



Toxicant default guideline values for aquatic ecosystem protection

Metsulfuron-methyl in freshwater

Technical brief



© Commonwealth of Australia 2021

Ownership of intellectual property rights

Unless otherwise noted, copyright (and any other intellectual property rights, if any) in this publication is owned by the Commonwealth of Australia (referred to as the Commonwealth).

Creative Commons licence

All material in this publication is licensed under a Creative Commons Attribution 4.0 Australia Licence, save for content supplied by third parties, photographic images, logos and the Commonwealth Coat of Arms.



Creative Commons Attribution 4.0 Australia Licence is a standard form licence agreement that allows you to copy, distribute, transmit and adapt this publication provided you attribute the work. See the <u>summary of the licence terms</u> or the <u>full licence terms</u>.

Inquiries about the licence and any use of this document should be emailed to copyright@agriculture.gov.au.

Cataloguing data

This publication (and any material sourced from it) should be attributed as: ANZG 2021, *Toxicant default guideline values for aquatic ecosystem protection: Metsulfuron-methyl in freshwater*. Australian and New Zealand Guidelines for Fresh and Marine Water Quality. CC BY 4.0. Australian and New Zealand Governments and Australian state and territory governments, Canberra, ACT, Australia.

This publication is available at <u>waterquality.gov.au/anz-guidelines/guideline-values/default/water-quality-toxicants/toxicants</u>.

Contact

Australian Government Department of Agriculture, Water and the Environment GPO Box 858 Canberra ACT 2601 Switchboard +61 2 6272 3933 or 1800 900 090 Email <u>waterguality@agriculture.gov.au</u>

Disclaimer

The author(s) of this publication, all other entities associated with funding this publication or preparing and compiling this publication, and the publisher of this publication, and their employees and advisers, disclaim all liability, including liability for negligence and for any loss, damage, injury, expense or cost incurred by any person as a result of accessing, using or relying on any of the information or data in this publication to the maximum extent permitted by law.

Acknowledgements

These default guideline values (DGVs) were derived by Olivia C King, Dr Rachael A Smith (Water Quality and Investigations, Environmental Monitoring and Assessment Sciences, Science Delivery, Department of Science, Information Technology and Innovation); Dr Michael St J Warne (School of Earth and Environmental Studies, Queensland University; Queensland Department of Environment and Science); and Gabrielle Dern (Griffith University). The DGVs were peer reviewed by two anonymous reviewers and by two contracted technical advisors, Dr Rick van Dam and Alicia Hogan. The DGVs were also reviewed and approved by jurisdictional technical and policy oversight groups and a National Water Reform Committee, prior to being published.



Contents

Sun	nmary .		iv
1	Introd	uction	1
2	Aquati	ic toxicology	2
	2.1	Mechanism of toxicity	2
	2.2	Toxicity	2
3	Factor	s affecting toxicity	3
4	Defaul	It guideline value derivation	4
	4.1	Toxicity data used in derivation	4
	4.2	Species sensitivity distribution	6
	4.3	Default guideline values	6
	4.4	Reliability classification	7
Glo	ssary		8
•••		A: Toxicity data that passed the screening and quality assessment and were used to default guideline values	10
Ref	erences	1	2

Figures

Figure 1 Structure of metsulfuron-methyl	. 1
Figure 2 Species sensitivity distribution, metsulfuron-methyl in freshwater	. 6

Tables

Table 1 Summary of selected physico-chemical properties of metsulfuron-methyl	1
Table 2 Summary of the single toxicity values, all species used to derive default guideline values for	
metsulfuron-methyl in freshwater	5
Table 3 Toxicant default guideline values, metsulfuron-methyl in freshwater, moderate reliability	7

Appendix tables

Table A 1 Summary, chronic toxicity data that passed the screening and quality assurance processes,	
metsulfuron-methyl in freshwater	

Summary

The default guideline values (DGVs) and associated information in this technical brief should be used in accordance with the detailed guidance provided in the Australian and New Zealand Guidelines for Fresh and Marine Water Quality website (www.waterquality.gov.au/anz-guidelines).

Metsulfuron-methyl (2-(4-methoxy-6-methyl-1,3,5-triazin-2-ylcarbamoylsulfamoyl)benzoate, CAS no. 74223-64-6) is a selective, systemic triazinylsulfonylurea herbicide that sits within the sulfonylurea group of the urea family of herbicides. Other triazinylsulfonylurea herbicides include iodosulfuron, ethametsulfuron, thifensulfuron and their methylated forms. In Australia and New Zealand, metsulfuron-methyl is typically used in agriculture to control broadleaf and other weeds in pastures, cereals, forestry and/or for other non-agricultural purposes (ACVM 2020, APVMA 2020). Metsulfuron-methyl exerts toxicity by binding to and inhibiting the acetolactate synthase (ALS) enzyme, which prevents the biosynthesis of amino acids and stops cell division. Non-agricultural uses of metsulfuron-methyl include weed control in forestry.

