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

Tessa L. Fojut, Amanda J. Palumbo, and Ronald S. Tjeerdema

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

Tubic I Thij break chies	mean properties of diagon
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	$1.15 \times 10^{-3} \text{ mPa (IUPAC 2008)}$
Henry's constant $(K_{\rm H})$	$173,205 \text{ Pa m}^3 \text{ mol}^{-1}$ (geomean, $n = 2$; Mackay et al. 2006; IUPAC 2008)
$\text{Log } K_{\text{oc}}^{\text{a}}$	2.61 (geomean, $n = 20$; Mackay et al. 2006)
$\text{Log } K_{\text{ow}}^{ \text{b}}$	2.78 (geomean, $n = 3$; Hansch et al. 1995; Sangster Research
	Laboratories 2008: HIPAC 2008)

^aLog-normalized organic carbon–water partition coefficient

Table 2 Environmental fate of diuron

	Half-life	Water	Temp (°C)	pН	Reference
Hydrolysis	>4 months	Phosphate buffer	20	5–9	Mackay et al. (2006)
	Stable	Sterile buffer	25	5, 7, 9	USEPA (2003)
Aqueous	2.25 h	Distilled	NR	NR	Mackay et al. (2006)
photolysis	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

^bLog-normalized octanol–water partition coefficient

Table 3 Final acute toxicity data set for diuron

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		Meas/	Chemical	Duration	Temp			LC/EC_{50} (µg/L)	
Species	Test type	e Nom g	grade (%)	(h)	(°C)	Nom grade (%) (h) (°C) End point	Age/size	Age/size (95% CI)	Reference
Daphnia magna	S	Nom	0.08	48	19.9	19.9 Mortality/	<24 h 12,000	12,000	Baer (1991)
						immobility		(10,000-13,000)	
Daphnia pulex	SR	Meas	8.66	96	22	Mortality	5 days 1	17,900	Nebeker and Schuytema
								(14,200–22,600) (1998)	(1998)
Hyalella azteca	SR	Meas	8.66	96	22	Mortality	<11 days	<11 days 19,400	Nebeker and Schuytema
								(17,700–21,300) (1998)	(1998)

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

 data set for diuron	
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Table 4 1 mai childre piant to the data set for diaron	re puu	IL LOAICI	ily data set in	or aranom								
	Test	Meas/	Meas/ Chemical		Temp			$NOEC^a$	NOEC ^a LOEC ^b	$MATC^{c}$		
Species	type	Nom	grade (%) Duration (°C)	Duration	(°C)	End point	Age/size $(\mu g/L)$ $(\mu g/L)$	(µg/L)	(µg/L)	(µg/L)	(95% CI)	Reference
Lemna gibba G3	S	Meas 99.1	99.1	7 days	24.7	Growth inhibition Plant with 2.47	Plant with	2.47	8.11	4.48	14.4	Ferrell
						(biomass	4				$(9.26-19.6)^{d}$	(2006)
						yield),	fronds					
						relative						
						growth rate (biomass)						
Navicula pelliculosa S	S	Nom	99.1	72 h	22–24	Growth inhibition	Cells	11	33	19.1	22 (9–56)	Dengler
						(biomass)						(2006b)
N. pelliculosa	S	Nom	99.1	72 h	22–24	Growth inhibition Cells	Cells	11	33	19.1	65 (33–160)	Dengler
						(growth rate)						(200pp)
N. pelliculosa						Growth inhibition				19.1		Geomean
Pseudokirchneriella	S	Meas	8.96	120 h	24	Growth inhibition 2-day-old	2-day-old	1.3	2.5	1.8	2.9 (2.5–3.5)	Blasberg
subcapitata							algal					et al.
(formerly							cells					(1991)
Selenastrum												
capricornutum												
Printz)												
Scenedesmus	S	Nom	Technical 24 h	24 h	21	Growth inhibition Algal cells NR	Algal cells	NR	NR	NR	10	Geoffroy
obliquus												et al.
												(7007)
Synechococcus	S	Nom	99.1	72 h	22–25	22-25 Growth inhibition Algal cells 3.7	Algal cells	3.7	Ξ	6.4	26 (4–100)	Dengler
leopoliensis						(biomass)						(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 $^{\rm a}$ No-observed effect concentration $^{\rm b}$ Lowest-observed effect concentration

