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ENVIRONMENTAL QUALITY BENCHMARKS FOR AQUATIC ECOSYSTEM PROTECTION: DERIVATION AND APPLICATION

Ecotoxicity thresholds for ametryn, diuron, hexazinone and simazine in fresh and marine waters

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Abstract

Triazine and urea herbicides are two groups of photosystem II inhibiting herbicides frequently detected in surface, ground and marine waters. Yet, there are few water quality guidelines for herbicides. Ecotoxicity thresholds (ETs) for ametryn, hexazinone and simazine (triazine herbicides) and diuron (a urea herbicide) were calculated using the Australian and New Zealand method for deriving guideline values to protect fresh and marine ecosystems. Four ETs were derived for each chemical and ecosystem that should theoretically protect 99, 95, 90 and 80% of species (i.e. PC99, PC95, PC90 and PC80, respectively). For all four herbicides, the phototrophic species were significantly more sensitive than non-phototrophic species, and therefore, only the former data were used to calculate the ETs. Comparison of the ET values to measured concentrations in 2606 samples from 15 waterways that discharge to the Great Barrier Reef (2011–2015) found three exceedances of the simazine PC99, regular exceedances (up to 30%) of the PC99 in a limited number of rivers for ametryn and hexazinone and frequent (> 40%) exceedances of the PC99 and PC95 ETs in at least four waterways for diuron. There were no exceedances of the marine ETs in inshore reef areas. Further, ecotoxicity data are required for ametryn and hexazinone to fresh and marine phototrophic species, for simazine to marine phototrophic species, for tropical phototrophic species, repeated pulse exposures and long-term (2 to 12 months) exposures to environmentally relevant concentrations.

Keywords Ecotoxicity thresholds · Ametryn · Diuron · Hexazinone · Simazine · Freshwater · Marine water · Ecosystem protection

Introduction

Annual global usage of pesticides has been relatively stable at greater than 2.27 billion kg (5 billion pounds) per year since 1997 (Donaldson et al. 2002; Kiely et al. 2004; Grube et al. 2011). Global annual herbicide usage has been approximately 900 million kg over the same period (Donaldson et al. 2002; Kiely et al. 2004; Grube et al. 2011) or approximately 40% of total pesticide usage. Herbicides that inhibit photosystem II (PSII inhibitors) are widely used. The PSII group includes amides, benzothiadiazinones, nitriles, phenylcarbamates, phenyl-pyridazines, pyridazinones, triazines, triazinones, triazolinones, uracils and ureas (HRAC 2010). Since 1997, figures supplied by Australia to the FAO indicate that between 20 and 25 million kg of herbicides are applied annually of which approximately 8 million kg was PSII herbicides (Australian Academy of Technological Sciences and Engineering 2002).

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Given the amounts of PSII herbicides applied annually to land and the amounts of diuron used as an anti-fouling agent, it is not surprising that triazine and urea herbicides have frequently been detected globally in rivers and lakes (e.g. Solomon et al. 1996; Gfrerer et al. 2002; Claver et al. 2006; Konstantinou et al. 2006), groundwater (e.g. Guzzella et al. 2006; Hildebrandt et al. 2008), oceans (e.g. Konstantinou and Albanis 2004 and references therein) and sediments (e.g. Thomas et al. 2000; Konstantinou and Albanis 2004). Within Australia, they have been frequently detected in rivers discharging to the Great Barrier Reef (GBR) (e.g. Smith et al. 2012; O'Brien et al. 2016; Wallace et al. 2016), in rivers of northern New South Wales draining cotton growing farmland (e.g. Muschal and Warne 2003), in Victoria (Wightwick and Allinson 2007 and references therein) and in groundwater in the states of New South Wales, Queensland, South Australia and Western Australia (Wightwick and Allinson 2007 and references therein). In addition, triazine and urea herbicides have been detected regularly at essentially every monitoring site in the GBR since 2005, when monitoring began (Kennedy et al. 2010a, b, 2011; Bentley et al. 2012; Gallen et al. 2013, 2014, 2016).

The GBR is a World Heritage Listed site that runs approximately 2500 km along the east coast of Queensland, Australia. It is the world's largest reef ecosystem and is a bioversity hotspot, but like most reefs, it faces a number of human and natural stressors that have the potential to adversely affect its health and resilience (e.g. Commonwealth of Australia 2015). The main water quality stressors impacting the GBR have been identified as suspended solids (eroded agricultural soil), nutrients (dissolved and total nitrogen and phosphorus) and pesticides (Baker 2003; Brodie et al. 2008, 2013; Department of Premier and Cabinet 2008). Consequently, the Australian and Queensland governments developed and implemented the Reef Water Quality Protection Plan (Australian Government and Queensland Government 2009, 2013) that included land management and water quality targets to reduce the loads (total mass) of each of these major pollutants being transported to the reef.

To assess the hazard and risk that pesticides pose to reef ecosystems and to develop pollution reduction targets (refer to Smith et al. 2017), it is essential to have estimates of the "safe environmental concentrations" such as water quality guidelines (WQGs, also referred to as criteria, standards, objectives) preferably derived using species sensitivity distributions, for all the pesticides present in the reef. Yet, despite pesticides being used globally, some for many decades, there is still a general lack of WQGs and/or SSDs for pesticides.

In Australia and New Zealand, the current Australian and New Zealand Guidelines for Fresh and Marine Water Quality (ANZECC and ARMCANZ 2000) are being revised. As part of the revision, numerical limits are being derived for 17 pesticides, predominantly to protect freshwater ecosystems. These pesticides were selected based on the priorities of government departments and stakeholders. However, even with this revision, there are still numerous pesticides regularly detected in rivers discharging to the reef and/or in the reef lagoon itself that will not have numerical limits. Therefore, the Queensland Department of Environment and Science, Information Technology and Innovation is deriving the numerical limits for a further 28 pesticides to protect both fresh and marine ecosystems.

Limits calculated using the Australian and New Zealand method for deriving water quality guideline values for ecosystem protection (Batley et al. 2014; Warne et al. 2015) are technically reviewed and then approved by a series of committees until they are nationally endorsed and become Default Guideline Values (DGVs). The approval process can take a considerable length of time, and hence, the limits derived in the current study are termed ecotoxicity thresholds (ETs) to make it clear that they have not yet been nationally endorsed, but in all other senses they are DGVs. The DGVs provide four levels of environmental protection that should theoretically protect 99, 95, 90 and 80% of species. The concentrations corresponding to these levels of protection are termed the PC99, PC95, PC90 and PC80 which are equivalent to the concentrations harmful to 1% (HC1), 5% (HC5), 10% (HC10) and 20% (HC20), respectively. In the current Australian and New Zealand Guidelines for Fresh and Marine Water Quality (ANZECC and ARMCANZ 2000), the numerical limits are termed trigger values (TVs), but in all other senses, they are identical to DGVs.

The aim of this paper was to develop ETs for four herbicides (ametryn, diuron, hexazinone and simazine) that are commonly detected in Queensland waterways and in the marine waters of the GBR, which either do not have TVs or only have low reliability TVs. Low reliability TVs and DGVs are based on ecotoxicity data for a limited number of species and taxa (Warne 2001; Warne et al. 2015).

Ametryn and simazine are both triazine herbicides (group C1 (HRAC 2010) and class 5 (WSSA 2016)), hexazinone is a triazinone herbicide but belongs to the same HRAC and WSSA classifications, while diuron is a urea herbicide belonging to group C2 (HRAC 2010) and class 7 (WSSA 2016)). The mode of action for all four herbicides is inhibition of photosystem II.

Methods

The revised method for the derivation of DGVs for the Australian and New Zealand Water Quality Guidelines (Batley et al. 2014; Warne et al. 2015) were followed. A thorough literature review was conducted for ecotoxicity data in both fresh and marine waters for the four herbicides. This search included the USEPA ECOTOX database (USEPA 2015a), the Office of the Pesticide Programs (USEPA

2015b), the Australasian Ecotoxicity Database (Warne et al. 1998) and the Australian and New Zealand Water Quality Guidelines toxicant database (Sunderam et al. 2000). In addition, physicochemical properties that are relevant to the environmental fate of the herbicides were collected (Table 1). Each publication was read and each datum was screened and their quality assessed using the methods set out in Warne et al. (2015), as the methods can vary within a paper. The data quality assessment process consists of answering 20 questions on how the data were generated (e.g. test organism, experimental design, chemical and statistical analysis) based on the information provided in the articles. This method is based on Hobbs et al. (2005) and is similar to other data evaluation methods (e.g. Klimisch et al. 1997; Durda and Preziosi 2000; Schneider et al. 2009; Brady 2011; Agerstrand et al. 2014). Data assessments were conducted and recorded using an electronic data quality assessment and reporting spreadsheet (Zhang et al. 2015). Toxicity data were classed as 'high' quality (score of 80 to 100), 'acceptable' quality (score of 51 to 79) or 'unacceptable' quality (score of 50 or less). 'Unacceptable' quality data were not used to derive ET values.