The previous Australian and New Zealand DGV for metsulfuron-methyl in freshwater environments was a low reliability value (using the ANZECC/ARMCANZ (2000) reliability scheme) as it was based on acute toxicity data for two freshwater fish species, one invertebrate and one microalga only (ANZECC/ARMCANZ 2000). More data on metsulfuron-methyl toxicity to freshwater species are now available, including data on phototrophic species (species that photosynthesise e.g. plants and algae), resulting in moderate reliability DGVs (Warne et al. 2018).

Due to the small sample size of available heterotrophic ecotoxicity data for metsulfuron-methyl, it was not possible to ascertain distinctions in sensitivity between different groups of species, for example between phototrophic and heterotrophic species. As a result, both phototrophic and heterotrophic species were used to derive the metsulfuron-methyl DGVs, as recommended in Warne et al. (2018). However, based on the mode of action of metsulfuron-methyl, it is expected that phototrophic species would be more sensitive than non-phototrophic species, as metsulfuron-methyl binds to and inhibits the ALS enzyme, which is a protein generally found in plants. Consequently, it is possible that the derived DGVs for metsulfuron-methyl may not provide adequate protection to all phototrophic species. In addition to this, as phototrophs are at the bottom of most aquatic food webs, the derived DGVs may not provide sufficient protection to non-phototrophic species (as a result of potential indirect effects).

The lowest reported chronic toxicity value to freshwater species is 0.054 µg/L (freshwater macrophyte, 8-day NOEC). The lowest reported acute toxicity value to freshwater species is 64.8 µg/L (freshwater microalga, 24-hour EC5).

The DGV derivation for metsulfuron methyl in freshwater incorporated chronic EC10, NOEC and NOEL data for eight freshwater, phototrophic and heterotrophic, species from five phyla and six classes. The (visual) fit of the model to the toxicity data was poor, resulting in moderate reliability DGVs. The DGVs derived here are expressed in terms of the active ingredient (metsulfuron-methyl) rather than commercial formulations. The DGVs for 99, 95, 90 and 80% species protection are 0.0037 μ g/L, 0.018 μ g/L, 0.048 μ g/L and 0.18 μ g/L, respectively. The 95% species protection level for metsulfuron-methyl in freshwater (0.018 μ g/L) is recommended for adoption in the assessment of slightly-to-moderately disturbed ecosystems.

1 Introduction

Metsulfuron-methyl is a herbicide ($C_{14}H_{15}N_5O_6S$; see Figure 1) that at room temperature is a white to pale-yellow solid with a characteristic ester-like odour. It is the active ingredient of a variety of commercial herbicide formulations. Metsulfuron-methyl is often recommended to be mixed with other herbicides (e.g. terbutryn and glyphosate formulations) in tank mixes to increase its efficacy. Physico-chemical properties of metsulfuron-methyl that may affect its environmental fate and toxicity are presented in Table 1.

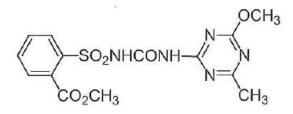


Figure 1 Structure of metsulfuron-methyl

Physico-chemical property	Value
Molecular weight	381.4 amu
Aqueous solubility	548 mg/L (pH 5), 2 790 mg/L (pH 7), 213 000 mg/L (pH 9) @ temperature of 25 °C ¹ 2 790 mg/L @ temperature of 20 °C ²
Logarithm of the octanol-water partition coefficient (log $K_{\mbox{\tiny ow}}$)	-1.87 at pH 7 and temperature of 20 °C ^{a, b}
Logarithm of the organic carbon water partition coefficient (log $\kappa_{\text{oc}})$	1.54 °
Logarithm of the bioconcentration factor (log BCF)	1 °
Half-life (t _{1/2}) in water	22 days at pH 5–9 and temperature of 25 °C ^b
Half-life (t _{1/2}) in soil	Typical: 10–30 days; up to 180 days ^{b, d}

Table 1 Summary of selected physico-chemical properties of metsulfuron-methyl

a BCPC (2012).

b Pesticide Properties Database (University of Hertfordshire 2013).

c Barcelö and Hennion (2003).

d Cornell University (1993).

Metsulfuron-methyl belongs to the triazinylsulfonylurea group that sits within the sulfonylurea group of the urea family of herbicides, which also includes iodosulfuron, ethametsulfuron, thifensulfuron and their methylated forms. It is a systemic herbicide and can be applied before and/or after weeds emerge (i.e. it is a pre-emergent and post-emergent herbicide). In Australia, metsulfuron-methyl has been approved for brush and broadleaf weed control on a range of crops including cereals (e.g. wheat, barley, canola, rye, triticale), linseed, chickpeas, mung beans and pastures, and also in other activities such as forestry, commercial and industrial areas, and for *Mimosa pigra* control on floodplains (APVMA 2020). In New Zealand, it is approved for weed control on pastures, and in forestry (radiata pine) and non-cropland areas (ACVM 2020).