 $^{\text{c}}$ Maximum acceptable toxicant concentration $^{\text{d}}$ EC $_{50}$ based on biomass yield end point

Table 5 Final chronic animal toxicity data set for diuron	nic anim	nal toxici	ity data set fo	ır diuron							
	Test	Meas/	est Meas/ Chemical Duration Temp	Duration	Temp			NOEC	NOEC LOEC MATC	MATC	
Species	type	Nom	type Nom grade (%) (days) (°C) End point	(days)	(°C)	End point	Age/size	(µg/L)	$(\mu g/L)$	(µg/L)	$(\mu g/L)$ $(\mu g/L)$ $(\mu g/L)$ Reference
Chironomus tentans		SR Meas 99.8	8.66	10	24	Mortality	2 days, first instar	1,900	3,400	2,540	3,400 2,540 Nebeker and Schuytema (1998)
Daphnia pulex	S	Meas	8.66	7	NR	Reduced number of 5 days young/mortality	5 days	4,000.0	7,700		5,550 Nebeker and Schuytema (1998)
Hyalella azteca	SR	Meas 99.8	8.66	10	22	Mortality/reduced weight	<11 days	7,900	15,700	11,140	15,700 11,140 Nebeker and Schuytema (1998)
Lumbriculus variegatus	SR	Meas	8.66	10	23	Reduced weight	Small, short adults	1,800	3,500		2,510 Nebeker and Schuytema (1998)
Physa gyrina	SR	Meas	8.66	10	24	Reduced weight	2 days, first instar	13,400		17,480	22,800 17,480 Nebeker and Schuytema

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21,100 17,490

14,500

Tadpole fry

20

7

8.66

Meas

SR

Pseudacris regilla

promelas Pimephales

Call et al. (1983, 1987)

51

78

33.4

Deformity, mortality Eggs < 24 h, hatched

25

4

98.6

Meas

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Nebeker and Schuytema (1998)

Table 5 (continued)	_										
Species	Test	Meas/	Meas/ Chemical Duration Temp Nom grade (%) (days) (°C) End point	Duration (davs)	Temp	End point	Age/size	NOEC (ug/L)	NOEC LOEC MATC (ug/L) (ug/L)	MATC (ug/L)	NOEC LOEC MATC (ug/L) (ug/L) Reference
1						Growth inhibition (length)		j j	ò	5	Schuytema and Nebeker (1998)
Rana aurora	SR	Meas	8.66	7	20	Growth inhibition (wet weight)	Tadpole	7,600	14,500	14,500 10,500	Schuytema and Nebeker (1998)
Rana catesbeiana	SR	Meas	8.66	21	24	Growth inhibition (dry weight)	Tadpole	$11,690^{a}$	$11,690^{a} ext{ } 16,430^{a} ext{ } 12,450^{a}$	12,450 ^a	Schuytema and Nebeker (1998)
Xenopus laevis	SR	Meas	8.66	4 days	24	Growth inhibition (length)	Embryo	10,490 ^b	20,540 ^b	10,490 ^b 20,540 ^b 14,680 ^b	Schuytema and Nebeker

All studies were rated RR S static, SR static renewal, FT flow through, NR not reported ^aSMCV calculated from three values ^bSMCV calculated from two values

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	Test	Meas/			Temp			LC/EC_{50} (µg/L)	MATC		for
Species	type	Nom		grade (%) Duration (°C)	(°C)	End point	Age/size	(95% CI)	(µg/L)	Reference	exclusion
Chironomus	SR	Meas	8.66	10 days	24	Reduced weight	2 days, first	I	4,910	Nebeker and	A
tentans							instar			Schuytema (1998)	
Daphnia magna	S	Nom	80.0	24 h	19.9	Mortality/ immobility	<24 h	68,000 (55,000–86,000)	1	Baer (1991)	О
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	I	14.5	Ferrell (2006)	A
P. promelas	SR	Meas	8.66	7 days	25	Reduced weight	2.5 days embryo	I	5,900	Nebeker and Schuytema (1998)	C
P. promelas	SR	Meas	8.66	10 days	24	Mortality	1.5 months juvenile	I	23,280	Nebeker and Schuytema (1998)	В
Pseudacris regilla	SR	Meas	8.66	10 days	20	Increased deformity	Embryo	I	20,540	Schuytema and Nebeker (1998)	A

