most sensitive or appropriate duration
[a]SMCV calculated from two values

Table 7 Supplemental diuron data rated RL, LR, LL with given reason for rating and exclusion (listed at the end of table)

Species	Test type	Meas/ Nom	Chemical grade (%)	Duration	Temp (°C)	End point	Age/size	LC/EC_{50} (µg/L) (95% CI)	MATC (µg/L)	Reference	Rating/ reason
Achnanthes brevipes	S	Nom	Technical	3 days	20	Reduced oxygen evolution	Algal cells	24 (SE = 1.0)	–	Hollister and Walsh (1973)	LL/1, 2, 6
Americamysis bahia	FT	Meas	96.8	28 days	25.3	Number of young surviving	<24 h juvenile	–	1,400	Ward and Boeri (1992b)	RL/2
Amphora exigua	S	Nom	Technical	3 days	20	Reduced oxygen evolution	Algal cells	31 (SE = 4)	–	Hollister and Walsh (1973)	LL/1, 2, 6
Apium nodiflorum	S	Nom	>99	14 days	NR	Relative growth rate	Single stem node with leaf	2.808	NOEC = 0.05	Lambert et al. (2006)	LL/1, 5, 6
A. nodiflorum	S	Nom	>99	14 days	NR	Growth inhibition (roots)[b]	Single stem node with leaf	0.00026	NOEC < 0.0005	Lambert et al. (2006)	LL/1, 5, 6, 7
A. nodiflorum	S	Nom	>99	14 days	NR	Change in chlorophyll fluorescence ratio	Single stem node with leaf	>5.0	NOEC = 5	Lambert et al. (2006)	LL/1, 5, 6
Artemia salina	S	NR	NR	24 h	25	Mortality	Instar II–III larvae	12,010 (11,420 –12,100)	–	Koutsaftis and Aoyama (2007)	LL/2, 5
Asellus brevicaudus	S	Nom	95.0	96 h	15	Mortality	Mature	15,500 (7,200–33,400)	–	Johnson and Finley (1980)	LL/5, 6
Chara vulgaris	S	Nom	>99	14 days	NR	Relative growth rate	Terminal lengths of shoots with 3 nodes	0.35	NOEC = 0.0005	Lambert et al. (2006)	LL/1, 5, 6

(continued)

Table 7 (continued)

Species	Test type	Meas/ Nom	Chemical grade (%)	Duration	Temp (°C)	End point	Age/size	LC/EC_{50} (µg/L) (95% CI)	MATC (µg/L)	Reference	Rating/ reason
C. vulgaris	S	Nom	>99	14 days	NR	Change in chlorophyll fluorescence ratio	Terminal lengths of shoots with 3 nodes	4.033	NOEC = 0.5	Lambert et al. (2006)	LL/1, 5, 6
Chlamydomonas moewusii Gerloff	S	Nom	80.0	7 days	21	Growth inhibition	7-day-old algal cell stock	559.44	–	Cain and Cain (1983)	RL/1, 6
Chlamydomonas sp.	S	Nom	Technical	3 days	20	Reduced oxygen evolution	Algal cells	37 (SE = 3)	–	Hollister and Walsh (1973)	LL/1, 2, 6
Chlamydomonas sp.	S	Nom	99.8	20 min	21.5	Change in chlorophyll fluorescence ratio	2–4-week-old algal cells	10.8 (8.5–13.6)	0.22	Podola and Melkonian (2005)	RL/1, 5, 8
Chlorella pyrenoidosa	S	Nom	95.0	4 days	25	Growth inhibition	Algal cells	25	–	Maule and Wright (1984)	LR/1, 6
C. pyrenoidosa	S	Nom	50.0	96 h	25	Growth inhibition	Algal cells	1.3	–	Ma et al. (2001), Ma (2002)	LL/1, 3, 6
Chlorella sp.	S	Nom	Technical	10 days	20.5	Growth inhibition	Algal cells	$EC_{66} = 4$	–	Ukeles (1962)	LL/1, 2, 6
Chlorella sp.	S	Nom	Technical	3 days	20	Reduced oxygen evolution	Algal cells	19 (SE = 2)	–	Hollister and Walsh (1973)	LL/1, 2, 6

Chlorella vulgaris	S	Nom	50.0	96 h	25	Growth inhibition	Algal cells	4.3	–	Ma (2002)	LL/1, 3, 6
C. vulgaris SAG211-11b	S	Nom	99.8	20 min	21.5	Change in chlorophyll fluorescence ratio	2–4-week-old algal cells	27.4 (21.1–35.5)	0.22	Podola and Melkonian (2005)	RL/1, 8
Chlorococcum sp.	S	Nom	Technical	7 days	20	Growth inhibition	Algal cells	$EC_{62} = 10$	NOEC < 1.0	Walsh and Grow (1971)	RL/1, 2
Chlorococcum sp.	S	Nom	Technical	10 days	20	Growth inhibition	Algal cells	10	–	Walsh (1972)	RL/1, 2
Chlorococcum sp.	S	Nom	Technical	90 min	20	Reduced oxygen evolution	Algal cells	20	–	Walsh (1972)	RL/1, 2
Chlorococcum sp.	S	Nom	Technical	3 days	20	Reduced oxygen evolution	Algal cells	20 (SE = 4)	–	Hollister and Walsh (1973)	LL/1, 2, 6
Crassostrea virginica	FT	Meas	96.8	96 h	23	Shell deposition	Neonates, <24 h	4,800 (4,400–5,200)	NOEC = 2,400	Ward and Boeri (1991)	RL/2
Cryptomonas sp.	S	Nom	99.8	20 min	21.5	Change in chlorophyll fluorescence ratio	2–4-week-old algal cells	6.4 (5.3–7.8)	0.22	Podola and Melkonian (2005)	RL/1, 5, 8
Ctenopharyngodon idella	FT	NR	100.0	96 h	13	Mortality	1+ year, 15.8 g, 9.5 cm	31,000 (28,000–34,000)	–	Tooby et al. (1980)	LL/1, 5, 6
Cyclotella nana	S	Nom	Technical	3 days	20	Reduced oxygen evolution	Algal cells	39 (SE = 7)	–	Hollister and Walsh (1973)	LL/1, 2, 6
Cyprinodon variegates	FT	Meas	96.8	32 days	30	Mortality	<24 h	–	2,500	Ward and Boeri (1992a)	RL/2

(continued)

Table 7 (continued)