Often, multiple ecotoxicity values for more than one endpoint and measure of toxicity were available for species. In such cases, a data reduction process was used to generate a single value for each species (Warne et al. 2015). The remaining data were then tested, based on the chemical's mode of action, to determine if they were uni-, bi- or multi-modal. As the selected chemicals are all herbicides, tests were conducted to determine if there were significant differences in the sensitivity of phototrophic species (species that photosynthesize) and non-phototrophic species. When the data were normally distributed and had equal variances, the parametric two-sample *t* test was used, and when the data were not, the non-parametric Mann-Whitney two-tailed test was used. When the data were not uni-modal, only ecotoxicity data for the most sensitive group of organisms (i.e. phototrophs in the case of herbicides) were used to derive ETs. In cases where there were insufficient data to permit a statistical comparison, then the fresh and marine ecotoxicity data were combined.

Many measures of ecotoxicity are reported in the literature. The revised Australian and New Zealand method for deriving guideline values has an order of preference for using ecotoxicity data. For chronic ecotoxicity data, the order is as follows: no effect concentration (NEC) values; effect, inhibition or lethal concentration (EC/IC/LCx) values where x is less than 10; 10% bounded effect concentration (BEC10) values; 15 to 20% effect, inhibition or lethal concentration (EC/IC/LC15–20) values and no observed effect concentration (NOEC) values (Warne et al. 2015). There is considerable criticism of the generation and use of NOEC and lowest observed effect concentration (LOEC) values to derive environmental quality standards (e.g. van Dam et al. 2012 and references therein), although this is not universal (Green et al. 2012). Much of the existing chronic ecotoxicity data are NOEC values and this will continue to be the case for the immediate future. To encourage the generation of EC/IC/LC10 type data and phase out the use of NOEC data, the revised method for deriving the Australian and New Zealand guideline values (Warne et al. 2015) states that when there are EC/IC/LC10 type data for at least eight species that belong to at least four taxonomic groups, NOEC values should not be used. However, the impact that this would have on the reliability of the DGVs should be considered (Warne et al. 2015).

Species sensitivity distributions for each chemical in fresh and marine waters were derived using the Burrlioz 2.0 software (CSIRO 2016). This software selects the log-logistic distribution that best fits the ecotoxicity data when there are less than eight values and selects the best Burr type III statistical distribution when there are eight or more ecotoxicity data. The software then calculates four different levels of protection (PCx values). These PCx values are applied to ecosystems in different conditions for each chemical in each ecosystem type (Table 2). The reliability of the derived ET values was determined based on the number of species and taxa for which there were data, the type of data (chronic, a mixture of chronic and converted acute or only converted acute data) and the fit of the statistical distribution to the ecotoxicity data (good or poor) (Table 3). The resulting ET values were classed as very high, high, moderate, low and very low reliability (Table 3).

Results and discussion

The logarithms of the octanol-water partition coefficient and the logarithms of the bioconcentration factor for all four herbicides were well below 4 (Table 1), and therefore, the ET values did not need to consider secondary poisoning (Warne et al. 2015).

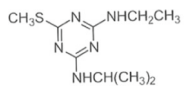
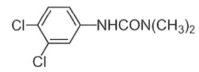
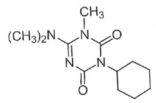
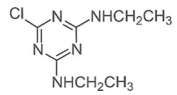
Phototrophic species were significantly ($p = 0.005$ for simazine and $p = < 0.0001$ for ametryn, diuron and hexazinone) more sensitive than non-phototrophic species for all four herbicides. Therefore, only ecotoxicity data for phototrophic species were used in all subsequent calculations of ETs as prescribed in Warne et al. (2015). The ETs should therefore theoretically protect set percentages of phototrophic species, and as the phototrophs are more sensitive than non-phototrophs, the ETs should provide an even higher level of protection to species overall.

Ametryn

Freshwater

There were 39 acceptable and high-quality acute and chronic toxicity data from 10 sources (Supplementary Material Table 1). The removal of non-phototrophic species and the

Table 1 Chemical structure, chemical abstract service number (CAS no.) and selected physicochemical properties of the selected herbicides

Herbicide and CAS no.	Molec. wgt (amu)	Aqueous sol. (mg/L)	Log Kow	Log Koc	Log BCF	Half-life in freshwater (days)	Half-life in marine water (days)
Ametryn 834-12-8 	227.3[a]	200 (pH 7.1, 22°C)	2.63 (pH 7, 20°C)	1.98 – 2.97[a], 2.5[b]	1.52[b]	> 7[c] Stable at normal aquatic pH[d]	419 ± 264[g] (dark, 25°C)
Diuron 330-54-1 	233.1[a]	37.4 (25°C)[a] 35.6 (20°C)[b]	2.85 (25°C)[a] 2.87 (20°C)[b]	2.60[a], 2.91[b]	0.975[b]	175 (lagoon prediction) with majority of diuron (90%) residing in sediment[e]	556 ± 14[g] (dark, 25°C) to 1568 ± 222[g] (dark, 25°C)
Hexazinone 51235-04-2 	252.3[a]	29.8[a] (pH 7, 25°C)	1.17[b] (pH 7, 25°C)	1.72[b] – 2.79[f]	0.85[b]	≥ 56[b, f] (pH 7, 25 C)	479 ± 240[g] (dark, 25°C) to 2799 ± 467[g] (light, 25°C)
Simazine 122-34-9 	201.7[a]	6.2[a]	2.1[a]	2.2[a]	>2.0[g]	8.8[a] (pH 1), 96[a] (pH 5), 3.7[a] (pH 13)	579 ± 294[g] (dark, 25°C)

[a] BCPC (2012)

[b] University of Hertfordshire (2013)

[c] USEPA (1987)

[d] USEPA (2013)

[e] Peterson and Batley (1991)

[f] DPR (1996)

[g] Mercurio et al. (2015)

conversion of the data to a single value per species resulted in chronic ecotoxicity data for two phototrophic species that belonged to two phyla (freshwater data in Table 4). This dataset did not meet the minimum data requirements to derive ET values using a SSD method, i.e. data for at least five species belonging to at least four phyla (Warne et al. 2015). In cases where there are insufficient chronic ecotoxicity data, Warne et al. (2015) recommend two methods to address this. The first converts acute toxicity data to estimates of chronic toxicity (i.e. chronic NOEC/EC10 type values). The second method permits the combination of ecotoxicity data for organic chemicals tested in freshwater and marine conditions, provided the two sets of data are not significantly different or

Table 2 The guideline values that correspond to the four levels of protection and examples of where they would apply (modified from ANZECC and ARMCANZ 2000)

Level of protection	Equivalent HC value	Ecosystems applied to
PC99	HC1	High conservation value systems, e.g. National Parks
PC95	HC5	Slightly to moderately disturbed sites, e.g. most urban and rural waterways
PC90	HC10	Highly disturbed sites, e.g. waterways receiving many industrial discharges, channelized waterways
PC80	HC20	

Table 3 Classification scheme for the reliability of ecotoxicity threshold values derived using the species sensitivity distribution method (modified from Warne et al. 2015)

No. species	Data type	Adequacy of distributions fit	Reliability
≥ 15	Chronic	Good	Very high
		Poor	Moderate
8–14		Good	High
		Poor	Moderate
5–7		Good	Moderate
		Poor	Low
≥ 15	Combined chronic and converted acute or Combined fresh and marine	Good	Moderate
		Poor	Low
8–14		Good	Moderate
		Poor	Low
5–7		Good	Moderate
		Poor	Low
≥ 15	Converted acute	Good	Moderate
		Poor	Low
8–14		Good	Moderate
		Poor	Low
5–7		Good	Low
		Poor	Very low

Table 4 Summary of the single toxicity values for each species used to derive the freshwater and marine ecotoxicity threshold values for ametryn. Data are arranged in alphabetical order for the media and then test species