Metsulfuron-methyl is a selective residual herbicide, and it retains its biological effectiveness in soil, with a half-life ranging from days to months (Cornell University 1993, University of Hertfordshire 2013) and recommended exclusion times for some crops of up to 22 months (Cornell University 1993). The higher the soil moisture content and temperature and the lower the acidity, the more rapidly metsulfuron-methyl is degraded in soil (Smith 1986).

Metsulfuron-methyl has a low affinity for binding to soil particles (Table 1); therefore, it has a high capacity to leach to groundwater and end up in surface waters. The aqueous hydrolysis of metsulfuron-methyl is relatively fast, with a half-life of 22 days at pH 5–9 and a temperature of 25 °C (University of Hertfordshire 2013) (Table 1).

2 Aquatic toxicology

2.1 Mechanism of toxicity

Metsulfuron-methyl is mainly absorbed through the roots and foliage of plants and is transported to the leaves and shoots where it exerts its toxicity. Metsulfuron-methyl binds to, and inhibits, the acetolactate synthase (ALS) enzyme, which is responsible for catalysing the formation of amino acids. As a result, the biosynthesis of amino acid branches within sensitive plants is inhibited (FAO UN 2015). Exposed plants typically die within two to four weeks due to cessation of cell division and growth processes.

2.2 Toxicity

2.2.1 Freshwater chronic toxicity data

There were freshwater chronic toxicity data for one fish, 12 macrophytes and six microalgae.

The toxicity values for the single fish species were:

• 90-day NOEL and LOEC values of 4 500 μg/Land 8 000 μg/L.

The toxicity values for macrophytes consisted of:

- a 6-day EC50 (dry weight) value of 11.95 μ g/L
- 7-day EC10 (frond count and frond area) values ranging from 0.11 μg/L to 1.45 μg/L
- 7-day EC50 (frond number and frond area) values ranging from 0.06 μg/L to 12.7 μg/L
- 8-day NOEC (dry weight, shoot length and root growth) values ranging from 0.054 $\mu g/L$ to 20 $\mu g/L$
- 8-day LOEC (shoot length) values ranging from 0.1 μ g/L to 1 μ g/L
- a 9-day EC50 (dry weight) value of 6.18 μg/L
- an 11-day EC50 (frond number) value of 0.68 μg/L
- a 12-day EC50 (dry weight) value of 2.61 μg/L
- 14-day NOEC/NOEL (root occurrence, dry weight, frond number and frond area) values ranging from 0.16 μg/L to 20 μg/L
- 14-day LOEC (chlorophyll-a content and root occurrence) values ranging from 1 μg/L to 2.7 μg/L

- 14-day EC50 (leaf area, fresh weight: dry weight, frond number, frond area, chlorophyll-a content and total shoot length) values ranging from 0.1 μg/L to 26.7 μg/L
- a 15-day EC50 (dry weight) value of 2.43 μg/L
- 42-day NOEC, LOEC and EC50 (frond count) values of 0.1 μg/L, 0.5 μg/L and 0.99 μg/L, respectively.

The toxicity values for microalgae were:

- a 48-hour EC10 (chlorophyll-a content) value of 292 μg/L
- two 48-hour EC50 (chlorophyll-a content) values of 677 μg/L and 1 934 μg/L
- a 72-hour IC50 (cell density) value of 612 μg/L
- two 96-hour NOEL (biomass yield, growth rate and area under the growth curve) values of 14.5 μ g/L and 92 800 μ g/L
- 96-hour EC50 (cell density, biomass, growth rate and area under the growth curve) values ranging from 130 μg/L to 72 782 μg/L
- two 5-day NOEL (biomass, growth rate and area under the curve) values of 10 $\mu g/L$ and 95.4 $\mu g/L$
- a 5-day EC50 (biomass, growth rate and area under the curve) value of 286 μg/L
- 6-day EC20 and EC50 (chlorophyll-a content) values of 68.6 μg/L and 1 564 μg/L, respectively.

2.2.2 Freshwater acute toxicity data

There were freshwater acute toxicity data for one microalga and one macrophyte.

The toxicity values for the single microalga species were:

24-hour NOEC, EC5 and EC50 (cell density) values of 165.1 μg/L, 64.8 μg/L and 1 163 μg/L, respectively.

The toxicity values for the single macrophyte species were:

• 96-hour LOEC and EC50 (frond count) values of 0.2 μg/L and 0.4 μg/L, respectively.