Species	Test type	Meas/ Nom	Chemical grade (%)	Duration	Temp (°C)	End point	Age/size	LC/EC_{50} (µg/L) (95% CI)	MATC (µg/L)	Reference	Rating/ reason
Daphnia magna	S	Nom	Technical	26 h	21.1	Mortality/ immobility	First instar	47,000 (41,600 –53,100)	–	Crosby and Tucker (1966)	LL/1, 5, 6
Daphnia pulex	S	Nom	95.0	48 h	15	Mortality/ immobility	First instar	1,400 (1,000–1,900)	–	Johnson and Finley (1980)	LL/5, 6
Dunaliella euchlora Lerche	S	Nom	Technical	10 days	20.5	Growth inhibition	Algal cells	EC_{56} = 0.4	–	Ukeles (1962)	LL/1, 2, 6
Dunaliella tertiolecta	S	Nom	99.0	96 h	20	Growth inhibition	Algal cells	5.9	–	Gatidou and Thomaidis (2007)	LL/2, 5
D. tertiolecta	S	Nom	Technical	3 days	20	Reduced oxygen evolution	Algal cells	10 (SE = 3)	–	Hollister and Walsh (1973)	LL/1, 2, 6
D. tertiolecta Butcher	S	Nom	Technical	10 days	20	Growth inhibition	Algal cells	20	–	Walsh (1972)	RL/1, 2
D. tertiolecta Butcher	S	Nom	Technical	90 min	20	Reduced oxygen evolution	Algal cells	10	–	Walsh (1972)	RL/2, 6, 8
Eudorina elegans	S	Nom	99.8	20 min	21.5	Change in chlorophyll fluorescence ratio	2–4-week-old algal cells	13.2 (10.4–16.9)	0.22	Podola and Melkonian (2005)	RL/1, 5, 8
Gammarus fasciatus	S	Nom	Technical	24 h	15.5	Mortality	Early instar	2,500 (1,000–5,500)	–	Sanders (1970)	LL/1, 5, 6
G. fasciatus	S	Nom	Technical	48 h	15.5	Mortality	Early instar	1,800 (800–5,200)	–	Sanders (1970)	LL/1, 5, 6
G. fasciatus	S	Nom	Technical	96 h	15.5	Mortality	Early instar	700 (190–8,200)	–	Sanders (1970)	LL/1, 5, 6

Gammarus lacustris	S	Nom	Technical	24 h	21.1	Mortality	2 months	700 (590–8,300)	–	Sanders (1969)	LL/1, 5, 6
G. lacustris	S	Nom	Technical	48 h	21.1	Mortality	2 months	380 (290–500)	–	Sanders (1969)	LL/1, 5, 6
G. lacustris	S	Nom	Technical	96 h	21.1	Mortality	2 months	160 (130–190)	–	Sanders (1969)	LL/1, 5, 6
Isochrysis galbana	S	Nom	Technical	3 days	20	Reduced oxygen evolution	Algal cells	10 (SE = 3)	–	Hollister and Walsh (1973)	LL/1, 2, 6
I. galbana Parke	S	Nom	Technical	90 min	20	Reduced oxygen evolution	Algal cells	10	–	Walsh (1972)	RL/1, 2, 8
I. galbana Parke	S	Nom	Technical	10 days	20	Growth inhibition	Algal cells	10	–	Walsh (1972)	RL/1, 2
Lemna gibba G3	S	Nom	98.0	7 days	25	Growth inhibition	NR	29 (27–31)	–	Okamura et al. (2003)	LR/6
Lemna minor	S	Nom	98.0	48 h	21	Reduced oxygen evolution	Plant fronds	–	LOEC = 5	Eullaffroy et al. (2007)	LL/1, 6, 7
L. minor 1769	S	Nom	98.0	7 days	25	Growth inhibition	NR	30 (28–31)	–	Okamura et al. (2003)	LR/6
L. minor	S	Nom	98.0	7 days	25	Growth inhibition	Plant fronds	25	LOEC = 5	Teisseire et al. (1999)	RL/1, 6
Lepomis macrochirus	S	Nom	Technical	96 h	12.7	Mortality	0.6–1.5 g	8,900 (8,200–9,600)	–	Macek et al. (1969)	LL/1, 5, 6
L. macrochirus	S	Nom	Technical	96 h	18.3	Mortality	0.6–1.5 g	7,600 (7,000–8,200)	–	Macek et al. (1969)	LL/1, 5, 6
L. macrochirus	S	Nom	Technical	96 h	23.8	Mortality	0.6–1.5 g	5,900 (5,300–6,500)	–	Macek et al. (1969)	LL/1, 5, 6

(continued)

Table 7 (continued)

Species	Test type	Meas/ Nom	Chemical grade (%)	Duration	Temp (°C)	End point	Age/size	LC/EC_{50} (μg/L) (95% CI)	MATC (μg/L)	Reference	Rating/ reason
Lymnaea spp.	S	Nom	NR	96 h	NR	Mortality	Adult	15,300	–	Christian and Tate (1983)	LL/1, 3, 6
Monochrysis lutheri	S	Nom	Technical	3 days	20	Reduced oxygen evolution	Algal cells	18 (SE = 3)	–	Hollister and Walsh (1973)	LL/1, 2, 6
M. lutheri Droop	S	Nom	Technical	10 days	20.5	Growth inhibition	Algal cells	EC_{100} = 0.02	–	Ukeles (1962)	LL/1, 2, 6
M. lutheri Droop	S	Nom	Technical	10 days	20.5	Mortality	Early instar	2,500 (1,000–5,500)	–	Sanders (1970)	LL/1, 5, 6
Myriophyllum spicatum	S	Nom	>99	14 days	NR	Relative growth rate	Terminal lengths of shoots with 3 nodes	5	NOEC = 0.0005	Lambert et al. (2006)	LL/1, 5, 6
M. spicatum	S	Nom	>99	14 days	NR	Change in chlorophyll fluorescence ratio	Terminal lengths of shoots with 3 nodes	>5	NOEC = 5	Lambert et al. (2006)	LL/1, 5, 6
Navicula forcipata	S	Nom	99.0	96 h	20	Growth inhibition	Algal cells	27	–	Gatidou and Thomaidis (2007)	LL/2, 5
Navicula inserta	S	Nom	Technical	3 days	20	Reduced oxygen evolution	Algal cells	93(SE = 12)	–	Hollister and Walsh (1973)	LL/1, 2, 6
Neochloris sp.	S	Nom	Technical	3 days	20	Reduced oxygen evolution	Algal cells	28 (SE = 5)	–	Hollister and Walsh (1973)	LL/1, 2, 6
Nitzschia (Ind. 684)	S	Nom	Technical	3 days	20	Reduced oxygen evolution	Algal cells	169 (SE = 17)	–	Hollister and Walsh (1973)	LL/1, 2, 6