Media	Taxonomic group	Species	Phyla	Duration (days)	Type (acute/chronic)	Toxicity endpoint	Toxicity value used (μg/L)
Freshwater	Microalgae	*Chlorella pyrenoidosa*	Chlorophyta	4	Chronic estimated NOEC	Population (Abundance)	0.06[a]
Freshwater	Microalgae	*Chlorococcum sp.*	Chlorophyta	10	Chronic estimated NOEC	Biomass yield	2000[a]
Freshwater	Macrophyte	*Lemna gibba*	Tracheophyta	7	Chronic NOEC	Total frond number, growth rate, mortality	2
Freshwater	Microalgae	*Neochloris* sp.	Chlorophyta	3	Chronic estimated NOEC	Biomass yield	7.2[a]
Freshwater	Microalgae	*Platymonas sp.*	Chlorophyta	3	Chronic estimated NOEC	Biomass yield	4.8[a]
Freshwater	Microalgae	*Scenedesmus quadricauda*	Chlorophyta	4	Chronic estimated NOEC	Population (abundance)	30[a]
Freshwater	Microalgae	*Selenastrum capricornutum*[b]	Chlorophyta	7	Chronic NOEC	Biomass yield	1.14
Freshwater	Microalgae	*Stauroneis amphoroides*	Bacillariophyta	3	Chronic estimated NOEC	Biomass yield	5.2 [a]
Marine	Microalgae	*Achnanthes brevipes*	Bacillariophyta	3	Chronic estimated NOEC	Biomass yield	3.8[a]
Marine	Microalgae	*Dunaliella tertiolecta*	Chlorophyta	4–10	Chronic estimated NOEC	Biomass yield	1.89[a]
Marine	Microalgae	*Isochrysis galbana*	Haptophyta	3	Chronic NOEC	Population (Abundance)	1.31
Marine	Microalgae	*Monochrysis lutheri*	Ochrophyta	3	Chronic estimated NOEC	Biomass yield	2.8[a]
Marine	Microalgae	*Navicula incerta*	Bacillariophyta	3	Chronic estimated NOEC	Biomass yield	19.4[a]
Marine	Microalgae	*Nitzschia closterium*[c]	Bacillariophyta	3	Chronic estimated NOEC	Biomass yield	12.4[a]
Marine	Microalgae	*Phaeodactylum tricornutum*	Bacillariophyta	10	Chronic estimated NOEC	Biomass yield	6.32[a]
Marine	Microalgae	*Thalassiosira fluviatilis*	Bacillariophyta	3	Chronic estimated NOEC	Biomass yield	11.6 [a]
Marine	Microalgae	*Thalassiosira guillardii*	Bacillariophyta	3	Chronic estimated NOEC	Biomass yield	11 [a]

[a] The chronic EC/LC50 values were converted to estimates of chronic NOEC/EC10 values. Chronic EC/LC50 values were divided by 5 (Warne 2001)

[b] This species has also been called *Raphidocelis subcapitata* and is currently called *Pseudokirchneriella subcapitata*

[c.] This species has previously been called *Ceratoneis closterium*

knowledge of the properties or mode of action of the chemical does not indicate there should be differences. So, acute ecotoxicity data were converted to estimates of chronic NOEC/EC10 values (Table 4). This resulted in a dataset for eight species that belonged to three phyla (Table 4), which still did not meet the minimum requirements. There was only chronic ecotoxicity data for a single marine species, so chronic and estimated chronic data for marine species were combined and compared to the freshwater data—with no significant differences being found ($p > 0.05$). The fresh and marine ecotoxicity data were therefore combined, resulting in data for 17 species (eight freshwater and nine marine) that belonged to five phyla. The resulting dataset met the minimum data requirements to use a SSD method (Warne et al. 2015). The statistical distribution selected by Burrlioz (CSIRO 2016) provided a 'good' fit to the data (Fig. 1a). This combined with the number and type of toxicity data (Table 3) available resulted in a 'moderate' reliability set of ET values (Table 5).

Marine

There were 26 acceptable and high-quality acute and chronic data from four sources (Supplementary Material, Table 2). The removal of non-phototrophic species, conversion of the acute to estimated chronic values and conversion of data to a single value per species resulted in chronic ecotoxicity data for nine phototrophic species that belonged to four phyla (marine data in Table 4). This dataset met the minimum data requirements (i.e. at least five species belonging to at least four phyla)

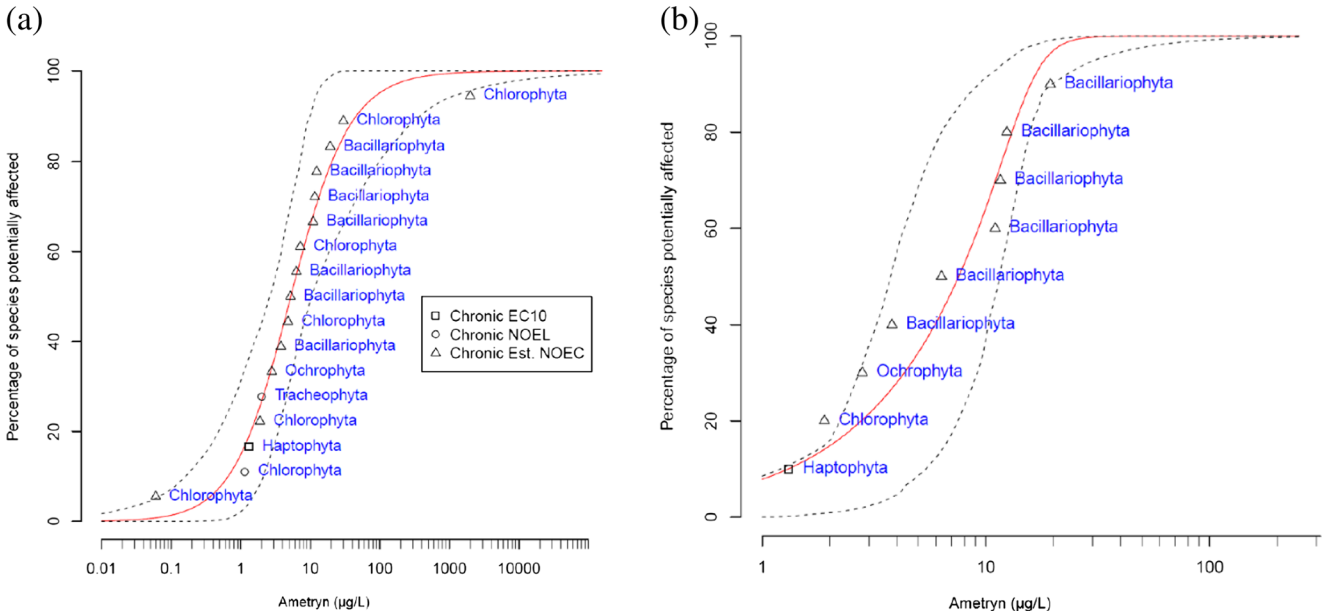


Fig. 1 Species sensitivity distribution plot of the toxicity data used to derive the **a** freshwater and **b** marine ecotoxicity threshold values for ametryn

to use a SSD method (Warne et al. 2015). The statistical distribution selected by Burrlioz (CSIRO 2016) provided a 'good' fit (Fig. 1b). This combined with the number and type of toxicity data available (Table 3) resulted in a set of 'moderate' reliability ET values (Table 5).

Diuron

Fresh

There were 243 acceptable and high-quality acute and chronic data from 43 sources (Supplementary Material, Table 3). The removal of non-phototrophic species and the conversion of the data to a single value per species resulted in chronic ecotoxicity data for 26 phototrophic species that belonged to four phyla (Table 6). This dataset met the minimum data requirements to derive ecotoxicity threshold values using a SSD method (Warne et al. 2015). The distribution selected by Burrlioz (CSIRO 2016) provided a 'good' fit (Fig. 2a) which combined with the number and type of ecotoxicity data available (Table 3) resulted in a set of 'very high' reliability ET values (Table 5).