As stated in Warne et al. (2018), acute EC10/NOEC and LOEC values should not be converted to chronic EC10/NOEC values, and these have not been used to derive DGVs.

3 Factors affecting toxicity

No factors have been reported as modifying the toxicity of metsulfuron-methyl. As with many organic chemicals, it might be expected that dissolved and particulate organic matter and suspended solids would affect its bioavailability and toxicity. Kah and Brown (2007) found that sorption to soil was negatively correlated to soil pH and positively correlated to soil organic carbon, such that relatively strong sorption was measured in soils with low pH and high organic carbon content. However, overall, sorption of metsulfuron-methyl to soil was still relatively weak compared to many other pesticides (Kah and Brown 2007), which is supported by its low organic carbon water partition coefficient (log K_{oc}) (Table 1).

4 Default guideline value derivation

The DGVs were derived in accordance with the method described in Warne et al. (2018) and using Burrlioz 2.0 software. Although some decisions on data selection/manipulation may reflect the Warne et al. (2015) method rather than the Warne et al. (2018) method, these were found to have no material effect on the final DGVs.

4.1 Toxicity data used in derivation

The previous Australian and New Zealand Guidelines for Fresh and Marine Water Quality (ANZECC/ARMCANZ 2000) included an environmental concern level (ECL) for metsulfuron-methyl in freshwater environments. This ECL had a low reliability based on the ANZECC/ARMCANZ (2000) reliability scheme as it was based on unscreened acute toxicity data for only two freshwater fish, one invertebrate and one microalga (ANZECC/ARMCANZ 2000).

To obtain toxicity data for metsulfuron-methyl for freshwater organisms, an extensive search of the scientific literature was conducted. In addition, the ECOTOXicology Database System (USEPA 2015a), Office of Pesticide Programs Database (USEPA 2015b), the Australasian Ecotoxicology Database (Warne et al. 1998) and the ANZECC/ARMCANZ (2000) toxicant database (Sunderam et al. 2000) were searched. There are now considerably more metsulfuron-methyl toxicity data available to enable the calculation of DGVs for freshwater (Appendix A: Toxicity data that passed the screening and quality assessment and were used to derive the default guideline values). However, as there are still insufficient chronic no or low effect toxicity data to meet the preferred dataset size (i.e. toxicity data for at least 15 species that belong to at least four taxonomic groups), it is recommended that additional chronic toxicity tests of metsulfuron-methyl with phototrophic (e.g. plants and algae) freshwater species be conducted.

In total, there were freshwater toxicity data for 20 species (five phyla and seven classes) that passed the screening and quality assessment processes. The represented phyla were Bacillariophyta, Chlorophyta, Chordata, Cyanobacteria and Tracheophyta. The seven classes were Actinopterygii (which accounts for approximately 99% of fish), Bacillariophyceae (diatoms; a major grouping of algae), Chlorophyceae (a major grouping of freshwater green algae), Cyanophyceae (a class of cyanobacteria), Liliopsida (monocots), Magnoliopsida (dicots) and Trebouxiophyceae (another grouping of green algae). Chronic toxicity data were available for 19 of the 20 species, comprising 18 phototrophs and one heterotroph, while only acute toxicity data were available for one species— a phototroph.

Based on the current understanding of the mode of action of metsulfuron-methyl, an ALS-inhibiting herbicide, it is expected that phototrophic species would be more sensitive than non-phototrophic species. However, due to the small sample size of heterotrophic species, it was not possible to discern differences in sensitivity between different groups of species, for example between phototrophic and heterotrophic species. Therefore, both phototrophic and heterotrophic species were used to derive the metsulfuron-methyl DGVs, as recommended in Warne et al. (2018).

From the dataset of toxicity values for 20 species, there were freshwater chronic no or low effect (i.e. EC10, NOEC, NOEL, LOEC) data for eight species (seven phototrophic and one heterotrophic) that

belonged to five phyla. This met the minimum data requirements necessary to use a species sensitivity distribution (SSD) to derive DGVs. However, the fit of the SSD to the data was poor and, combined with the number and type of toxicity data, this resulted in the DGVs having moderate reliability. In an attempt to improve the reliability of the DGVs, chronic EC50 type data (for the remaining 12 species; converted to no or low effect estimates by dividing by 5, as per Warne et al. 2018) were added to the dataset. However, the resulting SSD fitted this dataset worse than the SSD for the chronic no or low effect dataset, particularly for the more sensitive species. Therefore, the DGVs for metsulfuron-methyl were derived using only the chronic no or low effect data.

To identify species that were regionally relevant to Australia and New Zealand ecosystems, a search of AlgaeBase (Guiry & Guiry 2017), Atlas of Living Australia (ALA 2017), Catalogue of Life (Roskov et al. 2017), Integrated Taxonomic Information System (ITIS 2017) and the World Register of Marine Species (WoRMS 2017) was conducted. The dataset used in the DGV derivation process for metsulfuron-methyl in freshwater includes toxicity data for four freshwater species that either originated from or are distributed within Australia and/or New Zealand.