Nitzschia closterium	S	Nom	Technical	3 days	20	Reduced oxygen evolution	Algal cells	50 (SE = 6)	–	Hollister and Walsh (1973)	LL/1, 2, 6
Oscillatoria cf. chalybea	S	Nom	80.0	96 h	25	Growth inhibition	Algal cells	28	LOEC = 280	Schrader et al. (1998)	LR/1, 6
Oncorhynchus clarki (*Salmo clarki*)	S	Nom	95.0	96 h	10.0	Mortality	3.00 g	1,400 (1,100–1,900)	–	Johnson and Finley (1980)	LL/5, 6
Oncorhynchus mykiss (*Salmo gairdneri*)	S	Nom	95.0	96 h	13	Mortality	0.8 g	4,900 (4,100–5,900)	–	Johnson and Finley (1980)	LL/5, 6
O. mykiss (*Salmo gairdneri*)	S	Nom	80.0	96 h	13	Mortality	1.2 g	16,000 (11,300–22,700)	–	Johnson and Finley (1980)	LL/5, 6
O. mykiss	S	Nom	95	7 days	10	Mortality	Juveniles, hatched <24 h ago	74,000 (29,000–3,681,000)	–	Okamura et al. (2002)	LR/1, 6
O. mykiss	S	Nom	95	14 days	10	Mortality	Juveniles, hatched <24 h ago	15,000 (11,000–29,000)	–	Okamura et al. (2002)	LR/1, 6
O. mykiss	S	Nom	95	21 days	10	Mortality	Juveniles, hatched <24 h ago	5,900 (4,700–7,700)	–	Okamura et al. (2002)	LR/1, 6
O. mykiss	S	Nom	95	28 days	10	Mortality	Juveniles, hatched <24 h ago	230 (8.9–590)	–	Okamura et al. (2002)	LR/1, 6
Phaeodactylum tricornutum	S	Nom	Technical	3 days	20	Reduced oxygen evolution	Algal cells	10 (SE = 3)	–	Hollister and Walsh (1973)	LL/1, 2, 6
P. tricornutum Bohlin	S	Nom	Technical	90 min	20	Reduced oxygen evolution	Algal cells	10	–	Walsh (1972)	RL/1, 2, 8

(continued)

Table 7 (continued)

Species	Test type	Meas/ Nom	Chemical grade (%)	Duration	Temp (°C)	End point	Age/size	LC/EC_{50} (µg/L) (95% CI)	MATC (µg/L)	Reference	Rating/ reason
P. tricornutum Bohlin	S	Nom	Technical	10 days	20	Growth inhibition	Algal cells	10	–	Walsh (1972)	RL/1, 2
P. tricornutum Bohlin	S	Nom	Technical	10 days	20.5	Growth inhibition	Algal cells	$EC_{21} = 0.4$	–	Ukeles (1962)	LL/1, 2, 6
Pimephales promelas	FT	Meas	98.6	96 h	24.3	Mortality	30 days	14,200 (13,400–15,000)	–	Call et al. (1983, 1987)	RL/1, 5
Platymonas sp.	S	Nom	Technical	3 days	20	Reduced oxygen evolution	Algal cells	7 (SE = 3)	–	Hollister and Walsh (1973)	LL/1, 2, 6
Porphyridium cruentum	S	Nom	Technical	3 days	20	Reduced oxygen evolution	Algal cells	24 (SE = 3)	–	Hollister and Walsh (1973)	LL/1, 2, 6
Protcoccus sp.	S	Nom	Technical	10 days	20.5	Growth inhibition	Algal cells	$EC_{48} = 0.02$	–	Ukeles (1962)	LL/1, 2, 6
Pseudokirchneriella subcapitata (*Selenastrum capricornutum*)	S	Nom	80.0	96 h	25	Growth inhibition	Algal cells	36.4	LOEC = 280	Schrader et al. (1998)	LR/1, 6
P. subcapitata (*S. capricornutum*)	S	Nom	98.0	3 days	25	Growth inhibition	Algal cells	6.6 (5.9–7.2)	–	Okamura et al. (2003)	LL/5, 6
P. subcapitata (*S. capricornutum*)	S	Nom	99.8	20 min	21.5	Change in chlorophyll fluorescence ratio	2–4-week-old algal cells	13.8 (9.3–20.4)	0.22	Podola and Melkonian (2005)	RL/1, 8

P. subcapitata (*S. capricornutum*)	S	Nom	98	120 h	24	Growth inhibition	Algal cells	22	NOEC = 10	Douglas and Handley (1988)	RL/6
P. subcapitata (*S. capricornutum*)	S	Nom	98	72 h	24	Growth inhibition	Algal cells	18	–	Douglas and Handley (1988)	RL 6
Pteronarcys californica	S	Nom	95.0	96 h	15	Mortality	Second year class	1,200 (900–1,700)	–	Johnson and Finley (1980)	LL/5, 6
P. californica	S	Nom	Technical	24 h	15.5	Mortality	30–35 mm	3,600 (2,800–4,700)	–	Sanders and Cope (1968)	LL/1, 5, 6
P. californica	S	Nom	Technical	48 h	15.5	Mortality	30–35 mm	2,800 (2,100–3,800)	–	Sanders and Cope (1968)	LL/1, 5, 6
P. californica	S	Nom	Technical	96 h	15.5	Mortality	30–35 mm	1,200 (870–1,700)	–	Sanders and Cope (1968)	LL 1, 5, 6
Raphidocelis subcapitata	S	Nom	50.0	96 h	25	Growth inhibition	Algal cells	0.7	–	Ma et al. (2006)	LL/3, 5, 6
Salvelinus namaycush	S	Nom	95.0	96 h	10	Mortality	1.5 g	2,700 (2,400–3,000)	–	Johnson and Finley (1980)	LL/5, 6
Scenedesmus obliquus	S	Nom	50.0	96 h	25	Growth inhibition	Algal cells	4.09	–	Ma (2002)	LL/1, 3, 6
S. obliquus	S	Nom	98.0	1 min	22	Change in chlorophyll fluorescence ratio	Algal cells	1[a]	–	Eullaffroy and Vernet (2003)	LL/1, 4, 6, 8

(continued)

Table 7 (continued)

Species	Test type	Meas/ Nom	Chemical grade (%)	Duration	Temp (°C)	End point	Age/size	LC/EC_{50} (μg/L) (95% CI)	MATC (μg/L)	Reference	Rating/ reason
Scenedesmus quadricauda	S	Nom	50.0	96 h	25	Growth inhibition	Algal cells	2.7	–	Ma (2003)	LL/1, 3, 6
Scenedesmus subspicatus	S	Nom	Technical	24 h	20	Growth inhibition	Algal cells, 3-day old	NR	NOEC = 4	Schafer et al. (1994)	LR/5, 6
S. subspicatus	S	Nom	Technical	72 h	20	Growth inhibition	Algal cells, 3-day old	36	NOEC = 10	Schafer et al. (1994)	LR/5, 6
Scherffelia dubia	S	Nom	99.8	20 min	21.5	Change in chlorophyll fluorescence ratio	2–4-week-old algal cells	3.9 (2.5–6.2)	0.22	Podola and Melkonian (2005)	RL/1, 8
Simocephalus serrulatus	S	Nom	95.0	48 h	15	Mortality	First instar	2,000 (1,400–2,800)	–	Johnson and Finley (1980)	LL/5, 6
Staurodesmus convergens	S	Nom	99.8	20 min	21.5	Change in chlorophyll fluorescence ratio	2–4-week-old algal cells	4.1 (2.5–6.9)	0.22	Podola and Melkonian (2005)	RL/1, 5, 8
Stauroneis amphoroides	S	Nom	Technical	3 days	20	Reduced oxygen evolution	Algal cells	31 (SE = 2)	–	Hollister and Walsh (1973)	LL/1, 2, 6
Synechocystis sp.	S	Nom	99.8	20 min	21.5	Change in chlorophyll fluorescence ratio	2–4-week-old algal cells	7.6 (5.5–10.5)	0.22	Podola and Melkonian (2005)	RL/1, 5, 8
Tetraselmis elegans	S	Nom	99.8	20 min	21.5	Change in chlorophyll fluorescence ratio	2–4-week-old algal cells	3.0 (2.3–3.8)	0.22	Podola and Melkonian (2005)	RL/1, 8