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	Test	Meas/	Test Meas/ Chemical		Temp			LC/EC_{50} (µg/L)	MATC		for
Species	type	type Nom	grade (%) Duration (°C) End point	Duration	(°C)	End point	Age/size	(95% CI)	(µg/L)	(μg/L) Reference	exclusion
P. regilla	SR	SR Meas 99.8	8.66	14 days 20	20	Growth	Tadpole	1	24,720	Schuytema and	A
						inhibition				Nebeker	
						(wet weight)				(1998)	
P. regilla	SR	Meas	8.66	14 days	20	Growth	Tadpole	ı	$24,750^{a}$	Schuytema and	А
						inhibition				Nebeker	
						(dry weight)				(1998)	
Rana	SR	Meas	8.66	21 days	24	Growth	Tadpole	ı	$18,950^{a}$	Schuytema and	A
catesbeiana						inhibition				Nebeker	
						(length)				(1998)	
R. catesbeiana SR Meas	SR	Meas	8.66	21 days	24	Growth	Tadpole	ı	$22,560^{a}$	Schuytema and	A
						inhibition				Nebeker	
						(wet weight)				(1998)	
Synechococcus S	S	Nom	99.1	72 h	22–25	Growth	Algal cells	1	19.1	Dengler (2006a)	A
leopoliensis						inhibition					
						(growin rate)					
Xenopus laevis SR Meas	SR	Meas	8.66	4 days	24	Deformity	Embryo	1	22,560	Schuytema and Nebeker	V
										(1998)	

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

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	Test	Meas/			Temp			LC/EC_{50} (µg/			Rating/
Species	type	Nom	grade (%)	Duration (°C)	(°C)	End point	Age/size	L) (95% CI)	MATC (μg/L)	Reference	reason
Achnanthes brevipes	S	Nom	Technical 3 days		20	Reduced oxygen Algal cells evolution	Algal cells	24 (SE = 1.0)	I	Hollister and Walsh (1973)	LL/1, 2, 6
Americamysis bahia	FI	Meas 96.8	8.96	28 days	25.3	Number of young surviving	<24 h juvenile	I	1,400	Ward and Boeri (1992b)	RL/2
Amphora exigua	S	Nom	Technical	3 days	20	Reduced oxygen Algal cells evolution	Algal cells	31 (SE = 4)	I	Hollister and Walsh (1973)	LL/1, 2, 6
Apium nodiflorum	S	Nom	66<	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	66<	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,
A. nodiflorum	S	Nom	>66	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 R	NR	24 h	25	Mortality	Instar II—III larvae	12,010 (11,420 -12,100)	I	Koutsaftis and LL/2, 5 Aoyama (2007)	LL/2, 5
Asellus brevicaudus	S	Nom	95.0	96 h	15	Mortality	Mature	15,500 (7,200– 33,400)	I	Johnson and Finley (1980)	LL/5, 6
Chara vulgaris	S	Nom	>66	14 days	NR	Relative growth rate	Terminal lengths of shoots with 3 nodes	0.35	NOEC = 0.0005 Lambert et al. (2006)	Lambert et al. (2006)	LL/1, 5, 6
										9)	(continued)