A summary of the toxicity data used to calculate the DGVs for metsulfuron-methyl in freshwater is provided in Table 2. A summary of the acceptable quality raw toxicity data for all freshwater species that passed the screening and quality assurance processes is provided in Section 2.2 and Section 2.2.2. Further details on the data that passed the quality assessment and screening process and were used to derive the DGVs are presented in Appendix A: Toxicity data that passed the screening and quality assessment and were used to derive the default guideline values, Table A 1. Details of the <u>data quality assessment</u> and the <u>data that passed the quality assessment</u> are provided as supporting information.

Taxonomic group (Phylum)	Species	Life stage	Duration (d)	Type (acute/ chronic)	Toxicity endpoint	Final toxicity value (µg/L)
Blue–green alga (Cyanobacteria)	Anabaena flosaquae	Not stated	5	Chronic NOEL	Biomass yield, growth rate, AUC ª	95.4
Macrophyte (Tracheophyta)	Elodea canadensis b	Apical shoot (19.5 cm)	8	Chronic NOEC	Shoot length	0.054
Macrophyte (Tracheophyta)	Lemna gibba	Not stated	7	Chronic EC10	Frond count	0.193 ^c
Macrophyte Lemna minor b (Tracheophyta)		Exponential growth phase	42	Chronic NOEC	Frond count	0.1
Macrophyte (Tracheophyta)	Myriophyllum spicatum	Apical shoot	14	Chronic LOEC	Root occurrence	0.4 ^d
Diatom (Bacillariophyta)	Navicula pelliculosa Þ	Not stated	4	Chronic NOEL	Biomass yield, growth rate, AUC ^a	92 800
Fish (Chordata)	Oncorhynchus mykiss ^b	Early life	90	Chronic NOEL	Mortality	4 500
Green alga (Chlorophyta)	Pseudokirchneriella subcapitata ^e	Not stated	5	Chronic NOEL	Biomass yield, growth rate, AUC ^a	10

Table 2 Summary of the single toxicity values, all species used to derive default guideline values for metsulfuron-methyl in freshwater

a AUC = area under the growth curve.

b Species that originated from, or whose geographic distributions include, Australia and/or New Zealand.

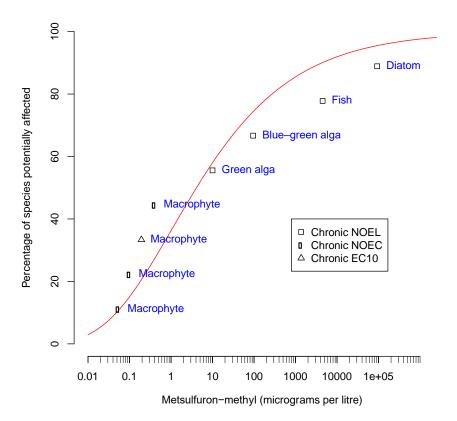
c Represents a geometric mean of four toxicity values.

d Converted to an estimated chronic NOEC/EC10 by dividing by 2.5 (Warne et al. 2018).

e This species has also been called Raphidocelis subcapitata and Selenastrum capricornutum.

4.2 Species sensitivity distribution

The cumulative frequency (species sensitivity) distribution (SSD) of the eight freshwater phototrophic and heterotrophic species that was used to derive the DGVs is presented in Figure 2. The SSD was plotted using the Burrlioz 2.0 software, and the model was judged to provide a poor fit to the data.





4.3 Default guideline values

It is important that the DGVs (Table 3) and associated information in this technical brief are used in accordance with the detailed guidance provided in the Australian and New Zealand Guidelines for Fresh and Marine Water Quality <u>website</u>. As with other pesticides that have DGVs, the DGVs for metsulfuron-methyl are expressed in terms of the concentration of the active ingredient.

The derived Australian and New Zealand DGVs for metsulfuron-methyl in freshwater are provided in Table 3. The 99% and 95% species protection DGVs may be below routine limits of reporting for most commercial laboratories, although some laboratories may be able to achieve lower limits of reporting. ANZG (2018; see <u>Accounting for local conditions</u>) provides guidance on what to do if DGVs are below analytical detection limits. By including phototrophic and heterotrophic species in the dataset used to derive DGVs for metsulfuron-methyl, which is expected to be more toxic to phototrophs, it is possible that the DGVs may not provide adequate protection to all phototrophic species. Additionally, as phototrophs are at the bottom of most aquatic food webs, the DGVs also may not provide sufficient protection to non-phototrophic species, as a result of potential indirect effects.