Thalassiosira fluviatilis	S	Nom	Technical	3 days	20	Reduced oxygen evolution	Algal cells	95 (SE = 10)	–	Hollister and Walsh (1973)	LL/1, 2, 6
Ulothrix fimbriata	S	Nom	95.0	7 days	25	Growth inhibition	Algal cells	540	–	Maule and Wright (1984)	LR/1, 6

S Static, *SR* static renewal, *FT* flow through, *NR* not reported, *95% CI* 95% confidence interval, *SE* standard error

Reasons for ratings

1. Not a standard method
2. Saltwater
3. Low chemical purity or purity not reported
4. Toxicity value not calculable
5. Control not described and/or response not reported
6. Low reliability score
7. End point not linked to growth, reproduction, or survival
8. Inappropriate test duration

[a] Value reported as toxicity threshold, which is conceptually very similar to an MATC, but calculated differently than an MATC or an EC_x

[b] Growth inhibition of roots is not a standard end point

including the rationale for the scores and ratings were created for each study, all of which are included in the Supporting Material (http://extras.springer.com/).

Because diuron is a herbicide, many of the single-species studies were plant toxicity tests. Plant data are more difficult to interpret than animal data because a variety of end points may be used, but the significance of each one is not clear. According to the UCDM, all plant studies were considered as chronic because the typical end points of growth or reproduction are inherently chronic. Only end points of growth or reproduction (measured by biomass) and tests lasting at least 24 h had the potential to be rated highly, and to be used for criteria calculation, which is in accordance with standard methods (ASTM 2007a, 2007b, USEPA 1996). The four main end points identified in plant toxicity tests are described below, including whether the end point is clearly linked to survival, growth, or reproduction.

2.1 Growth Inhibition

All of these end points are evaluated relative to a control growth measurement. Depending on the plant, the endpoint measurement may have been assessed by direct cell counts with a hemacytometer, cell counts with a spectrophotometer, cell counts with an electronic particle counter, chlorophyll concentration measured by absorbance, turbidity measured by absorbance, or number of fronds (*Lemna* spp.). In all cases, growth of exposed samples was compared statistically to controls.

2.2 Relative Growth Rate

The biomass of macrophytes was measured before and after exposure to calculate a growth rate as (final mass–initial mass)/initial mass $\times$ 100. This end point is very similar to growth inhibition, except that it is expressed as a positive effect while growth inhibition is expressed as a negative effect. In all cases, the growth rate of exposed samples was compared statistically to controls.

2.3 Change in Chlorophyll Fluorescence Ratio

Chlorophyll fluorescence was measured at a maximal fluorescence and either a variable or steady-state fluorescence and a ratio were computed. An increase in the ratio indicates a disruption of photosystem II (PSII), which may lead to a decrease in carbohydrate production and thus decreased growth. With this end point, one measures physiological stress in plants (Lambert et al. 2006). This ratio is a valid measurement that is related to algal growth according to ASTM Standard Method E1218-04 (ASTM 2004), but is described as being less definitive than measuring

chlorophyll *a* content, and is therefore not a preferred end point if one more directly related to growth is available.

2.4 Reduced Oxygen Evolution

Plants evolve oxygen during photosynthesis, and reduced photosynthesis has been shown by Walsh (1972) to correlate well with the concentrations that inhibit growth, but it is not clear that this end point is a good predictor of growth inhibition across all plant species. The value for this end point is always calculated as being relative to controls.

To ensure that the derived criteria are protective of ecosystems and used all available data, all multispecies mesocosm, microcosm, and ecosystem (field and laboratory) studies that were rated as being acceptable and reliable (R) or less reliable (L) were compared to the criteria. Studies on the effects of diuron on mallard ducks were rated for reliability using the terrestrial wildlife evaluation table. Mallard studies that were rated as being reliable (R) or less reliable (L) were used to evaluate the bioaccumulation of diuron.

3 Data Reduction

The data reduction procedure is described by Palumbo et al. (2012). Multiple toxicity values for diuron for the same species were reduced down to a species mean acute value (SMAV) or a species mean chronic value (SMCV). Acceptable (RR) data were excluded from the final data sets that were employed for criteria calculations for the following reasons: more appropriate exposure durations were available, flow-through tests are preferred over static tests, a test with a more sensitive life stage of the same species was available, and tests with more sensitive end points were available. Excluded data are given in Table 6. The final acute data set contains three animal SMAVs (Table 3), the final chronic plant data set contains three SMCVs (Table 4), and the final chronic animal data set contains ten SMCVs (Table 5).

4 Acute Criterion Calculation

Although plants are more sensitive to diuron, the acute criterion was calculated from acute animal toxicity data because plant toxicity tests are considered as being chronic. Three SMAVs from two different taxa were available: planktonic crustaceans (*Daphnia magna* and *Daphnia pulex*) and a benthic invertebrate (*Hyalella azteca*). Because there were so few data, the acute criterion was not

calculated using a species sensitivity distribution (SSD). At least five data values are required to fit an SSD to a data set, and the data must fulfill five different taxa requirements (planktonic crustacean, benthic invertebrate, fish from the family Salmonidae, warm water fish, and insect). Instead, the acute criterion was calculated using the assessment factor (AF) procedure (TenBrook et al. 2010). The AFs in the UCDM were derived by randomly sampling 12 organic pesticide data sets to give estimates of the median fifth percentile of a distribution (TenBrook et al. 2010). AFs are recognized as a conservative approach for dealing with uncertainty in assessing risks posed by chemicals and are widely used in other methods for deriving criteria.