Table 7 (continued)	ned)										
	Test	Meas/	Meas/ Chemical		Temp			LC/EC ₅₀ (µg/			Rating/
Species	type	Nom	grade (%) Duration (°C)	Duration	(°C)	End point	Age/size	L) (95% CI)	MATC (µg/L)	Reference	reason
C. vulgaris	∞	Nom	66<	14 days	NR R	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	I	Cain and Cain RL/1, 6 (1983)	RL/1, 6
Chlamydomonas sp.	S	Nom	Technical 3 days	3 days	20	Reduced oxygen evolution	Algal cells	37 (SE = 3)	I	Hollister and Walsh (1973)	LL/1, 2, 6
Chlamydomonas sp.	N	Nom	8.66	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	I	Maule and Wright (1984)	LR/1, 6
C. pyrenoidosa	S	Nom	50.0	96 h	25	Growth inhibition	Algal cells	1.3	1	Ma et al. (2001), Ma (2002)	LL/1, 3, 6
Chlorella sp.	S	Nom	Technical 10 days		20.5	Growth inhibition	Algal cells	$EC_{66} = 4$	ſ	Ukeles (1962)	LL/1, 2, 6
Chlorella sp.	S	Nom	Technical 3 days	3 days	20	Reduced oxygen evolution	Algal cells	19 (SE = 2)	I	Hollister and Walsh (1973)	LL/1, 2, 6

Chlorella vulgaris	v	Non	20.0	96 h	35	Growth	Alastoelle	4.3	ı	Ma (2002)	9 8 1/11
Cingletia varsalis	2	TACK	2.		ì	bition	mgar coms	<u>;</u>		(2002)	1, 2, 0
C. vulgaris SAG211-11b	S	Nom	8.66	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	7 days	20	Growth	Algal cells	$EC_{62} = 10$	NOEC < 1.0	Walsh and Grow (1971)	RL/1, 2
Chlorococcum sp.	S	Nom	Technical 10 days	10 days	20	Growth inhibition	Algal cells	10	I	Walsh (1972)	RL/1, 2
Chlorococcum sp.	S	Nom	Technical	90 min	20	Reduced oxygen evolution	Algal cells	20	I	Walsh (1972)	RL/1, 2
Chlorococcum sp.	S	Nom	Technical 3 days	3 days	20	Reduced oxygen evolution	Algal cells	20 (SE = 4)	I	Hollister and Walsh (1973)	LL/1, 2, 6
Crassostrea virginica	FI	Meas	8.96	4 96 h	23	Shell deposition Neonates, <24 h	Neonates, <24 h	4,800 (4,400– 5,200)	4,800 (4,400- NOEC = 2,400 5,200)	Ward and Boeri (1991)	RL/2
Cryptomonas sp.	S	Nom	8.66	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
Ctenophary- ngodon idella	FI	NR	100.0	4 96 h	13	Mortality	1+ year, 15.8 g, 9.5 cm	31,000 (28,000 –34,000)	I	Tooby et al. (1980)	LL/1, 5, 6
Cyclotella nana	S	Nom	Technical 3 days	3 days	20	Reduced oxygen evolution	Algal cells	39 (SE = 7)	I	Hollister and Walsh (1973)	LL/1, 2, 6
Cyprinodon variegates	FT	Meas	8.96	32 days	30	Mortality	<24 h	1	2,500	Ward and Boeri (1992a)	RL/2

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	Test	Meas/	Meas/ Chemical		Temp			LC/EC ₅₀ (µg/			Rating/
Species	type	Nom	grade (%)	Duration	(°C)	End point	Age/size	L) (95% CI)	MATC (μg/L)	Reference	reason
Daphnia magna	S	Nom	Technical	26 h	21.1	Mortality/	First instar	47,000	1	Crosby and	LL/1, 5, 6
						immobility		(41,600 -53,100)		Tucker (1966)	
Daphnia pulex	S	Nom	95.0	48 h	15	Mortality/ immobility	First instar	1,400 (1,000– 1,900)	I	Johnson and Finley (1980)	LL/5, 6
Dunaliella euchlora Lerche	S	Nom	Technical 10 days	10 days	20.5	Growth inhibition	Algal cells	$EC_{56}=0.4$	I	Ukeles (1962)	LL/1, 2, 6
Dunaliella tertiolecta	w	Nom	0.66	ч 96	20	Growth inhibition	Algal cells	5.9	I	Gatidou and Thomaidis (2007)	LL/2, 5
D. tertiolecta	S	Nom	Technical 3 days	3 days	20	Reduced oxygen evolution	Algal cells	10 (SE = 3)	I	Hollister and Walsh (1973)	LL/1, 2, 6
D. tertiolecta Butcher	S	Nom	Technical 10 days	10 days	20	Growth inhibition	Algal cells	20	I	Walsh (1972)	RL/1, 2
D. tertiolecta Butcher	S	Nom	Technical	90 min	20	Reduced oxygen evolution	Algal cells	10	I	Walsh (1972)	RL/2, 6, 8
Eudorina elegans	_∞	Nom	8.66	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)	I	Sanders (1970)	LL/1, 5, 6
G. fasciatus	S	Nom	Technical	48 h	15.5	Mortality	Early instar	1,800 (800– 5,200)	I	Sanders (1970)	LL/1, 5, 6
G. fasciatus	S	Nom	Technical 96 h	96 h	15.5	Mortality	Early instar	700 (190– 8,200)	I	Sanders (1970)	LL/1, 5, 6