Measured log BCF values for metsulfuron-methyl are low (Table 1) and are below the threshold at which secondary poisoning must be considered (i.e. threshold log BCF = 4, Warne et al. 2018). Therefore, the DGVs for metsulfuron-methyl do not need to account for secondary poisoning.

Table 3 Toxicant default guideline values, metsulfuron-methyl in freshwater, moderate reliability

Level of species protection (%)	DGV for metsulfuron-methyl in freshwater (µg/L) $^{\rm a}$			
99	0.0037			
95	0.018			
90	0.048			
80	0.18			

a DGVs were derived using the Burrlioz 2.0 software and rounded to two significant figures.

4.4 Reliability classification

The metsulfuron-methyl in freshwater DGVs have a moderate reliability classification (Warne et al. 2018) based on the outcomes for the following three criteria:

- Sample size—8 (good)
- Type of toxicity data—chronic EC10, NOEC, LOEC
- SSD model fit—poor (Inverse Weibull model).

Glossary

Term	Definition
acute toxicity	A lethal or adverse sub-lethal effect that occurs as the result of a short exposure period to a chemical relative to the organism's life span.
ANZECC	Australian and New Zealand Environment and Conservation Council
ARMCANZ	Agricultural and Resource Management Council of Australia and New Zealand
CAS no. (Chemical Abstracts Service number)	Each chemical has a unique identifying number that is allocated to it by the American Chemical Society.
chronic toxicity	A lethal or sublethal adverse effect that occurs after exposure to a chemical for a period of time that is a substantial portion of the organism's life span or an adverse effect on a sensitive early life stage.
default guideline value (DGV)	A guideline value recommended for generic application in the absence of a more specific guideline value (e.g. site-specific guideline value), in the Australian and New Zealand Guidelines for Fresh and Marine Water Quality. Formerly known as 'trigger values'.
EC50 (median effective concentration)	The concentration of a substance in water or sediment that is estimated to produce a 50% change in the response being measured or a certain effect in 50% of the test organisms relative to the control response, under specified conditions.
ECx	The concentration of a substance in water or sediment that is estimated to produce an x% change in the response being measured or a certain effect in x% of the test organisms, under specified conditions.
endpoint	The specific response of an organism that is measured in a toxicity test (e.g. mortality, growth, a particular biomarker).
environmental fate	The behaviour (e.g. movement, transformation, degradation, partitioning) of a chemical in the environment.
guideline value (GV)	A measurable quantity (e.g. concentration) or condition of an indicator for a specific community value below which (or above which, in the case of stressors such as pH, dissolved oxygen and many biodiversity responses) there is considered to be a low risk of unacceptable effects occurring to that community value. Guideline values for more than one indicator should be used simultaneously in a multiple lines of evidence approach. (Also refer to 'default guideline value' and 'site-specific guideline value'.)
ICx	The concentration of a substance in water or sediment that is estimated to produce an x% inhibition in the response being measured relative to the control response, under specified conditions.
LC50 (median lethal concentration)	The concentration of a substance in water or sediment that is estimated to be lethal to 50% of a group of test organisms, relative to the control response, under specified conditions.
lowest observed effect concentration (LOEC)	The lowest concentration of a material used in a toxicity test that has a statistically significant adverse effect on the exposed population of test organisms as compared to the controls.
Macrophyte	A member of the macroscopic plant life of an area, especially of a body of water; large aquatic plant.
no observed effect concentration (NOEC) or	The highest concentration of a material used in a toxicity test that has no statistically significant adverse effect on the exposed population of test organisms as compared with the controls.
no observed effect level (NOEL)	
phototrophs	Organisms that photosynthesize as their main means of obtaining energy e.g. plants and algae.

Toxicant default guideline values for aquatic ecosystem protection: Metsulfuron-methyl in freshwater

Term	Definition
site-specific guideline value	A guideline value that is relevant to the specific location or conditions that are the focus of a given assessment or issue.
Species (biological)	A group of organisms that resemble each other to a greater degree than members of other groups and that form a reproductively isolated group that will not produce viable offspring if bred with members of another group.
species sensitivity distribution (SSD)	A method that plots the cumulative frequency of species' sensitivities to a toxicant and fits a statistical distribution to the data. From the distribution, the concentration that should theoretically protect a selected percentage of species can be determined.
toxicity	The inherent potential or capacity of a material to cause adverse effects in a living organism.
toxicity test	The means by which the toxicity of a chemical or other test material is determined. A toxicity test is used to measure the degree of response produced by exposure to a specific level of stimulus (or concentration of chemical) for a specified test period.