The acute criterion was calculated by dividing the lowest SMAV (12 mg/L for *D. magna*) from the acceptable (RR) data set by an AF. The magnitude of the AF was determined by the number of taxa available in the data set. The acute data set fulfilled two of the five taxa requirements, corresponding to an AF of 36 (TenBrook et al. 2010). The acute value calculated using the AF represents an estimate of the median fifth percentile of the SSD, which is the recommended acute value. The recommended acute value is divided by a factor of 2 to calculate the acute criterion. Because the toxicity datum used to calculate the criterion was presented in only two significant figures, the criterion is rounded to two significant figures.

$$\begin{aligned} \text{Acute value} &= \frac{\text{LowestSMAV}}{\text{Assessment factor}}, \\ &= 0.33 \text{ mg/L}. \end{aligned} \tag{1}$$

$$\begin{aligned} \text{Acute criterion} &= \frac{\text{Acutevalue}}{2}, \\ &= 0.17 \text{ mg/L } (170 \ \ \mu\text{g/L}). \end{aligned} \tag{2}$$

5 Chronic Criterion Calculation

The chronic data demonstrate that plants are more sensitive to diuron than animals. Because diuron is a herbicide and the data demonstrates that plants are the most sensitive taxon, only plant data were used to derive the chronic criterion. The chronic criterion is likely to also be protective of animals because they are less sensitive to diuron. Four acceptable maximum acceptable toxicant concentrations (MATCs) and five acceptable EC_{50}s were available for vascular plants or alga. MATCs are recommended for derivation of the chronic criterion because they approximate a no-effect concentration (unlike EC_{50}s). EC_x toxicity values are not recommended for chronic criteria derivation unless there is data for the relevant species indicating what level of x corresponds to a no-effect level, which was not available for the diuron data set. Since there were too few MATCs to fit a distribution to the data, the chronic criterion was derived by setting the chronic criterion equal to the lowest

NOEC from an important alga or vascular aquatic plant species that has measured concentrations and a biologically relevant end point (TenBrook et al. 2010). In this scheme, the NOEC of 1.3 μg/L for the green algae *Pseudokirchneriella subcapitata* (formerly *Selenastrum capricornutum*) serves as the chronic criterion.

6 Water Quality Effects and Bioavailability

Temperature and pH do not appear to have a significant effect on the toxicity of diuron, as it is only a very weak base and no such effects have been documented in the literature. Because diuron has a moderate octanol–water partition coefficient ($\log K_{ow} = 2.78$), decreased bioavailability due to surface sorption is possible. Knauer et al. (2007) demonstrated that the addition of black carbon (BC) in its native form to water only slightly decreased the toxicity of diuron to the freshwater green algae *P. subcapitata* (formerly *S. capricornutum*). BC is ubiquitous in the environment because it is a product of incomplete combustion and can act as a supersorbent for some organic contaminants as a result of its large surface area, but it represents only a small fraction of total organic carbon, which is usually responsible for the majority of sorption to solids. Studies in which the sorption of diuron to dissolved organic carbon and clays were investigated are not currently available in the literature, but sorption to these materials is also likely to inhibit bioavailability in a similar manner as sorption to BC. Because there is little information regarding which phases of diuron (freely dissolved, sorbed to dissolved organic carbon, or sorbed to suspended solids) are bioavailable, it is recommended that criteria compliance is based on whole water concentrations.

7 Chemical Mixtures

Diuron is a PSII inhibitor, as are all phenylurea herbicides. Other widely used herbicides, such as the triazines, are also PSII inhibitors, but have different binding sites than the phenylurea herbicides. The concentration addition model is recommended because it has been tested and shown to successfully predict the toxicity of compound mixtures that possess the same mode of action (Mount 2003). It has been confirmed in several studies that the toxicity of a mixture of PSII-inhibitor herbicides, including diuron, can be predicted by the concentration addition method (Arrhenius et al. 2004; Backhaus et al. 2004; Knauert et al. 2008). When diuron is detected with other PSII-inhibitor herbicides, the toxicity of the mixture should be predicted by the concentration addition model and used to determine criteria compliance. If numeric water quality criteria are not available for other PSII-inhibitor herbicides, the model cannot be used and diuron should be considered alone.

The toxicity of diuron in mixtures with other chemicals that work by different modes of action has been reported (e.g., Hernando et al. 2003; Walker 1965), but interaction coefficients for multiple species have not been calculated. Therefore, nonadditive mixture toxicity cannot yet be incorporated into criteria compliance. Lydy and Austin (2005) demonstrated a nonadditive form of toxicity when mixtures of diuron and organophosphate insecticides were tested; these authors found that some acted as synergists with diuron. Teisseire et al. (1999) examined the phytotoxicity of the herbicide combined with two fungicides (copper and folpet) on duckweed (*Lemna minor*) because these pesticides are often used in combination in vineyards. They found that growth inhibition from the combination of diuron and copper depended on the concentrations of both chemicals used, whereas it only depended on the herbicide's concentration when combined with folpet. Diuron is widely used as an antifouling biocide in paint for ship hulls and is often used in combination with other antifouling agents. Several articles were found in which researchers studied the toxicity of mixtures of diuron or diuron metabolites and other antifouling agents, including Irgarol (cybutryne), Sea nine 211 (4, 5-dichloro-2-*n*-octyl-3(2H)-isothiazolone), copper, chlorothalonil, copper pyrithione, zinc pyrithione, and tri-*n*-butyltin (Chesworth et al. 2004; Fernandez-Alba et al. 2002; Gatidou and Thomaidis 2007; Koutsaftis and Aoyama 2007; Manzo et al. 2008; Molander et al. 1992). Resulting toxicities were synergistic, additive, or antagonistic for different mixtures, and were sometimes dependent on concentration ratios and how many compounds were in the mixture.

8 Sensitive Species

The derived criteria were compared to the most sensitive toxicity values in both the acceptable (RR) and supplemental (RL, LR, LL) data sets to ensure that these species are adequately protected. The lowest acute value in the data sets is 160 μg/L for the amphipod *Gammarus lacustris* (Sanders 1969), which is below the derived acute criterion of 170 μg/L. This study was rated LL because the control response was not reported, many other study details were not documented, and the test concentrations were not measured. Additionally, data for another amphipod, *Gammarus fasciatus*, is the next lowest acute value in the data set (700 μg/L), indicating that *Gammarus* species are particularly sensitive to diuron. Because the *G. lacustris* toxicity value is based on nominal, instead of measured, concentrations, the acute criterion was not adjusted downward. If measured data that is highly rated becomes available for *Gammarus* species in the future, it should be examined to determine if the acute criterion is protective of this sensitive genus.

Although there are several supplemental chronic data values that are below the derived chronic criterion (1.3 μg/L), the criterion was not adjusted because the lower toxicity values were lacking at least one of the following critical parameters: (1) the use of an end point that directly related to survival, growth, or reproduction; (2) the use of an exposure duration of $\geq$24 h (ASTM 2007a, 2007b; USEPA 1996);

(3) proper design of hypothesis tests and reporting of parameters used to evaluate the reasonableness of the resulting toxicity values; (4) the use of diuron ≥80% purity; and (5) the use of freshwater species. These studies are discussed in detail below.