Gammarus lacustris	S	Nom	Technical 24 h	24 h	21.1	Mortality	2 months	700 (590– 8,300)	ı	Sanders (1969)	LL/1, 5, 6
G. lacustris	S	Nom	Technical 48 h	48 h	21.1	Mortality	2 months	380 (290–500)	I	Sanders (1969)	LL/1, 5, 6
G. lacustris	S	Nom	Technical 96 h	96 h	21.1	Mortality	2 months	160 (130–190)	ı	Sanders (1969)	LL/1, 5, 6
Isochrysis galbana	S	Nom	Technical 3 days	3 days	20	Reduced oxygen Algal cells evolution	Algal cells	10 (SE = 3)	I	Hollister and Walsh (1973)	LL/1, 2, 6
I. galbana Parke	S	Nom	Technical 90 min	90 min	20	Reduced oxygen Algal cells evolution	Algal cells	10	ı	Walsh (1972)	RL/1, 2, 8
I. galbana Parke	S	Nom	Technical 10 days	10 days	20	Growth inhibition	Algal cells	10	I	Walsh (1972)	RL/1, 2
Lemna gibba G3	S	Nom	0.86	7 days	25	Growth inhibition	NR	29 (27–31)	I	Okamura et al. LR/6 (2003)	LR/6
Lemna minor	S	Nom	0.86	48 h	21	Reduced oxygen evolution	Plant fronds	1	LOEC = 5	Eullaffroy et al. (2007)	LL/1, 6, 7
L. minor 1769	S	Nom	0.86	7 days	25	Growth inhibition	NR	30 (28–31)	I	Okamura et al. (2003)	LR/6
L. minor	S	Nom	0.86	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)	ı	Macek et al. (1969)	LL/1, 5, 6
L. macrochirus	S	Nom	Technical	ч 96	18.3	Mortality	$0.6-1.5 \mathrm{\ g}$	7,600 (7,000– 8,200)	I	Macek et al. (1969)	LL/1, 5, 6
L. macrochirus	ω	Nom	Technical 96 h	96 h	23.8	Mortality	0.6–1.5 g	5,900 (5,300– 6,500)	ı	Macek et al. (1969)	LL/1, 5, 6

