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

A.J. Palumbo • T.L. Fojut (✉) • I.R. Faria • R.S. Tjeerdema
Department of Environmental Toxicology, College of Agricultural and Environmental Sciences, University of California, Davis, CA 95616-8588, USA
e-mail: tlfojut@ucdavis.edu

P.L. TenBrook
Department of Environmental Toxicology, College of Agricultural and Environmental Sciences, University of California, Davis, CA 95616-8588, USA

Current affiliation: USEPA Region 9*, 75 Hawthorne Street, San Francisco, CA 94195, USA
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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

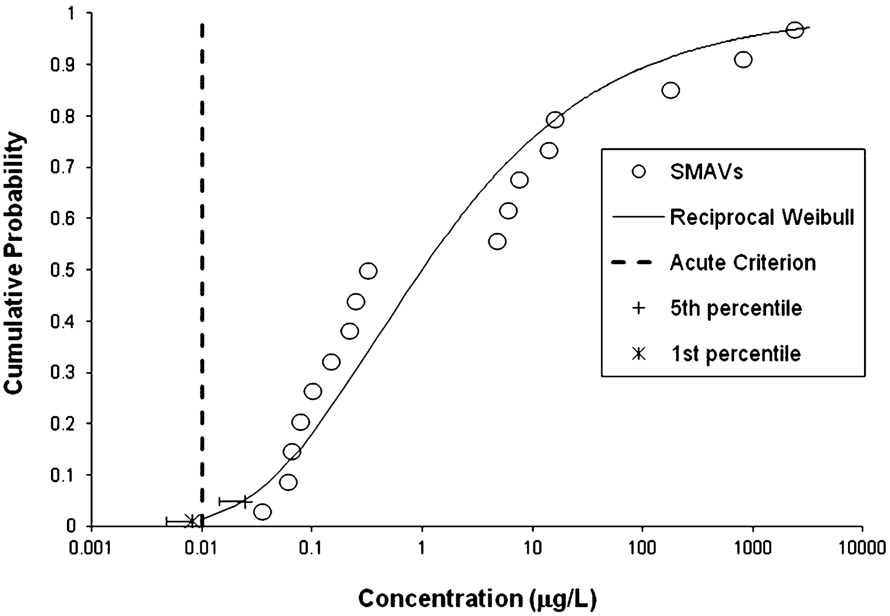

Fig. 1 Plot of species mean acute values for chlorpyrifos and fit of the Reciprocal Weibull distribution. The graph shows the median fifth and first percentiles with the lower 95% confidence limits and the acute criterion at 0.01 µg/L

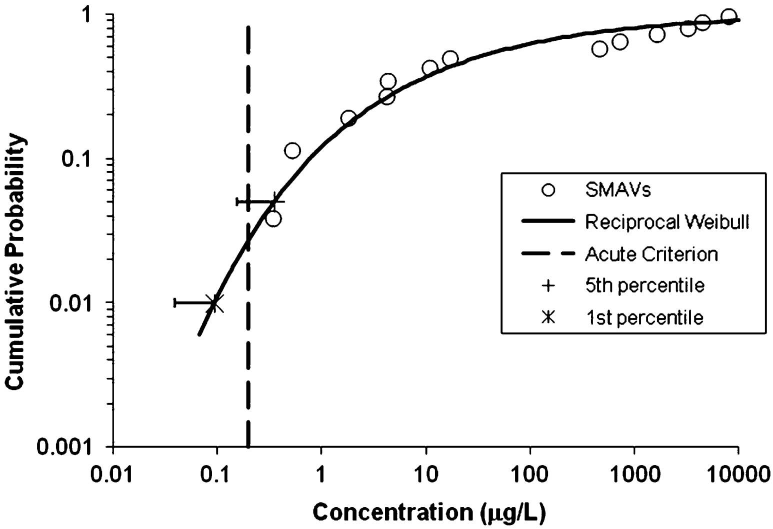

Fig. 2 Plot of species mean acute values for diazinon and fit of the Reciprocal Weibull distribution. The graph shows the median fifth and first percentiles with the lower 95% confidence limits and the acute criterion at 0.2 μg/L

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

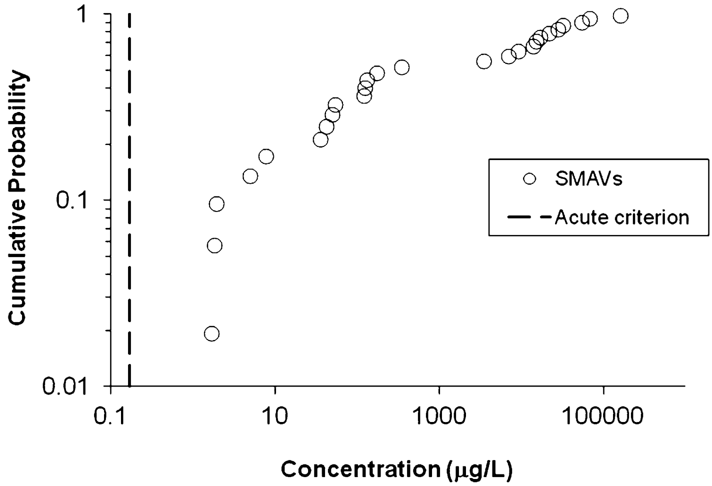

Fig. 3 Malathion species mean acute values with the acute criterion displayed at 0.17 µg/L

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*.

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

Using Eq. 1:

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

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

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

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 *K*s 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):

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

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:

$$C_{\text{a}} = C_{\text{m}}\ (K), \tag{3}$$

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 *K*s ($p<0.005$; 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:

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

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. azteca*, 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

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

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 $\leq$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 $\geq$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.

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

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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