The lowest measured chronic value in the data sets is an EC_{50} of 0.00026 µg/L for the rooted macrophyte *Apium nodiflorum*—for a nonstandard end point of root growth (Lambert et al. 2006). This value was calculated by extrapolation, not interpolation, is lower than the NOEC reported for this test, and is below the lowest concentration tested; thus, it was not used for criterion adjustment. There are several other NOECs reported in this study for an appropriate end point (relative growth rate) that are below the proposed chronic criterion (0.0005–0.05 µg/L), but it was not possible to evaluate the reasonableness of these NOECs because the control responses were not reported, the *p*-value selected was not reported, and a minimum significant difference was not calculated.

Podola and Melkonian (2005) report NOEC and LOEC values of 0.1 and 0.5 µg/L, respectively, for nine different algae. These values are below the proposed criteria, but this study used a less preferred end point, change in chlorophyll fluorescence, and a nonstandard exposure duration of 20 min. The authors proposed the use of a biosensor to detect and identify herbicides in the environment, and do not discuss the link between the effects they quantify and survival, growth, or reproduction of the algal strains. Similarly, Eullaffroy and Vernet (2003) reported a toxicity threshold of 1 µg/L for green algae, which is slightly below the chronic criterion. The exposure duration was only 1 min, and its purpose was to rapidly detect herbicides in the environment. This study did not follow a standard method, used extremely short exposure durations, and did not include an acceptable toxicity value (e.g., NOEC, LOEC, MATC, or EC_x). Values from these studies cannot be directly related to survival, growth, or reproduction, and probably only demonstrate exposure to diuron, not adverse effects. Therefore, the chronic criterion was not adjusted downward based on these data.

Ma et al. (2001) and Ma (2002) performed studies that contained the same data for the alga *Chlorella pyrenoidosa*, an EC_{50} equal to the derived criterion. These studies used diuron with a purity of 50% and did not report a control response. In another study by Ma et al. (2006), an EC_{50} below the derived criterion (0.7 µg/L) was reported, but also used diuron of 50% purity. The low-purity compound used in these tests precludes the use of them for criterion adjustment. One study that used saltwater organisms (Ukeles 1962) reported toxicity values below the derived chronic criterion (0.02 and 0.4 µg/L), but such organisms are suspected to have different sensitivities than freshwater species; therefore, they are not used to derive or adjust freshwater criteria.

9 Ecosystem-Level Studies

The chronic criterion was compared to multispecies studies to ensure that the results from single-species studies are protective of multispecies systems. Ten mesocosm, microcosm, or ecosystem (field and laboratory) studies were identified (Table 10),

which were almost all indoor or laboratory studies mimicking small river or pond natural environments and in which microbial, phytoplanktonic, or bacterial communities were examined. An initial drop in phytoplankton biomass was noted in most of these studies, which led to a decrease in dissolved oxygen from the decay of the phytoplankton.

Planktonic communities have displayed varying degrees of response to diuron, depending on, among other things, the concentrations applied. Hartgers et al. (1998) set up microcosms containing phyto-, peri-, bacterio-, and zoo-plankton and monitored them for a 28-day exposure to a mixture of diuron, atrazine, and metolachlor, followed by a 28-day recovery period. An NOEC for the mixture based on phytoplankton was determined to be 1.5 μg/L diuron; thus, the criterion of 1.3 μg/L would likely be protective of phytoplankton based solely on diuron. Flum and Shannon (1987) reported a 96-h EC_{50} of 2,205 μg/L (1,630–3,075 μg/L 95% CI) for an artificial microecosystem containing zooplankton, amphipods, ostracods, unicellular and filamentous algae, protozoans, and microbes, which is much higher than the derived chronic criterion. The EC_{50} was based on monitoring the redox potential, pH, and dissolved oxygen as a measure of toxicity.

Planktonic and algal communities exposed to diuron have been studied in regard to the aquaculture industry because some algae give fish an "off" flavor, yet plankton is necessary for healthy ponds. Zimba et al. (2002) assessed the effect of 9 weeks of diuron application (10 μg/L) on catfish pond ecology. The only significant effect from the exposure was a change in the phytoplankton composition; its biomass was not altered. Perschbacher and Ludwig (2004) also studied plankton communities in outdoor pool mesocosms simulating aquaculture ponds. Three diuron concentrations were tested and monitored for 4-weeks post application. Diuron depressed primary production and biomass of phytoplankton for at least 4-weeks post application, which in turn caused a decrease in dissolved oxygen to levels that are potentially lethal to fish. The concentrations were not measured, and were reported as field rate (1.4 kg a.i./ha), 1/10 field rate, and 1/100 field rate of Direx without adjuvants.

Tlili et al. (2008) studied biofilm communities in a small river with chronic exposure to 1 μg/L diuron, as well as 3-h pulses of 7 or 14 μg/L diuron with and without prior exposure. The results indicate that photosynthesis was never significantly inhibited by any of the treatments, but the pulses did alter the community structure of the microalgae. The pulses affected the eukaryotic community structure in microcosms that did not have prior chronic diuron exposure, but had no significant impact on those that did have prior exposure. Dorigo et al. (2007) assessed prokaryotic and eukaryotic communities and microalgae exposed to vineyard runoff water in a small stream containing diuron concentrations of 0.09 and 0.43 μg/L. The diuron tolerance in these communities increased in the downstream direction and the pristine control site had the lowest tolerance, following the concept that contaminant exposure increases the tolerance of biofilms either by adaptation or species changes. The end points in these studies are not clearly linked to survival, growth, and reproduction and do not exhibit a clear dose–response relationship, so it is not clear if diuron exposure at these levels impacted the

diversity of species in biofilm communities. Community restructuring may have long-term effects on an ecosystem; however, the studies available only provide preliminary data on this subject. The authors of two other studies also reported adverse effects on microbes from diuron exposure (Pesce et al. 2006; Sumpono et al. 2003), but the concentrations tested were well-above the derived criteria and do not provide information regarding protection at levels near the criterion.

The literature shows that herbicides in aquatic ecosystems may have detrimental effects on the bottom trophic levels of the food chain, which may indirectly impact species up the food chain via changes in water quality or decreased food supply. However, many of these studies only tested a single concentration, and no dose–response relationship can be inferred and no-effect concentrations are not available. Considering the available studies, it appears that the derived acute and chronic criteria could be protective of these types of negative effects because most studies used much higher exposure concentrations. The only studies that reported effects at concentrations lower than the derived chronic criterion examined biofilm community restructuring, and provided preliminary data that cannot be incorporated into criteria derivation until more in-depth studies are available.