Table 5 Derived ecotoxicity threshold values for the four selected herbicides in fresh and marine ecosystems

Chemical	media	Reliability	Ecotoxicity threshold values (µg/L)			
			PC99	PC95	PC90	PC80
Ametryn	Freshwater	Moderate	0.07	0.33	0.66	1.4
	Marine	Moderate	0.10	0.61	1.3	2.8
Diuron	Freshwater	Very high	0.08	0.23	0.42	0.9
	Marine	Very high	0.43	0.67	0.86	1.2
Hexazinone	Freshwater	Low	0.31	1.1	1.9	3.4
	Marine	Low	1.8	2.5	3.1	4.0
Simazine	Freshwater	High	3.2	10	17	29
	Marine	Low	28	63	89	130

Marine

There were 97 acceptable and high-quality acute and chronic data from 28 sources (Supplementary Material, Table 4). The removal of non-phototrophic species and the conversion of the data to a single value per species resulted in chronic EC10/NOEC ecotoxicity data for seven phototrophic species that belonged to five phyla (Table 7). This dataset met the minimum data requirements to use a SSD method (Warne et al. 2015). The distribution selected by Burrlioz (CSIRO 2016) provided a 'poor' fit (Fig. 2b), which combined with the number and type of ecotoxicity data available (Table 3) resulted in a set of 'low' reliability ET values (Table 5 and Supplementary Material, Table 5). The resulting PC99 and PC95 values (the most widely used ecotoxicity numerical limits) differed from the corresponding freshwater values by factors between 3- and 5-fold, which raised concerns about the marine ET values. Therefore, the dataset was expanded by including single species ecotoxicity values based on chronic estimated values (chronic LOEC or EC50 data converted to chronic EC10/NOEC values using the conversion factors stated in Warne et al. 2015) (Table 7). This increased the dataset to 20 phototrophic species that belonged to six phyla (Table 7) and the resulting SSD was used to derive ET values. The distribution selected by Burrlioz (CSIRO 2016) for the

Table 6 Summary of the single toxicity values for each species used to derive the freshwater ecotoxicity threshold values for diuron

Taxonomic group	Species	Phyla	Class	Duration (days)	Type (acute/chronic)	Toxicity endpoint	Toxicity value (μg/L)
Microalgae	*Achnanthidium minutissimum*	Bacillariophyta	Bacillariophyceae	4	Chronic EC05	Cell density	3.15
Bacteria	*Anabaena variabilis*	Cyanobacteria	Cyanophyceae	12	Chronic estimated NOEC	Chlorophyll-a	16[a]
Microalgae	*Chlorella pyrenoidosa*[b]	Chlorophyta	Trebouxiophyceae	4	Chronic estimated NOEC	Cell count	0.47[a]
Cyanobacteria	*Chroococcus minor*	Cyanobacteria	Cyanophyceae	7	Chronic estimated NOEC	Cell density	0.94[a]
Microalgae	*Craticula accomoda*	Bacillariophyta	Bacillariophyceae	4	Chronic EC05	Cell density	261
Microalgae	*Cyclotella meneghiniana*	Bacillariophyta	Mediophyceae	4	Chronic EC05	Cell density	1.59
Microalgae	*Cyclotella nana*	Bacillariophyta	Mediophyceae	3	Chronic estimated NOEC	Biomass yield, Growth rate, AUC	7.8[a]
Microalgae	*Encyonema silesiacum*	Bacillariophyta	Bacillariophyceae	4	Chronic EC05	Cell density	3.11
Microalgae	*Eolimna minima*	Bacillariophyta	Bacillariophyceae	4	Chronic EC05	Cell density	3007
Microalgae	*Fragilaria capucina var. vaucheriae*	Bacillariophyta	Fragilariophyceae	4	Chronic EC05	Cell density	0.069
Microalgae	*Fragilaria rumpens*	Bacillariophyta	Fragilariophyceae	4	Chronic EC10	Cell density	4.77
Microalgae	*Fragilaria ulna*[c]	Bacillariophyta	Fragilariophyceae	4	Chronic EC05	Cell density	12.6
Microalgae	*Gomphonema parvulum*	Bacillariophyta	Bacillariophyceae	4	Chronic EC10	Chlorophyll-a	232.1
Macrophyte	*Lemna gibba*	Tracheophyta	Liliopsida	7	Chronic NOEL	Total frond number, Growth rate, Mortality	2.49
Macrophyte	*Lemna minor*	Tracheophyta	Liliopsida	7	Chronic estimated NOEC	Total chlorophyll	3.16[a]
Macrophyte	*Lemna paucicostata*	Tracheophyta	Liliopsida	8	Chronic estimated NOEC	Frond cover area	2.19[a]
Microalgae	*Mayamaea fossalis*	Bacillariophyta	Bacillariophyceae	4	Chronic EC05	Cell density	74
Microalgae	*Nitzschia palea*	Bacillariophyta	Bacillariophyceae	3	Chronic EC05	Cell density	106
Microalgae	*Scenedesmus acutus*	Chlorophyta	Chlorophyceae	8	Chronic estimated NOEC	Cell count	2.66[a]
Microalgae	*Scenedesmus obliquus*	Chlorophyta	Chlorophyceae	4	Chronic estimated NOEC	Cell count	0.82[a]
Microalgae	*Scenedesmus quadricauda*	Chlorophyta	Chlorophyceae	4	Chronic estimated NOEC	Cell count	0.54[a]
Microalgae	*Scenedesmus subspicatus*[d]	Chlorophyta	Chlorophyceae	3	Chronic NOEC	Cell count	10
Microalgae	*Scenedesmus vacuolatus*	Chlorophyta	Chlorophyceae	2	Chronic estimated NOEC	Cell density	2.86[a]
Microalgae	*Selenastrum capricornutum*[e]	Chlorophyta	Chlorophyceae	4	Chronic NOEL	Biomass yield, Growth rate, AUC	0.44
Microalgae	*Sellaphora minina*	Bacillariophyta	Bacillariophyceae	4	Chronic EC10	Chlorophyll-a	1493.3
Microalgae	*Stauroneis amphoroides*	Bacillariophyta	Bacillariophyceae	4	Chronic estimated NOEC	Biomass yield, Growth rate, AUC	6.2[a]

AUC area under the growth curve

[a] Chronic NOEC/NOEL = no conversions applied; chronic est. NOEC = chronic LOEC values that were converted to chronic NOEC/NOEL/EC10 values by dividing by 5 (Warne et al. 2015)

[b] This species has also been called *Chlorella vulgaris* and *Chlorella pyrenoidosa*

[c] This species has also been called *Ulnaria ulna*

[d] This species has also been called *Desmodesmus subspicatus*

[e] This species has also been called *Raphidocelis subcapitata* and *Pseudokirchneriella subcapitata*

expanded dataset (chronic and chronic estimated EC10/NOEC values) provided a 'good' fit (Fig. 2c) which combined with the number and type of ecotoxicity data available (Table 3) resulted in a set of 'very high' reliability ET values (Table 5). The resulting ET values (Table 5) were similar to those based solely on chronic EC10/NOEC data, but