Appendix A: Toxicity data that passed the screening and quality assessment and were used to derive the default guideline values

Table A 1 Summary, chronic toxicity data that passed the screening and quality assurance processes, metsulfuron-methyl in freshwater

Taxonomic group (Phylum)	Species	Life stage	Exposure duration (d)	Toxicity measure (test endpoint)	Test medium	Temperature (°C)	рН	Concentration (µg/L)	Reference					
Diatom	Navicula	Not stated	4	NOEL	ASTM Type I	24 ± 2	7.5 ± 0.1	92 800	USEPA (2015b)					
(Bacillariophyta)	pelliculosa			(Biomass, growth rate, AUC ^b)	water									
-								92 800	VALUE USED IN SSD					
Green alga	Selenastrum	Not stated	5	NOEL	ASTM Type I	24 ± 2	7.5 ± 0.1	10	USEPA (2015b)					
(Chlorophyta)	capricornutum ª	pricornutum ª		(Biomass, growth rate, AUC ^b)	water									
-								10	VALUE USED IN SSD					
Fish	Oncorhynchus	Early life	90	NOEL	Dilution water	12 ± 2	Not stated	4 500	USEPA (2015b)					
(Chordata)	mykiss	mykiss	mykiss	mykiss	mykiss	mykiss			(Mortality)					
-								4 500	VALUE USED IN SSD					
Blue–green alga	Anabaena	Not stated	5	NOEL	ASTM Type I	24 ± 2	7.5 ± 0.1	95.4	USEPA (2015b)					
(Cyanobacteria)	flosaquae			(Biomass, growth rate, AUC ^b)	water									
-								95.4	VALUE USED IN SSD					

Taxonomic group (Phylum)	Species	Life stage	Exposure duration (d)	Toxicity measure (test endpoint)	Test medium	Temperature (°C)	рН	Concentration (µg/L)	Reference
Macrophyte	Elodea	Apical shoot	8	NOEC	Filtered	22 ± 2	Not stated	0.054	Wendt-Rasch et al.
(Tracheophyta)	canadensis	(19.5 cm)		(Shoot length)	freshwater				(2003)
-								0.054	VALUE USED IN SSD
Macrophyte	Lemna gibba	Not stated	7	EC10	20 × AAP	24 ± 2	7.5	0.27	Rosenkrantz et al.
(Tracheophyta)				(Frond count)	medium				(2013)
		Not stated	7	EC10	20 × AAP	24 ± 2	7.5	0.16	Rosenkrantz et al.
				(Frond count)	medium				(2013)
		Not stated	7	EC10	20 × AAP	24 ± 2	6.0	0.12	Rosenkrantz et al.
				(Frond count)	medium				(2013)
		Not stated	7	EC10	20 × AAP	24 ± 2	9.0	0.27	Rosenkrantz et al.
				(Frond count)	medium				(2013)
-								0.193	VALUE USED IN SSD
									(GEOMETRIC MEAN)
Macrophyte	Lemna minor	Exponential	42	NOEC	Swedish	20 ± 1	6.5 ± 0.2	0.1	Boxall et al. (2013)
(Tracheophyta)		growth phase		(Frond count)	standard (SIS)				
-								0.1	VALUE USED IN SSD
Macrophyte	Myriophyllum	Apical shoot	14	LOEC	Filtered	22 ± 2	Not stated	1.0	Wendt-Rasch et al.
(Tracheophyta)	spicatum			(Root occurrence)	freshwater				(2003)
-								0.4 ^c	VALUE USED IN SSD

a This species has been called *Raphidocelis subcapitata*, *Pseudokirchneriella subcapitata* and *Selenastrum capricornutum*.

b AUC = area under the growth curve.

c LOEC converted to an estimated chronic NOEC/EC10 by dividing by 2.5 (Warne et al. 2018).

References

ACVM 2020. <u>Agricultural Compounds and Veterinary Medicines (ACVM) register</u>. Minister for Primary Industries New Zealand.

ALA 2017. <u>Atlas of Living Australia</u>. Developed by the National Research Infrastructure for Australia (NCRIS) and the Commonwealth Scientific and Industrial Research Organisation (CSIRO). Accessed May 2017.

ANZECC/ARMCANZ 2000. Australian and New Zealand Guidelines for Fresh and Marine Water Quality/Aquatic Ecosystems: Rationale and background information (Chapter 8), Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand, Canberra, Australia, 678 pp.

ANZG 2018. <u>Australian and New Zealand Guidelines for Fresh and Marine Water Quality</u>. Australian and New Zealand Governments and Australian state and territory governments, Canberra, ACT, Australia.

APVMA 2020. <u>Public Chemical Registration Information System Search</u>. Australian Pesticide and Veterinary Medicine Authority.

Barcelö, D & Hennion MC 2003. Pesticides and their degradation products: Characteristics, usage and environmental behaviour. In: Trace determination of pesticides and their degradation products in water. Techniques and Instrumentation in Analytical Chemistry. *Elsevier Science*, 19, 1–89.

BCPC 2012. A world compendium. The Pesticide Manual. Sixteenth Edition. C MacBean (ed). British Crop Production Council, Alton, United Kingdom, 782–783 pp.