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	Test	Meas/	Chemical		Temp			LC/EC_{50} (µg/			Rating/
Species	type	Nom	grade (%)	Duration (°C)	(°C)	End point	Age/size	L) (95% CI)	MATC (μg/L)	Reference	reason
Lymnaea spp.	S	Nom	NR	4 96	NR	Mortality	Adult	15,300	1	Christian and	LL/1, 3, 6
										1 ate (1983)	
Monochrysis lutheri	N	Nom	Technical 3 days	3 days	20	Reduced oxygen Algal cells evolution	Algal cells	18 (SE = 3)	I	Hollister and Walsh	LL/1, 2, 6
M. lutheri Droop	S	Nom	Technical 10 days		20.5	Growth	Algal cells	$EC_{100} = 0.02$	I	(1973) Ukeles (1962)	LL/1, 2, 6
M. lutheri Droop	S	Nom	Technical 10 days	10 days	20.5	Mortality	Early instar	2,500 (1,000– 5,500)	I	Sanders (1970)	LL/1, 5, 6
Myriophyllum spicatum	∞	Nom	>66	14 days	NR	Relative growth rate	Terminal lengths of shoots with 3 nodes	S	NOEC = 0.0005 Lambert et al. (2006)	Lambert et al. (2006)	LL/1, 5, 6
M. spicatum	N	Nom	>66	14 days	Z Z	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	S	Nom	0.66	ч 96	20	Growth inhibition	Algal cells	27	I	Gatidou and Thomaidis (2007)	LL/2, 5
Navicula inserta	S	Nom	Technical 3 days	3 days	20	Reduced oxygen Algal cells evolution	Algal cells	93(SE = 12)	I	Hollister and Walsh (1973)	LL/1, 2, 6
Neochloris sp.	∞	Nom	Technical 3 days	3 days	20	Reduced oxygen Algal cells evolution	Algal cells	28 (SE = 5)	I	Hollister and Walsh (1973)	LL/1, 2, 6
Nitzschia (Ind. 684)	ω	Nom	Technical 3 days	3 days	20	Reduced oxygen Algal cells evolution	Algal cells	169 (SE = 17)	I	Hollister and Walsh (1973)	LL/1, 2, 6

Nitzschia closterium	S	Nom	Technical	3 days	20	Reduced oxygen Algal cells 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 L	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 – – – – – – – – – – – – – – – – – –		Johnson and Finley (1980)	LL/5, 6
0. 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
0. mykiss	S	Nom	95	14 days	10	Mortality	Juveniles, hatched <24 h ago	15,000 (11,000 –29,000)		Okamura et al. LR/1, 6 (2002)	LR/1, 6
0. mykiss	S	Nom	95	21 days	10	Mortality	Juveniles, hatched <24 h ago	5,900 (4,700 7,700)		Okamura et al. LR/1, 6 (2002)	LR/1, 6
0. mykiss	S	Nom	95	28 days	10	Mortality	Juveniles, hatched <24 h ago	230 (8.9–590) –		Okamura et al. LR/1, 6 (2002)	LR/1, 6
Phaeodactylum tricornutum	S	Nom	Technical 3 days	3 days	20	Reduced oxygen Algal cells evolution	Algal cells	10 (SE = 3) –		Hollister and Walsh (1973)	LL/1, 2, 6
P. tricornutum Bohlin	S	Nom	Nom Technical 90 min	90 min	20	Reduced oxygen Algal cells evolution	Algal cells			Walsh (1972)	RL/1, 2, 8

(continued)

Change in chlorophyll fluorescence ratio

 Table 7 (continued)

	Test	Meas/	Chemical		Temp			LC/EC ₅₀ (µg/			Rating/
Species	type			grade (%) Duration (°C)	$^{\circ}C$	End point	Age/size	L) (95% CI)	MATC (µg/L)	Reference	reason
P. tricornutum	S	Nom	Technical 10 days	10 days	20	Growth	Algal cells	10	ı	Walsh (1972)	RL/1, 2
Bohlin						inhibition					
P. tricornutum Bohlin	S	Nom	Technical 10 days	10 days	20.5	Growth inhibition	Algal cells	$EC_{21} = 0.4$	I	Ukeles (1962) LL/1, 2, 6	LL/1, 2, 6
Pimephales promelas	Ħ	Meas	9.86	ч 96 н	24.3	Mortality	30 days	14,200 (13,400– 15,000)	I	Call et al. (1983, 1987)	RL/1, 5
Platymonas sp.	ω	Nom	Technical 3 days	3 days	20	Reduced oxygen Algal cells evolution	Algal cells	7 (SE = 3)	I	Hollister and Walsh (1973)	LL/1, 2, 6
Porphyridium cruentum	ω	Nom	Technical 3 days	3 days	20	Reduced oxygen Algal cells evolution	Algal cells	24 (SE = 3)	I	Hollister and Walsh (1973)	LL/1, 2, 6
Protcoccus sp.	S	Nom	Technical 10 days	10 days	20.5	Growth inhibition	Algal cells	$EC_{48}=0.02$	I	Ukeles (1962) LL/1, 2, 6	LL/1, 2, 6
Pseudokirch- neriella subcapitata (Selenastrum capricor- nutum)	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. capricorn utum)	S	Nom	0.86	3 days	25	Growth inhibition	Algal cells	6.6 (5.9–7.2)	ı	Okamura et al. LL/5, 6 (2003)	LL/5, 6
P. subcapitata (S. capricorn utum)	S	Nom	8.66	20 min	21.5	Change in chlorophyll fluorescence	2-4-week-old algal cells	13.8 (9.3–20.4)	0.22	Podola and Melkonian (2005)	RL/1, 8