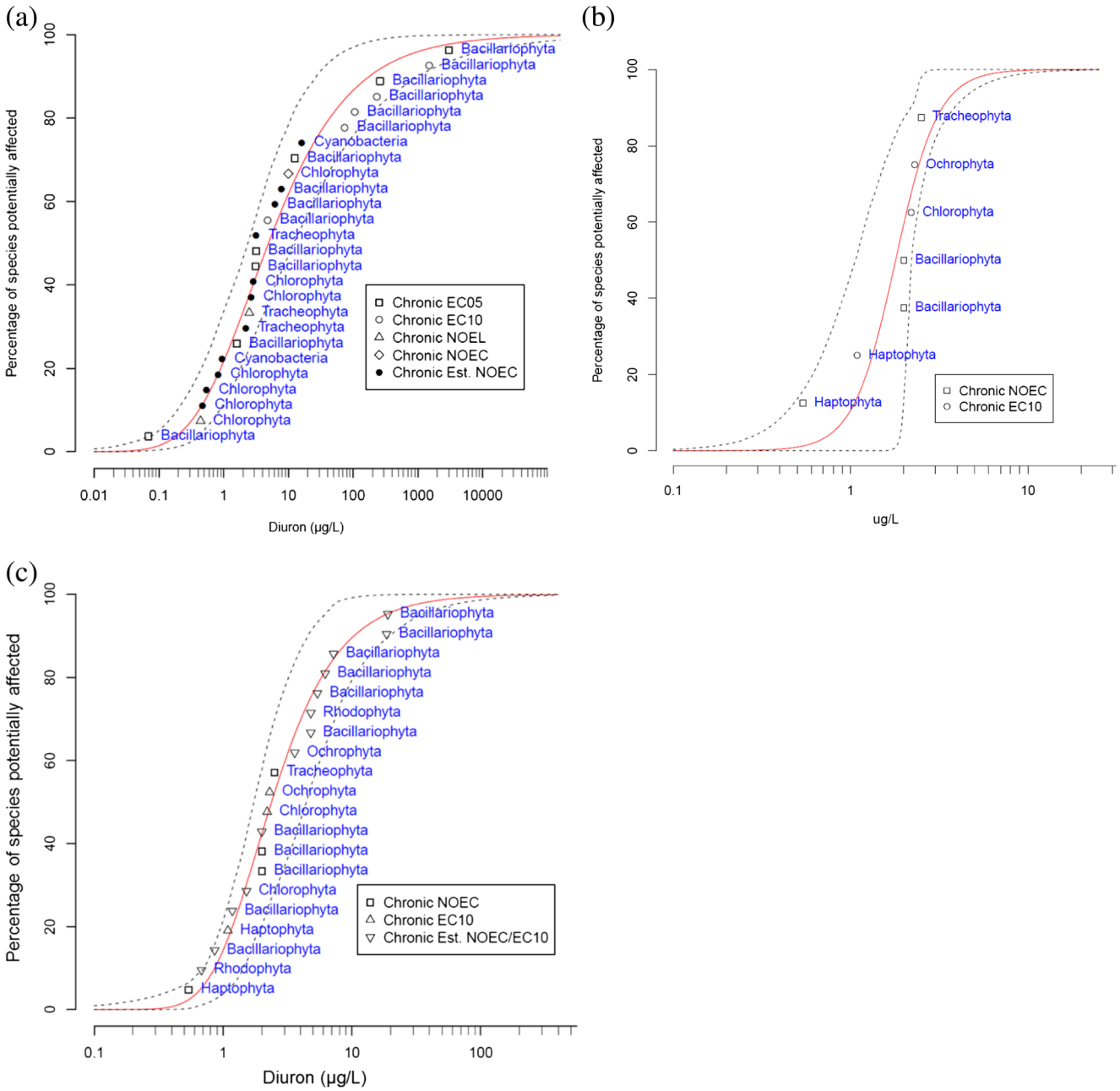


Fig. 2 Diuron species sensitivity distribution plots of **a** chronic freshwater ecotoxicity data, **b** chronic marine ecotoxicity data for seven species and **c** chronic EC10/NOEC and chronic estimated EC10/NOEC data for 20 marine species. The SSDs of **a** and **c** were used to generate the ecotoxicity thresholds

Table 7 Summary of the single toxicity values for each species used to derive the marine ecotoxicity threshold values for diuron

Taxonomic group	Species	Phyla	Class	Duration (days)	Type (acute/chronic)	Toxicity endpoint	Toxicity value (μg/L)
Microalgae	*Achnanthes brevipes*	Bacillariophyta	Bacillariophyceae	3	Chronic estimated NOEC	Biomass yield, growth rate, AUC	4.8[a]
Microalgae	*Amphora exigua*	Bacillariophyta	Bacillariophyceae	3	Chronic estimated NOEC	Biomass yield, growth rate, AUC	6.2[a]
Macroalgae	*Ceramium tenuicorne*	Rhodophyta	Florideophyceae	7	Chronic estimated NOEC	Final length	0.68[a]
Microalgae	*Chaetoceros gracilis*	Bacillariophyta	Mediophyceae	3	Chronic estimated NOEC	Cell number	7.2[a]
Microalgae	*Dunaliella tertiolecta*	Chlorophyta	Chlorophyceae	4	Chronic estimated NOEC	Cell density	1.52[a]
Microalgae	*Emiliania huxleyi*	Haptophyta	Coccolithophyceae	3	Chronic NOEC	Mortality	0.54
Microalgae	*Entomoneis punctulata*	Bacillariophyta	Bacillariophyceae	3	Chronic NOEC	Cell density	2.0
Microalgae	*Isochrysis galbana*	Haptophyta	Coccolithophyceae	3	Chronic EC10	Cell density	1.09
Microalgae	*Monochrysis lutheri*	Ochrophyta	Chrysophyceae	3	Chronic estimated NOEC	Biomass yield, growth rate, AUC	3.6[a]
Microalgae	*Navicula forcipata*	Bacillariophyta	Bacillariophyceae	4	Chronic estimated NOEC	Cell density	5.4[a]
Microalgae	*Navicula incerta*	Bacillariophyta	Bacillariophyceae	3	Chronic estimated NOEC	Biomass yield, growth rate, AUC	18.6[a]
Microalgae	*Nephroselmis pyriformis*	Chlorophyta	Nephrophyceae	3	Chronic EC10	Cell density	2.2
Microalgae	*Nitzschia closterium*[b]	Bacillariophyta	Bacillariophyceae	3	Chronic NOEC	Cell density	2.0
Microalgae	*Phaeodactylum tricornutum*	Bacillariophyta	Bacillariophyta incertae sedis	10	Chronic estimated NOEC	Biomass yield, growth rate, AUC	2.0[a]
Microalgae	*Porphyridium cruentum*	Rhodophyta	Porphyridiophyceae	3	Chronic estimated NOEC	Biomass yield, growth rate, AUC	4.8[a]
Macroalgae	*Saccharina japonica*	Ochrophyta	Phaeophyceae	15	Chronic EC10	Fresh weight	2.3
Microalgae	*Skeletonema costatum*	Bacillariophyta	Mediophyceae	4	Chronic estimated NOEC	Cell density	1.18[a]
Microalgae	*Thalassiosira fluviatilis*	Bacillariophyta	Mediophyceae	3	Chronic estimated NOEC	Biomass yield, growth rate, AUC	19[a]
Microalgae	*Thalassiosira pseudonana*	Bacillariophyta	Mediophyceae	4	Chronic estimated NOEC	Cell density	0.86[a]
Macrophyte	*Zostera marina*	Tracheophyta	Liliopsida	10	Chronic NOEC	Biomass (Old and new growth)	2.5

AUC area under the growth curve

[a] Chronic NOEC/NOEL = no conversions applied; Chronic est. NOEC = chronic LOEC values that were converted to chronic NOEC/NOEL/EC10 values by dividing by 5 (Warne et al. 2015)

[b] This species has previously been called *Ceratoneis closterium*

the second set of ET values were adopted as they were based on a larger dataset and the fit of the distribution was better resulting in greater confidence in these values.

Hexazinone

Fresh

There were 57 acceptable and high-quality acute and chronic data from eight sources (Supplementary Material, Table 6). The removal of non-phototrophic species and the conversion of the data to a single value per species resulted in chronic ecotoxicity data for five species that belonged to four phyla (freshwater data in Table 8). This dataset met the minimum data requirements to use a SSD method (Warne et al. 2015). The distribution selected by Burrlioz (CSIRO 2016) provided a 'poor' fit (Fig. 3a) which combined with the number and type of ecotoxicity data (Table 3) available resulted in a set of 'low' reliability ET values (Table 5).

Marine

There were 13 acceptable and high-quality acute and chronic data from four sources (Supplementary Material, Table 7). The removal of non-phototrophic species and the conversion of the data to a single value per species resulted in chronic

Table 8 Summary of the single toxicity values for each species used to derive the freshwater and marine ecotoxicity threshold values for hexazinone

Media	Taxonomic group	Species	Phyla	Class	Duration (days)	Type (acute/chronic)	Toxicity endpoint	Toxicity value (μg/L)
Freshwater	Cyanobacteria	*Anabaena flosaquae*	Cyanobacteria	Cyanophyceae	5	Chronic NOEC	Population (Abundance)	150
Marine	Microalgae	*Isochrysis galbana*	Haptophyta	Coccolithophyceae	3	Chronic NOEC	Population (Abundance)	19.34
Freshwater	Macrophyte	*Lemna gibba*	Tracheophyta	Liliopsida	14	Chronic NOEC	Population (Abundance)	8.82
Freshwater	Macrophyte	*Lemna minor*	Tracheophyta	Liliopsida	7	Chronic estimated NOEC	Population (Growth)	14.4[a]
Freshwater	Microalgae	*Navicula pelliculosa*	Bacillariophyta	Bacillariophyceae	5	Chronic NOEC	Population (Abundance)	3.5
Marine	Microalgae	*Nephroselmis pyriformis*	Chlorophyta	Nephrophyceae	3	Chronic NOEC	Population (Abundance)	3.8
Freshwater	Microalgae	*Pseudokirchneriella subcapitata*[b]	Chlorophyta	Chlorophyceae	5	Chronic NOEC	Population (Abundance)	4
Marine	Microalgae	*Skeletonema costatum*	Bacillariophyta	Mediophyceae	5	Chronic NOEC	Population (Abundance)	4.1

[a] The chronic EC/LC50 values were converted to estimates of chronic NOEC/EC10 values. Chronic LOEC values were divided by 2.5 while chronic EC/LC50 values were divided by 5 (Warne 2001)

[b] Previously, this species has been called Rhaphidocelis subcapitata and Selenastrum capricornutum

ecotoxicity data for three species that belonged to three phyla (Table 8). This dataset did not meet the minimum data requirements to derive ET values using a SSD method (Warne et al. 2015). The distributions of the ecotoxicity data for marine and freshwater species were not significantly different ($p > 0.05$). As per the methods for dealing with insufficient ecotoxicity data (Warne et al. 2015), chronic toxicity data for freshwater and marine phototrophic species were therefore combined, resulting in data for eight species (five freshwater and three marine) that belonged to five phyla (Table 8). The resulting dataset met the minimum data requirements to use a SSD method (Warne et al. 2015). The distribution selected by Burrlioz (CSIRO 2016) provided a 'poor' fit (Fig. 3b) which combined with the number and type of data (Table 3) available resulted in a set of 'low' reliability ET values (Table 5).