10 Threatened and Endangered Species

Threatened and endangered species (TES) may be more sensitive than standard test species, and their protection is considered by comparing toxicity values for TES to the derived criteria. Several listed animal species are represented in the data set (CDFG 2010a, 2010b; USFWS 2010). There is an RR study for *Rana aurora*, which has a related subspecies that is endangered (California red-legged frog, *R. a. draytonii*). The *R. aurora* 14-day LC_{50} is 22.2 mg/L, which is well above the acute criterion of 0.17 mg/L. The supplemental data set includes acute toxicity values for the listed salmonids *Oncorhynchus mykiss* and *Oncorhynchus clarki* (listed subspecies is *Oncorhynchus clarki henshawi*). There are two 96-h LC_{50}s for *O. mykiss* of 4.9 (4.1–5.9) mg/L and 16 (11.3–22.7) mg/L, and an LC_{50} of 1.4 (1.1–1.9) mg/L for cutthroat trout (*O. clarki*), which are both well above the acute criterion of 0.17 mg/L.

The USEPA interspecies correlation estimation (Web-ICE v. 3.1; Raimondo et al. 2010) software was used to estimate toxicity values for the listed animals represented in the acute data set by members of the same family or genus. The estimated toxicity values (Table 8) range from 0.729 to 4.491 mg/L for various salmonids.

No plant studies used in the criteria derivation were performed on state or federal endangered, threatened, or rare species. Plants are particularly sensitive to diuron because it is a herbicide, but there are no aquatic plants listed as state or federal endangered, threatened, or rare species; so they could not be considered in this section.

Table 8 Threatened, endangered, or rare species predicted values by Web-ICE (v. 3.1; Raimondo et al. 2010)

Surrogate		Predicted	
Species	LC_{50} (mg/L)	Species	LC_{50} (95% confidence interval) (mg/L)
Rainbow trout (*Oncorhynchus mykiss*)	4.9	*Oncorhynchus aguabonita whitei*	4.491 (3.613–5.581)
		Oncorhynchus gilae apache	4.491 (3.613–5.581)
		Oncorhynchus gilae	4.491 (3.613–5.581)
		Oncorhynchus nerka	5.983 (3.225–11.097)
		Oncorhynchus tshawytscha	8.086 (6.104–4.016)
		Oncorhynchus kisutch	4.758 (3.545–6.387)
		Oncorhynchus clarki henshawi	
Cutthroat trout (*O. clarki*)	1.4	*Oncorhynchus clarkii henshawi*	1.206 (0.967–1.504)
			1.206 (0.967–1.504)
		Oncorhynchus clarkii seleniris	1.206 (0.967–1.504)
		Oncorhynchus clarkii stomias	0.729 (0.290–1.832)
		O. gilae apache	0.729 (0.290–1.832)
		O. gilae	1.673 (1.156–2.421)
		O. kisutch	1.206 (0.967–1.504)
		O. nerka	1.206 (0.967–1.504)
		O. tshawytscha	

11 Bioaccumulation and Partitioning to Air and Sediment

Diuron has a log K_{ow} of 2.78 (Sangster Research Laboratories 2008), and a molecular weight of 233.1, which indicates a low bioaccumulative potential. There is a USEPA pesticide tolerance established for farm-raised freshwater finfish tissue of 2.0 mg/kg (USEPA 2007), but there are no FDA food tolerances for diuron (USFDA 2000). The bioconcentration of diuron has been measured in various species (Table 9) and these bioconcentration factors (BCFs) indicate that it has a low potential for bioaccumulation in the environment. Because diuron has a low potential to bioaccumulate and low toxicity to mallard ducks (lowest dietary $LC_{50} = 1{,}730$ mg/kg feed; USEPA 2003), the protection of terrestrial wildlife from bioaccumulation was not assessed further. Because diuron has a low vapor pressure and a moderate log K_{ow}, it is also not likely to partition to the air or sediment, and currently there were no state or federal air quality or sediment quality standards identified for diuron (CARB 2008; CDWR 1995; NOAA 1999).

Table 9 Bioconcentration factors (BCFs) for diuron

Species	BCF	Exposure	Reference
Gambusia affinis	290	S	Isensee (1976)
Physa sp.	40	S	Isensee (1976)
Daphnia magna	260	S	Isensee (1976)
Oedogonium cardiacum	90	S	Isensee (1976)
Pimephales promelas	2.00	FT	Call et al. (1983, 1987)

FT flow through, *S* static
Values are on a wet weight basis and are not lipid normalized

Table 10 Acceptable multispecies field, semifield, laboratory, microcosm, mesocosm studies

Reference	Habitat	Rating
Devilla et al. (2005)	Laboratory model ecosystem	L
Dorigo et al. (2007)	Lotic outdoor stream	L
Flum and Shannon (1987)	Laboratory microcosm	L
Hartgers et al. (1998)	Laboratory microcosm	R
Molander and Blanck (1992)	Laboratory microcosm	L
Perschbacher and Ludwig (2004)	Outdoor pond	L
Pesce et al. (2006)	Laboratory microcosm	L
Sumpono et al. (2003)	Indoor pond	R
Tlili et al. (2008)	Laboratory microcosm	R
Zimba et al. (2002)	Outdoor pond	L

R reliable, *L* less reliable

12 Assumptions, Limitations, and Uncertainties

Environmental managers have the discretion to choose how to use water quality criteria, as such, they should be aware of the assumptions, limitations, and uncertainties involved in the calculations, and the accuracy and confidence in criteria. The UCDM (TenBrook et al. 2010) identifies these points for the various recommended procedures, and this section summarizes any specific data limitations that affected the procedure used to determine the final diuron criteria.

One major limitation was the lack of highly rated acute toxicity data for diuron, which prevented the use of an SSD for acute criterion derivation. Only two of the five taxa required for use of an SSD were available; the three missing taxa were a warm water fish, a fish from the family Salmonidae, and an insect. Because of this lack of data, an AF was used to calculate the acute criterion. Uncertainty cannot be quantified using the AF procedure, as it is based on only one toxicity value. There were no highly rated amphipod data available, which is an important data gap, as this taxon appears to be the most sensitive animal taxa.

The most important limitation is the lack of acceptable plant data because plants are much more sensitive to diuron than animals. Plant and algal data can be difficult to interpret and do not use consistent end points. The chronic data set contained five EC_{50}s and four MATCs, which are the preferred toxicity values for chronic tests.

The methodology requires that MATCs are used to derive chronic criteria by the SSD procedure, unless studies are available with EC_x values that show what level of x is appropriate to represent a no-effect level. Thus, the chronic criterion was calculated as the lowest NOEC in the data set. In this approach, the chronic criterion was derived with the absolute minimum amount of data, and uncertainty cannot be quantified because it is based on only one toxicity value.