RL/6	RL 6	LL/5, 6	LL/1, 5, 6	LL/1, 5, 6	LL 1, 5, 6	LL/3, 5, 6	LL/5, 6	LL/1, 3, 6	LL/1, 4, 6, 8
Douglas and Handley (1988)	Douglas and Handley (1988)	Johnson and Finley (1980)	Sanders and Cope (1968)	Sanders and Cope (1968)	Sanders and Cope (1968)	Ma et al. (2006)	Johnson and Finley (1980)	Ma (2002)	Eullaffroy and LL/1, 4, 6, Vernet 8 (2003)
NOEC = 10	I	I	I	I	I	I	I	1	1
22	18	1,200 (900–1,700)	3,600 (2,800– 4,700)	2,800 (2,100– 3,800)	1,200 (870– 1,700)	0.7	2,700 (2,400– 3,000)	4.09	l a
Algal cells	Algal cells	Second year class	30–35 mm	30–35 mm	30–35 mm	Algal cells	1.5 g	Algal cells	Algal cells
Growth inhibition	Growth inhibition	Mortality	Mortality	Mortality	Mortality	Growth inhibition	Mortality	Growth inhibition	Change in chlorophyll fluorescence ratio
24	24	15	15.5	15.5	15.5	25	10	25	22
120 h	72 h	96 h	24 h	48 h	96 h	96 h	96 h	96 h	1 min
86	86	95.0	Technical 24 h	Technical 48 h	Technical 96 h	50.0	95.0	50.0	98.0
Nom	Nom	Nom	Nom	Nom	Nom	Nom	Nom	Nom	Nom
S	S	S	S	S	S	S	S	S	S
P. subcapitata (S. capricorn utum)	P. subcapitata (S. capricorn utum)	Pteronarcys californica	P. californica	P. californica	P. californica	Raphidocelis subcapitata	Salvelinus namaycush	Scenedesmus obliquus	S. obliquus

(continued)

Table 7 (continu	,										
	Test	Meas/	Test Meas/ Chemical		Temp			LC/EC_{50} (µg/			Rating
Species	type	Nom	type Nom grade (%) Duration (°C) End point	Duration	(°C)	End point	Age/size	L) (95% CI)	L) (95% CI) MATC (µg/L) Reference reasor	Reference	reasc
Scenedesmus	S	Nom	Nom 50.0 96 h 25 Growth	4 96	25	Growth	Algal cells 2.7	2.7	I	Ma (2003)	LL/1,
quadricauda						inhibition					

	Test	Meas/	Meas/ Chemical		Temp		:	LC/EC ₅₀ (μg/	1	,	Rating/
Species	type	Nom	grade (%)	Duration (°C)	(°C)	End point	Age/size	L) (95% CI)	MATC (µg/L)	Reference	reason
Scenedesmus quadricauda	S	Nom	50.0	4 96 h	25	Growth inhibition	Algal cells	2.7	1	Ma (2003)	LL/1, 3, 6
Scenedesmus subspicatus	S	Nom	Technical 24 h	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	72 h	20	Growth inhibition	Algal cells, 3- day old	36	NOEC = 10	Schafer et al. (1994)	LR/5, 6
Scherffelia dubia	S	Nom	8.66	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	N	Nom	95.0	48 h	15	Mortality	First instar	2,000 (1,400– 2,800)	1	Johnson and Finley (1980)	LL/5, 6
Staurodesmus convergens	S	Nom	8.66	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	N	Nom	Technical 3 days	3 days	20	Reduced oxygen Algal cells evolution	Algal cells	31 (SE = 2)	1	Hollister and Walsh (1973)	LL/1, 2, 6
Synechocystis sp.	S	Nom	8.66	20 min	21.5	Change in chlorophyll fluorescence ratio	2-4-week-old algal cells	7.6 (5.5–10.5) 0.22	0.22	Podola and Melkonian (2005)	RL/1, 5, 8
Tetraselmis elegans	ω.	Nom	8.66	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

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

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 ^bGrowth 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.