Simazine

Fresh

There were 229 acceptable and high-quality acute and chronic data from 33 sources (Supplementary Material, Table 8). The

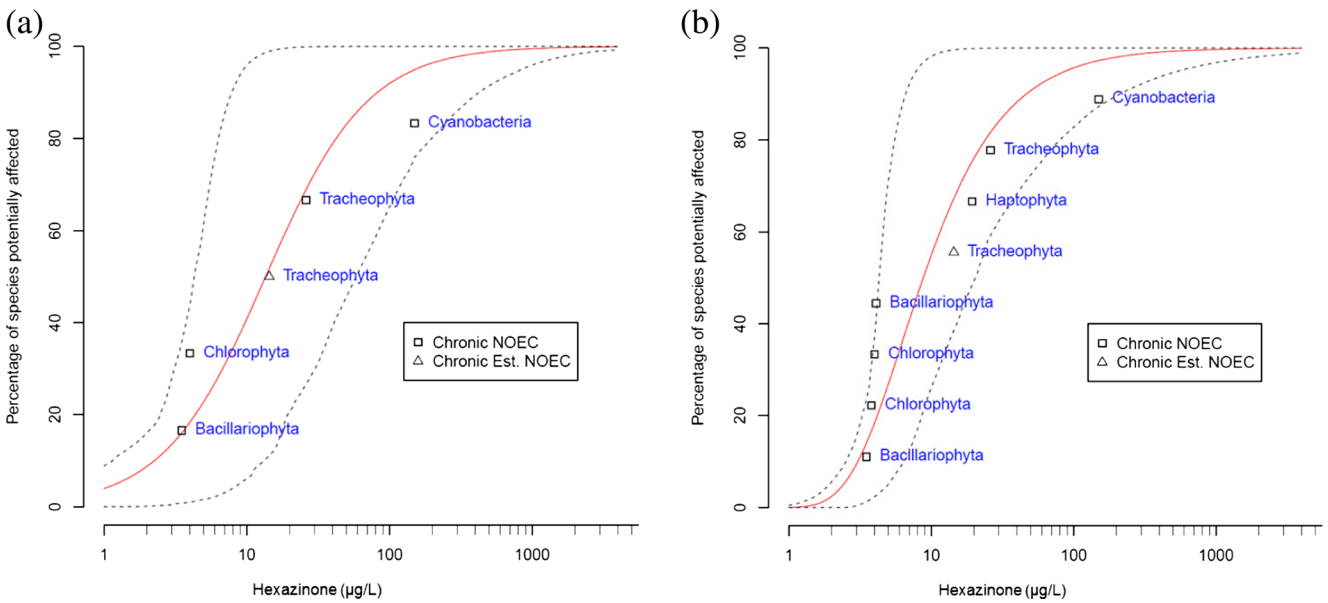


Fig. 3 Species sensitivity distribution plot of the toxicity data used to derive the **a** freshwater and **b** marine ecotoxicity threshold values for hexazinone

Table 9 Summary of the single toxicity values for each species used to derive the freshwater and marine ecotoxicity threshold values for simazine. Data are arranged alphabetically by media and then species name

Media	Taxonomic group	Species	Phyla	Life stage	Duration (days)	Type (acute/chronic)	Toxicity endpoint	Toxicity value (μg/L)
Freshwater	Microalga	*Chlamydomonas geitleri*	Chlorophyta	Exponential growth	3	Chronic estimated NOEC	Chlorophyll-a content	171[a]
Freshwater	Microalga	*Chlorella vulgaris*	Chlorophyta	–	4	Chronic estimated NOEC	Growth rate	84.4[a]
Freshwater	Microalga	*Pseudokirchneriella subcapitata*[b]	Chlorophyta	–	3	Chronic NOEC	Growth rate	32
Freshwater	Microalga	*Scenedesmus obliquus*	Chlorophyta	Exponential growth	*	Chronic estimated NOEC	Growth rate	51.4[a]
Freshwater	Microalga	*Scenedesmus quadricauda*	Chlorophyta	–	4	Chronic estimated NOEC	Abundance	30[a]
Freshwater	Microalga	*Anabaena flosaquae*	Cyanobacteria	–	5	Chronic estimated NOEC	Cell density	7.2[a]
Freshwater	Microalga	*Navicula pelliculosa*	Ochrophyta	–	5	Chronic estimated NOEC	Cell density	18[a]
Freshwater	Macrophyte	*Acorus gramineus*	Tracheophyta	–	7	Chronic NOEC	Fresh weight	100
Freshwater	Macrophyte	*Elodea canadensis*	Tracheophyta	–	*	Chronic NOEC	*	83
Freshwater	Macrophyte	*Glyceria maxima*	Tracheophyta	–	*	Chronic NOEC	*	83
Freshwater	Macrophyte	*Lemna gibba*	Tracheophyta	–	14	Chronic estimated NOEC	Biomass yield	28[a]
Freshwater	Macrophyte	*Myriophyllum aquaticum*	Tracheophyta	2 weeks old	7	Chronic estimated NOEC	Fresh weight	20
Freshwater	Macrophyte	*Myriophyllum spicatum*	Tracheophyta	–	*	Chronic NOEC	*	83
Freshwater	Macrophyte	*Persicaria amphibia*	Tracheophyta	–	*	Chronic NOEC	*	83
Freshwater	Macrophyte	*Pontederia cordata*	Tracheophyta	–	7	Chronic NOEC	Fresh weight	100
Freshwater	Macrophyte	*Typha latifolia*	Tracheophyta	–	7	Chronic NOEC	Fresh weight	300
Freshwater	Macrophyte	*Vallisneria americana*	Tracheophyta	–	13	Chronic NOEC	Fresh weight and length	58
Marine	Microalgae	*Ceratoneis closterium*[c]	Bacillariophyta	Exponential growth	3	Chronic NOEC	Growth rate	310
Marine	Microalgae	*Chlorococcum sp.*	Chlorophyta	–	10	Chronic estimated NOEC	Cell density	400[a]
Marine	Microalgae	*Dunaliella tertiolecta*	Chlorophyta	–	10	Chronic estimated NOEC	Cell density	1000[a]
Marine	Microalgae	*Isochrysis galbana*	Haptophyta	–	10	Chronic estimated NOEC	Cell density	100[a]
Marine	Microalgae	*Phaeodactylum tricornutum*	Bacillariophyta	Exponential growth	3	Chronic NOEC	Growth rate	100
Marine	Microalgae	*Skeletonema costatum*	Ochrophyta	–	5	Chronic estimated NOEC	Cell density	250[a]

[a] The chronic EC/LC50 values were converted to estimates of chronic NOEC/EC10 values. Chronic LOEC values were divided by 2.5 while chronic EC/LC50 values were divided by 5 (Warne 2001). *Refer to Supplementary Material Table 8 for information, as there are multiple durations and endpoints that apply to this species toxicity value

[b] Previously, this species has been called *Rhaphidocelis subcapitata* and *Selenastrum capricornutum*

[c] This species has also been called *Nitzschia closterium*

removal of non-phototrophic species and the conversion of the data to a single value per species resulted in chronic and chronic estimated EC10/NOEC data for 17 phototrophic species that belonged to four phyla (freshwater data in Table 9). This dataset met the minimum data requirements to use a SSD method (Warne et al. 2015). The distribution selected by Burrlioz (CSIRO 2016) provided a 'good' fit (Fig. 4a), which combined with the number and type of data (Table 3) available resulted in a set of 'high' reliability ET values (Table 5).