Other limitations include the lack of information about diuron and mixture toxicity and ecosystem-level effects. There is evidence that diuron exhibits synergism with some other chemicals, including organophosphate pesticides, but there is a lack of multispecies interaction coefficients available to incorporate the presence of chemical mixtures into criteria compliance. Biofilms displayed sublethal effects to low-level diuron exposures, but these effects need to be further investigated to determine if the exposures are linked to survival, growth, or reproduction of organisms in biofilms. Another issue to consider is the averaging periods of the acute and chronic criteria. The chronic 4-day averaging period should be protective based on available data. However, the acute criterion is very high when compared to plant data, and it may allow for a pulse that could kill off a large amount of algae, resulting in increased biological demand and potential fish kills due to low dissolved oxygen, as discussed in Sect. 9. Clear data on the timing and concentrations that could cause this effect are not currently available, but should be considered when more data is available.

13 Comparison to Existing Criteria

The European Union has derived an environmental quality standard for diuron of 20 μg/L as a maximum allowable concentration and 2 μg/L as the annual average (Killeen 1997), which are analogous to the acute and chronic criterion, respectively. The maximum allowable concentration is lower than the UCDM acute criterion of 170 μg/L, and the annual average is very similar to the UCDM chronic criterion of 1.3 μg/L. These criteria were derived using safety factors, which are analogous to assessment factors. A safety factor of 10 was applied to the lowest credible lethal concentration, which was an LC_{50} of 160 μg/L for *G. fasciatus*, to calculate the maximum allowable concentration. A safety factor of 100 was applied to this datum to calculate the annual average. The authors noted that while algae demonstrated higher sensitivity to diuron, the effects on algae were algistatic, not algicidal, and that based on the algal data the environmental quality standards derived from the animal data are sufficiently protective of these species.

The Netherlands has derived a maximum permissible concentration (MPC) for diuron of 0.43 μg/L (Crommentuijn et al. 2000), which is analogous to a UCDM chronic criterion. This MPC was derived using a statistical extrapolation on the combined freshwater and marine data set, which included data for algae, crustaceans, insects, plants, and fish (Crommentuijn et al. 1997). The lowest reported NOEC was 0.056 μg/L for *Scenedesmus subspicatus*, which is more sensitive than any data in the acceptable UCDM data set.

14 Comparison to the USEPA 1985 Method

Water quality criteria for diuron were also calculated by using the USEPA (1985) method, which requires a total of eight taxa to use an SSD—three additional taxa beyond the five required by the UCDM. Only two of the eight total acute taxa requirements were fulfilled, a planktonic crustacean (*D. magna* or *D. pulex*) and a benthic invertebrate (*H. azteca*). Because of this lack of data, no diuron acute criterion could be calculated according to the USEPA (1985) methodology.

According to the USEPA (1985) methodology, the chronic criterion is equal to the lowest of the Final Chronic Value, the Final Plant Value, and the Final Residue Value. To calculate the Final Chronic Value, animal data is used and the same taxa requirements must be met as in the calculation of the acute criterion. Seven of the eight taxa requirements are available in the RR chronic animal data set (Table 5). The missing taxon is a fish from the family Salmonidae; the seven available taxa are as follows: (1) planktonic crustacean (*D. pulex*), (2) benthic invertebrate (*H. azteca*), (3) insect (*Chironomus tentans*), (4) warm water fish (*Pimephales promelas*), (5) a third family in the phylum Chordata (*Pseudacris regilla*, *R. aurora*, *Rana catesbeiana*, or *Xenopus laevis*), (6) a family in a phylum other than Arthropoda or Chordata (*Physa* sp.), and (7) a family in any order of insect or any phylum not already represented (*Lumbriculus variegatus*).

The California Department of Fish and Game has derived criteria using the USEPA (1985) SSD method with fewer than the eight required families, using professional judgment to determine that species in the missing categories were relatively insensitive and their addition would not lower the criteria (Menconi and Beckman 1996; Siepmann and Jones 1998). It is not clear that a fish from the family Salmonidae would be relatively insensitive to diuron because the lowest animal chronic toxicity value is for a fish (*P. promelas*). As an example, the data in Table 5 were used to calculate genus mean chronic values from the given SMCVs, and the log-triangular distribution was employed to yield a fifth percentile estimate.

$$\begin{aligned}\text{Final Chronic Value} &= \text{Fifth percentile estimate},\\ &= 23\ \mu\text{g/L}.\end{aligned}$$

The Final Plant Value is calculated as the lowest result from a 96-h test conducted with an important plant species, in which the concentrations of test material were measured and the end point was biologically important. None of the plant toxicity values in the RR data set (Table 4) are for a 96-h test, and two use measured concentrations. The closest test that fits this description is the 120-h NOEC of 1.3 µg/L reported for *P. subcapitata* (Blasberg et al. 1991). This test has an exposure duration that is 24 h longer than the specified duration.

$$\begin{aligned}\text{Final Plant Value} &= \text{Lowest result from a plant test},\\ &= 1.3\ \mu\text{g/L}.\end{aligned}$$

The Final Residue Value is calculated by dividing the maximum permissible tissue concentration by an appropriate BCF or bioaccumulation factor (BAF). A maximum allowable tissue concentration is either (a) an FDA action level for fish oil or for the edible portion of fish or shellfish or (b) a maximum acceptable dietary intake based on observations on survival, growth, or reproduction in a chronic wildlife feeding study or long-term wildlife field study. While no FDA action level exists for fish tissue, there is an EPA pesticide tolerance for farm-raised freshwater finfish tissue of 2.0 mg/kg (USEPA 2007). There is no relevant study that meets the requirement of part (b) above. A BCF of 2.0 for *P. promelas* (Table 9) was used to calculate the Final Residue Value.

$$\begin{aligned}\text{Final Residue Value} &= \frac{\text{Maximum permissible tissue concentration}}{\text{BCF}},\\ &= 1\ \text{mg/L}\ (1,000\ \mu\text{g/L}).\end{aligned}$$

The Final Plant Value is lower than both the Final Chronic Value and the Final Residue Value; therefore, the chronic criterion by the USEPA (1985) methodology would be 1.3 μg/L, and the example USEPA chronic criterion is equivalent to the UCDM chronic criterion.

15 Summary and Final Criteria Statement

Acute and chronic water quality criteria for the protection of aquatic life were derived for diuron using the UCDM. The acute criterion is based only on acute animal data and was derived using an assessment factor because there were insufficient data to use a SSD while the chronic criterion was derived using only plant data, which are more sensitive to diuron. The lowest NOEC of a highly rated plant study was used as the criterion because there were insufficient data for use of an SSD for criterion calculation. Plant toxicity data are essential when considering diuron usage and regulations because plants and algae are the most sensitive taxa; however, plant data are difficult to interpret. The criteria should be updated whenever relevant and reliable new data become available.

Aquatic life in the Sacramento River and San Joaquin River basins should not be affected unacceptably if the 4-day average concentration of diuron does not exceed 1.3 μg/L (1,300 ng/L) more than once every 3 years on the average and if the 1-h average concentration does not exceed 170 μg/L more than once every 3 years on the average. Mixtures of diuron and other PSII-inhibitor herbicides should be considered to be additive (see Sect. 7).

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