Acute value =
$$\frac{LowestSMAV}{Assessment factor}$$
, (1)
= 0.33 mg/L.

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

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 ($\log K_{\rm ow} = 2.78$), 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 $160 \,\mu\text{g/L}$ for the amphipod *Gammarus lacustris* (Sanders 1969), which is below the derived acute criterion of $170 \,\mu\text{g/L}$. 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 ($700 \,\mu\text{g/L}$), 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 μ g/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 >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 \geq 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 EC₅₀ of $0.00026 \,\mu g/L$ 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 ($0.0005-0.05 \,\mu g/L$), 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 μ g/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 μ g/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 EC₅₀ 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 EC₅₀ below the derived criterion (0.7 μ g/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 μ g/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 μ g/L diuron; thus, the criterion of 1.3 μ g/L would likely be protective of phytoplankton based solely on diuron. Flum and Shannon (1987) reported a 96-h EC₅₀ of 2,205 μ g/L (1,630–3,075 μ g/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 EC₅₀ 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 $\mu g/L$) 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 μ g/L diuron, as well as 3-h pulses of 7 or 14 μ g/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 μ g/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 LC₅₀ 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 LC₅₀s for *O. mykiss* of 4.9 (4.1–5.9) mg/L and 16 (11.3–22.7) mg/L, and an LC₅₀ 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 Oncorhynchus gilae apache Oncorhynchus gilae Oncorhynchus nerka Oncorhynchus tshawytscha Oncorhynchus kisutch Oncorhynchus clarki henshawi	4.491 (3.613–5.581) 4.491 (3.613–5.581) 4.491 (3.613–5.581) 4.491 (3.613–5.581) 5.983 (3.225–11.097) 8.086 (6.104–4.016) 4.758 (3.545–6.387)
Cutthroat trout (O. clarki)	1.4	Oncorhynchus clarkii henshawi Oncorhynchus clarkii seleniris Oncorhynchus clarkii stomias O. gilae apache O. gilae O. kisutch O. nerka O. tshawytscha	1.206 (0.967–1.504) 1.206 (0.967–1.504) 1.206 (0.967–1.504) 0.729 (0.290–1.832) 0.729 (0.290–1.832) 1.673 (1.156–2.421) 1.206 (0.967–1.504) 1.206 (0.967–1.504)

11 Bioaccumulation and Partitioning to Air and Sediment

Diuron has a log $K_{\rm ow}$ 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 $K_{\rm ow}$, 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).

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)

Table 9 Bioconcentration factors (BCFs) for diuron

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 $20~\mu g/L$ as a maximum allowable concentration and $2~\mu g/L$ 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 $170~\mu g/L$, and the annual average is very similar to the UCDM chronic criterion of $1.3~\mu g/L$. These criteria were derived using safety factors, which are analogous to assessment factors. A safety factor of $10~\mu g/L$ for G.~fasciatus, to calculate the maximum allowable concentration. A safety factor of $100~\mu g/L$ for G.~fasciatus, to calculate the maximum allowable concentration. A safety factor of $100~\mu g/L$ of 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 μ g/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 μ g/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.

Final Chronic Value = Fifth percentile estimate,
=
$$23 \mu g/L$$
.

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 μ g/L reported for *P. subcapitata* (Blasberg et al. 1991). This test has an exposure duration that is 24 h longer than the specified duration.

Final Plant Value = Lowest result from a plant test,
=
$$1.3 \mu g/L$$
.

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.

Final Residue Value =
$$\frac{Maximum \ permissible \ tissue \ concentration}{BCF}$$
 = 1 mg/L (1,000 μ g/L).

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 $1.3~\mu g/L$, 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 μ g/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 μ g/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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