Marine

There were 23 acceptable and high-quality acute and chronic data from five sources (Supplementary Material, Table 9). The removal of non-phototrophic species and the conversion of the data to a single value per species resulted in chronic ecotoxicity data for six phototrophic species that belonged to four phyla (marine data in Table 9). This dataset met the minimum data requirements to use a SSD method (Warne et al.

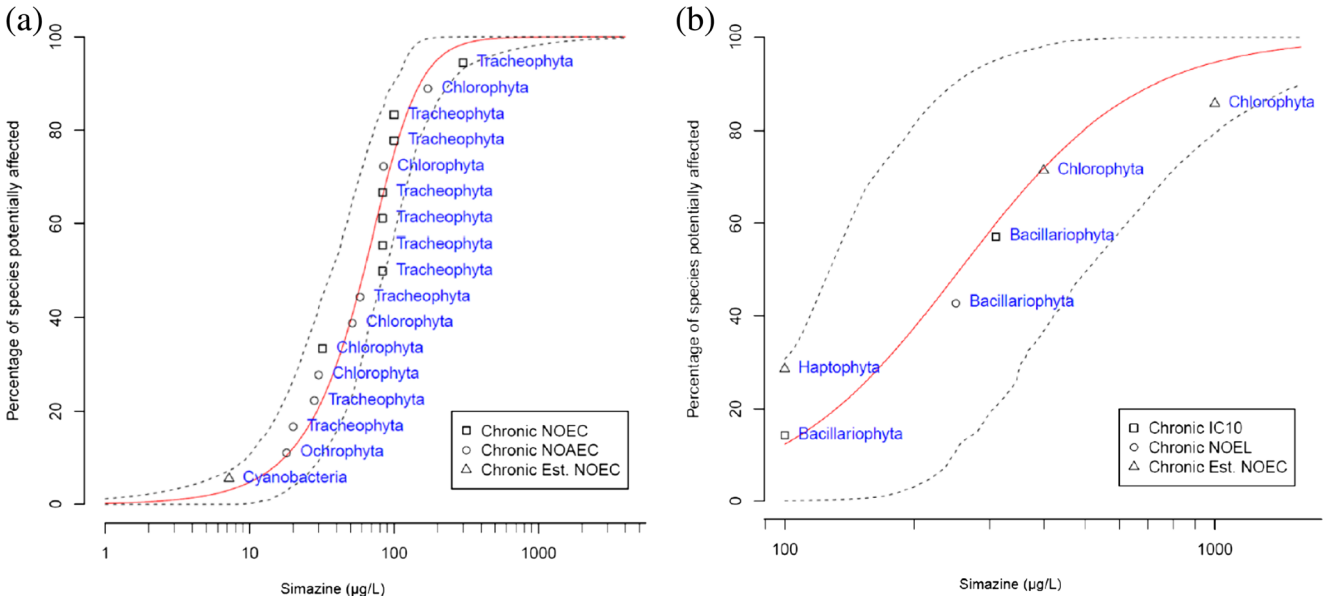


Fig. 4 Simazine species sensitivity distribution plots of **a** the chronic and chronic estimated toxicity data for freshwater species, **b** chronic and chronic estimated ecotoxicity data for marine species

2015). However, the distribution selected by Burrlioz (CSIRO 2016) provided a 'poor' fit to the ecotoxicity data (Fig. 4b), which combined with the number and type of data (Table 3) available resulted in a set of 'low' reliability ET values (Supplementary Material, Table 10). Despite the limited amount of marine ecotoxicity data, it was not combined with the ecotoxicity data for freshwater species as the two datasets had significantly different distributions ($p = 0.02$, compare Fig. 4a, b).

Comparison to international water quality guidelines for the same chemicals

A review of international water quality guidelines (including Australia and New Zealand, Canada, China, England, European Union (EU), France, Germany, Japan, Singapore, South Africa, South Korea and the USA) was conducted for the four herbicides. While comparing the numerical values of guidelines from different countries is not particularly useful (as different methods are used, different levels of protection are provided, and they are derived at different times with different ecotoxicity data available), this comparison clearly highlights the general paucity of guidelines for pesticides. In some countries, the lack of WQGs is due to some of the herbicides no longer being used, e.g. ametryn, hexazinone and simazine are not approved for use in the EU. In other countries such as the USA, WQGs are limited to the chemicals which were viewed as the major pollutants at the time the guidelines were derived (1980s) with few guidelines derived for additional chemicals since then. Given the amounts of pesticides used globally and that they are designed to kill pest species, this lack of guidelines is surprising.

There is a guideline for ametryn in Germany (an annual average (AA) concentration of 0.5 µg/L) (Federal Ministry of Justice and Customer Protection 2016) which is very similar to the PC95 value in marine waters derived by the current study (0.54 µg/L, Table 10). However, the ametryn PC99 for marine waters (0.087 µg/L) and the PC99 and PC95 values for fresh waters (0.013 and 0.16 µg/L, respectively) derived in the current study are considerably lower.

Despite being calculated using slightly different methods, the Swiss proposed maximum acceptable concentration (PMAC) and proposed annual average (PAA) values (0.25 and 0.07 µg/L, respectively (EAWAG 2016b) for diuron are essentially identical to the PC95 and PC99 values (0.23 and 0.08 µg/L) for diuron that were derived in the current project. Both sets of these numerical limits for diuron are considerably smaller than the current EU AA and maximum acceptable concentration (MAC) values of 1.9 and 0.2 µg/L, respectively. The difference in the EU (EU 2005a) and Swiss guidelines (EAWAG 2016b) for diuron is most likely due to availability of new ecotoxicity data as they were derived using the same method (EC 2011).

The only other WQGs available for hexazinone were from Germany (AA of 0.07 µg/L) which is at least one order of magnitude lower than the guidelines derived in the current project (Table 10). This most probably relates to the German value being derived by a conservative assessment factor method.

The simazine ETs (freshwater PC99 and PC95 of 3.4 and 9.9 µg/L, respectively, and marine PC99 and PC95 of 4.4 and 12 µg/L, respectively) derived in this study are higher than the EU guideline values (AA and MAC of 1 and 4 µg/L, respectively, Table 10) (EU 2005b), again reflecting the availability

Table 10 Comparison of ecotoxicity thresholds from this study and international water quality guidelines/standards/criteria

Country	Reference	Published	Media	Ametryn	Diuron	Hexazinone	Simazine
This study		2018	Freshwater	MR PC99: 0.074 MR PC95: 0.33	VHR PC99: 0.08 VHR PC95: 0.23	LR PC99: 0. 31 LR PC95: 1.1	HR PC99: 3.2 HR PC95: 10
			Marine	MR PC99: 0.10 MR PC95: 0.61	VHR PC99: 0.43 VHR PC95: 0.67	LR PC99: 1.8 LR PC95: 2.5	LR PC99: 28 LR PC95: 63
Australia and New Zealand	1	2000	Freshwater	–	LR (AF) 0.2	LR (AF) 75	MR PC99 = 0.2 MR PC95 = 3.2
			Marine	–	LR (AF) 1.8	= Freshwater value	= Freshwater PC95
Canada	2	1999	Freshwater	–	–	–	(AF) 10
			Marine	–	–	–	–
EU	3, 4	2005	Freshwater	–	MAC: 1.8 AA: 0.2	–	MAC: 4 AA: 1
			Marine		EU Freshwater values		EU freshwater values
Germany	5, 6	2016–ametryn 1993–simazine	Freshwater	AA: 0.5	EU Freshwater values	AA: 0.07	0.1
			Marine	AA: 0.5	EU freshwater values	AA: 0.07	–
Switzerland	7	2016	Freshwater	–	PMAC: 0.25 PAA: 0.07	–	–
China, Japan, Korea, Singapore, South Africa and USA	8, 9, 10, 11, 12 and 13		Freshwater and marine	–	–	–	–

VHR very high reliability, *HR* high reliability, *MR* moderate reliability, *LR* low reliability, *PC99* the concentration that should protect 99% of species, *PC95* the concentration that should protect 95% of species, *AF* derived by an assessment factor method, *MAC* maximum acceptable concentration, *AA* annual average concentration, *PMAC* proposed maximum acceptable concentration, *PAA* proposed annual average concentration

[1] ANZECC and ARMCANZ (2000)

[2] CCME (1999)

[3] EU (2005a)

[4] EU (2005b)

[5] Federal Ministry of Justice and Customer Protection (2016)

[6] IKSR (1993)

[7] EAWAG (2016a, b)

[8] https://www.env.go.jp/en/water/wq/wp.pdf. Accessed 30/11/2016

[9] *Pers. Comm.* Prof. Youn-Joo An, Konkuk University, Republic of Korea

[10] http://www.nea.gov.sg/anti-pollution-radiation-protection/water-pollution-control/recreational-water-quality Accessed 30/11/2016