Boxall, AB, Fogg, LA, Ashauer, R, Bowles, T, Sinclair CJ, Colyer, A & Brain RA 2013. Effects of repeated pulsed herbicide exposures on the growth of aquatic macrophytes. *Environmental Toxicology and Chemistry*, 32, 193–200.

Cornell University 1993. <u>EXTOXNET (Extension Toxicology Network): Metsulfuon-methyl</u>. Developed by the Pesticide Management Education Program (PMEP), Cornell University. Accessed 9 November 2015.

FAO UN 2015. <u>FAO Specifications and evaluations for plant protection products: Metsulfuron-methyl,</u> <u>methyl 2-(4-methoxy-6-methyl-1,3,5-triazin-2-ylcarbamoylsulfamoyl)benzoate</u>. Food and Agriculture Organisation of the United Nations, Rome, Italy. Accessed 12 September 2015.

Guiry, MD & Guiry, GM 2017. <u>AlgaeBase</u>. World-wide electronic publication, National University of Ireland, Galway. Accessed May 2017.

ITIS 2017. Integrated Taxonomic Information System. Accessed May 2017.

Kah, M & Brown, CD 2007. Behaviour of ionisable pesticides in soils. Earth Sciences. The University of York.

Rosenkrantz, RT, Cedergreen, N, Baun, A & Kusk, KO 2013. Influence of pH, light cycle, and temperature on ecotoxicity of four sulfonylurea herbicides towards *Lemna gibba*. *Ecotoxicology*, 22, 33–41.

Roskov, Y, Abucay, L, Orrell, T, Nicolson, D, Bailly, N, Kirk, PM, Bourgoin, T, DeWalt, RE, Decock, W, De Wever, A, Nieukerken, E, Zarucchi, J, Penev, L (eds) 2017. <u>Species 2000 & ITIS Catalogue of Life, 30th April 2017</u>. Species 2000: Naturalis, Leiden, the Netherlands. ISSN 2405-8858. Accessed May 2017.

Smith, AE 1986. Persistence of the herbicides [14c] chlorsulfuron and [14C] metsulfuron-methyl in prairie soils under laboratory conditions. *Bulletin of Environmental Contamination and Toxicology*, 37, 698–704.

Sunderam, RIM, Warne, MStJ, Chapman, JC, Pablo, F, Hawkins, J, Rose, RM & Patra, RW 2000. The ANZECC and ARMCANZ Water Quality Guideline Database for Toxicants. Supplied as part of a CD-ROM in the ANZECC/ARMCANZ (2000) Australian and New Zealand Guidelines for Fresh and Marine Water Quality.

University of Hertfordshire 2013. <u>The Pesticide Properties Data Base (PPDB)</u>. Developed by the Agriculture & Environment Research Unit (AERU), University of Hertfordshire, 2006–2013. Accessed 13 May 2016.

USEPA 2015a. <u>ECOTOX User Guide: ECOTOXicology Database System</u>. Version 4.0. United States Environmental Protection Agency. Accessed May–September 2015.

USEPA 2015b. <u>Office of Pesticide Programs Database</u>. United States Environmental Protection Agency, Office of Prevention, Pesticides, and Toxic Substances. Office of Pesticide Programs. Washington, D.C. January 23, 2004. Accessed February–April 2016.

Warne MStJ, Batley GE, van Dam RA, Chapman JC, Fox DR, Hickey CW & Stauber JL 2015. Revised Method for Deriving Australian and New Zealand Water Quality Guideline Values for Toxicants – update of 2014 version. Prepared for the revision of the Australian and New Zealand Guidelines for Fresh and Marine Water Quality, Department of Science, Information Technology and Innovation, Brisbane, Queensland, 49 pp.

Warne MStJ, Batley GE, van Dam RA, Chapman JC, Fox DR, Hickey CW & Stauber JL 2018. Revised Method for Deriving Australian and New Zealand Water Quality Guideline Values for Toxicants – update of 2015 version. Prepared for the revision of the Australian and New Zealand Guidelines for Fresh and Marine Water Quality. Australian and New Zealand Governments and Australian state and territory governments, Canberra, 48 pp.

Warne, MStJ, Westbury, A-M & Sunderam, R 1998. A compilation of toxicity data for chemicals to Australasian aquatic species. Part 1: Pesticides. *Australasian Journal of Ecotoxicology*, 4, 93–144.

Wendt-Rasch, L, Pirzadeh, P & Woin, P 2003. Effects of metsulfuron methyl and cypermethrin exposure on freshwater model ecosystems. *Aquatic Toxicology*, 63, 243–256.

WoRMS Editorial Board 2017. <u>World Register of Marine Species</u>. VLIZ. doi:10.14284/170. Accessed May 2017.