[11] file:///C:/Users/ac2458/Downloads/AQUATIC%20ecosystems.pdf Accessed 30/11/2016

[12] USEPA (2016)

[13] *Pers. Comm.* Prof. Liu Zhengtao, China Academy of Environmental Sciences

Table 11 Percentage of monitoring samples collected from 15 waterways by the Great Barrier Reef Catchment Loads Monitoring Program[a] between 2011 and 2015 that exceeded the ecotoxicity threshold values (protective concentration values for 99 and 95% of species) derived by the current project. Data presented in descending order of exceedances

Herbicide	% Exceedances of Freshwater PC99 (no. samples[b])	Waterway and long-term mean annual flow (GL[b,c])	% Exceedances of freshwater PC95 (no. samples[b])	Waterway
Ametryn	18.6 (140)	Sandy Creek (170)	6.4 (140)	Sandy Creek
	9.6 (335)	Pioneer River (810)	3.0 (336)	Barratta Creek
	3.9 (336)	Barratta Creek (160)	1.5 (335)	Pioneer River
	0.3 (346)	Tully River (3100)	0.0 (1795)	All others
	0.0 (1449)	All others		
Diuron	82.6 (140)	Sandy Creek (170)	68.6 (140)	Sandy Creek
	63.0 (335)	Pioneer River (810)	54 (243)	Herbert River
	53.4 (148)	Russell River (1200)	48.3 (236)	Barratta Creek
	47.5 (236)	Barratta Creek (160)	43.3 (335)	Pioneer River
	40.5 (346)	Tully River (3100)	22.0 (59)	O'Connell River
	36.8 (136)	Tinana Creek (270)	21.6 (148)	Russell River
	33.9 (59)	O'Connell River (700)	14.7 (136)	Tinana Creek
	17.1 (146)	Mulgrave River (1800)	14.2 (346)	Tully River
	16.9 (243)	Herbert River (3400)	4.1 (146)	Mulgrave River
	5.6 (18)	Theresa Creek (310)	2.3 (44)	Comet River
	3.2 (126)	Burdekin River (9400)	0.8 (126)	Burdekin River
	2.3 (176)	Burnett River (1400)	0.0 (647)	All others
	2.3 (44)	Comet River (910)		
	1.7 (175)	Mary River (1500)		
	0.9 (113)	North Johnstone River (1800)		
	0.0 (165)	All others		
Hexazinone	30.0 (140)	Sandy Creek (170)	12.1 (140)	Sandy Creek
	10.2 (335)	Pioneer River (810)	0 (2466)	All others
	5.1 (59)	O'Connell River (700)		
	0.4 (243)	Herbert River (3400)		
	0.3 (346)	Tully River (3100)		
	0.0 (1205)	All others		
Simazine	1.7 (175)	Mary River (1500)	0.0 (2606)	All waterways
	0.0 (2603)	All others		

[a] Turner et al. 2012, 2013; Wallace et al. 2014, 2015, 2016; Garzon-Garcia et al. 2015

[b] Wallace et al. 2016

[c] GL = 1×10^9 L

of new data but also the fact that in the EU derivation method, the final HC values are divided by an assessment factor while those of Australia and New Zealand are not (Warne et al. 2015).

Comparison of the ecotoxicity thresholds to measured herbicide concentrations

Environmental concentrations of these four herbicides in rivers that discharge to the GBR and in the GBR lagoon were compared to the derived ET values to illustrate the risk these herbicides can pose. Grab samples collected from 15 waterways since 2011, as part of the Great Barrier Reef Catchment Loads Monitoring Program (Turner et al. 2012, 2013; Wallace et al. 2014, 2015; Garzon-Garcia et al. 2015; Wallace et al. 2016), were used for this assessment. Information about the location and characteristics of the sites and upstream catchments can be obtained from the original references. This assessment reveals that more than 50% of the 2606 samples did not contain concentrations of ametryn, hexazinone or simazine that exceeded the PC95 ET values (Table 11), while more than 40% of samples did not exceed the corresponding PC99 ET values. For example, there have been only three exceedances of the simazine freshwater PC99

ET value and no exceedances of the PC95 ET value, only Sandy Creek had exceedances of the hexazinone freshwater PC95 ET value and no waterway had more than 10% of samples exceeding the ametryn PC95 ET value (Table 11). In contrast, there are seven waterways where more than 30% of the samples exceeded the freshwater PC99 ET value for diuron and four waterways where more than 30% of samples exceeded the freshwater PC95 ET value. Exceedances of the diuron ETs pose by far the greatest environmental threat of these four herbicides—with Sandy Creek and the Herbert River both having more than 50% of the samples exceeding the PC95 ET value. Monitoring (using passive samplers replaced monthly) of inshore waters of the GBR lagoon since 2009 has recorded no exceedances of the marine ET values, and only one instance where the marine concentration was equal to the ET—for diuron (Gallen et al. 2016). This is not surprising given the extent of dilution of river waters discharged to the reef.

Limitations of the existing ecotoxicity data

It is preferred to have ecotoxicity data for at least 15 species in order to derive GVs using the SSD approach in Australia and New Zealand but five is the minimum (Warne et al. 2015). There were sufficient chronic IC/EC/LC10 and NOEC type ecotoxicity data to reach the preferred status (ecotoxicity data for ≥ 15 species) for only diuron in fresh and marine water and simazine in freshwater. Diuron in freshwater ecosystems had chronic ecotoxicity data for 26 species, and for 20 marine species when chronic and chronic estimated data were combined. Simazine had ecotoxicity data for 17 freshwater species when chronic and chronic estimated data were combined. For the two other herbicides, ametryn and hexazinone, there is a need for more ecotoxicity data to fresh and marine phototrophic species that have not yet been tested. For the purpose of the current study and to protect the ecosystems in the catchments and lagoon of the GBR, there is a specific need for additional ecotoxicity data on tropical phototrophic species that inhabit these ecosystems—particularly corals, macrophytes (including sea-grasses) and microalgae. While the concentrations in the rivers and creeks that discharge to the GBR are highly variable both spatially and temporarily (e.g. Smith et al. 2012; O'Brien et al. 2016), the concentrations of these herbicides, away from estuaries of the waterways, are fairly uniform throughout the GBR (e.g. Gallen et al. 2016). Therefore, in addition to the above, it is recommended that:

- repeated exposure ecotoxicity tests are conducted to mimic the episodic exposure in rivers and the inshore marine ecosystems; and
- long-term exposure ecotoxicity tests of up to 1 year in duration are conducted using marine organisms.

Only with such data will it be possible to accurately assess the risk posed by pesticides to the ecosystems of the waterways that discharge to the GBR and the ecosystems that compose the GBR.

Conclusions

Ecotoxicity threshold values were derived for ametryn, diuron, hexazinone and simazine to protect freshwater and marine ecosystems using the revised method to derive Australian and New Zealand water quality guideline values for toxicants. The reliability of the ET values ranged from low (hexazinone in freshwater and hexazinone and simazine in marine water) to very high (diuron in freshwater and marine water). The derived ET values to protect 99 and 95% of species in freshwater ecosystems were as follows: 0.07 and 0.33 μg/L, 0.08 and 0.23 μg/L, 0.31 and 1.1 μg/L and 3.2 and 10 μg/L for ametryn, diuron, hexazinone and simazine, respectively. The derived ET values to protect 95 and 99% of species in marine ecosystems were as follows: 0.10 and 0.61 μg/L, 0.43 and 0.67 μg/L, 1.8 and 2.5 μg/L and 28 and 63 μg/L, for ametryn, diuron, hexazinone and simazine, respectively. The PC99 ET values for ametryn and hexazinone were exceeded in up to 30% of samples in a limited number of Queensland waterways that discharge to the GBR, while the PC99 and PC95 ET values for diuron were regularly exceeded (> 40% of samples) in five and four waterways that discharge to the GBR, respectively. Only three exceedances of the PC99 ET value occurred for simazine. In 6 years of monitoring, there have been no exceedances of the marine ET values in the inshore waters of the GBR and only once was a marine ET value equalled. Despite these herbicides being widely used for many decades, there are limited amounts of high-quality ecotoxicity data publically available for hexazinone and to a lesser extent ametryn and there is a general lack of marine ecotoxicity data for all four herbicides, but particularly for simazine. Future research should address this knowledge gap and this would permit the derivation of higher reliability ET values.

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