# Toxicant default guideline values for aquatic ecosystem protection

Agenda item 16

Attachment D

Sulfometuron-methyl in freshwater

Technical brief

August 2024

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## Summary

Sulfometuron-methyl (C15H16N4O5S) is a non-selective herbicide that provides broad-spectrum pre-emergence and post-emergence control of annual and perennial grasses and broad-leaf weeds in the forestry industry, as well as in commercial/industrial settings and transport corridors (e.g., road and railway verges) (APVMA n.d.). Sulfometuron-methyl is a sulfonylurea (SU) herbicide that inhibits the activity of the enzyme acetolactate synthase (ALS), which is required for cell growth in plants, fungi and bacteria (ATSE 2002; BLM and ENSR 2005; Chipman et al. 2005; US EPA 2008; US EPA 2012; US EPA 2015a, 2015b) but is absent in higher organisms (BLM and ENSR 2005; Zhou et al. 2007; US EPA 2012). Relatively low concentrations of sulfometuron-methyl affect target organisms, as evidenced by the generally low range of labelled application rates (BLM and ENSR 2005).

Sulfometuron-methyl is a weak acid with a pKa (acid dissociation constant; see ‘Glossary and acronyms’ for definitions) of 5.2 (Harvey et al. 1985; NCBI n.d.). This pH effect alters the solubility of sulfometuron-methyl, its partition coefficients, its rate of hydrolysis, and, consequently, its behaviour in soil and water (Harvey et al. 1985). Sulfometuron-methyl is more soluble, stable (resistant to hydrolysis) and mobile in neutral or alkaline water (BLM and ENSR 2005). Sulfometuron-methyl has a low potential to bioaccumulate, although reported log *K*ow values vary, depending on pH (BLM and ENSR 2005; Harvey et al. 1985; US EPA 2008).

Sulfometuron-methyl has low acute toxicity to fish and aquatic invertebrates. It is toxic to aquatic plants (BLM and ENSR 2005), which is to be expected given it is used as a herbicide. Aquatic macrophytes are generally more sensitive than aquatic algae (APVMA n.d.; US EPA 2012).

Overall, acceptable toxicity data for sulfometuron-methyl were available for only 6 species from 6 taxonomic groups – 4 phototroph species (a macrophyte, green alga, diatom and cyanobacterium) and 2 animal species (a crustacean and an amphibian). The herbicide likely exhibits a bimodal toxicity relationship, with plants, algae and bacteria being more sensitive than higher organisms that lack the ALS enzyme. This is due to the highly specific mechanism of sulfometuron-methyl toxicity and the nature of the acceptable toxicity data. The final acceptable dataset of 4 phototroph species (from 4 taxonomic groups) was insufficient to use the species sensitivity distribution (SSD) method for deriving default guideline values (DGVs). Consequently, a DGV for sulfometuron-methyl of 0.02 µg/L was derived using the assessment factor (AF) method, by dividing the lowest-acceptable-effect concentration (*Lemna gibba* 5-day no-observed-effect concentration [NOEC] of 0.207 µg/L for growth) by an AF of 10. A DGV derived using this approach is classed as having ‘unknown’ reliability. The DGV is below current routine analytical limits of reporting for sulfometuron-methyl, although lower limits of reporting may be achievable.

## Introduction

Sulfometuron-methyl (C15H16N4O5S, CASRN 74222-97-2, IUPAC name: methyl 2-{[(4,6-dimethylpyrimidin-2-yl)carbamoyl}sulfamoyl]benzoate) is a non-selective SU herbicide that provides broad-spectrum pre-emergence and post-emergence control of annual and perennial grasses and broad-leaf weeds. It is registered for use in Australia for various forestry and commercial and industrial applications (e.g. around agricultural buildings) and transport corridors (e.g. road and railway verges) (APVMA n.d.). It is registered for use in many herbicide products, either alone or in combination with other active ingredients, and is formulated as a dry flowable product or as water-dispersible granules (APVMA n.d.). Sulfometuron-methyl was introduced in the Australian forestry industry in the late 1980s to control brush weeds (FWPRDC 2006) and was being used for second-season weed control and in some pre-planting mixtures for forestry operations by the 1990s (FWPRDC 2006). Sulfometuron-methyl may be applied using ground (boom, handgun or back-pack) or aerial methods (APVMA n.d.; US EPA 2012). Herbicidal action requires adequate soil moisture. Although sulfometuron-methyl is listed on the New Zealand Inventory of Chemicals, there were no products in New Zealand that contained this herbicide at the time of publication of this technical brief (L. Harjadinata, New Zealand Environmental Protection Authority, pers comm, January 2020).

Sulfometuron-methyl is a solid that is colourless to white and has a molecular weight of 364.38 g/mol (BLM and ENSR 2005). The SU moiety of sulfometuron-methyl serves as a ‘bridge’ between an amino-pyrimidine and an esterified benzoic acid ring structure (HRAC 2015; SERA 2004; US EPA 2012), as shown in Figure 1. Several SU herbicides share similar amino-pyrimidine and esterified benzoic acid moieties.

![The chemical structure of sulfometuron-methyl is a benzoate ester that is the methyl ester of 2-{[(4,6-dimethylpyrimidin-2-yl)carbamoyl]sulfamoyl}benzoic acid.]()

Figure 1 Structure of sulfometuron-methyl

Reported solubilities are 6.42–10 mg/L at pH 5, 244–300 mg/L at pH 7 and 12,500 mg/L at pH 8.6 (Harvey et al. 1985; NCBI n.d.; US EPA 2008; US EPA 2012; US EPA 2015b). In general, the pH of soil and water significantly affects the degradation rate and mobility of sulfometuron-methyl in the environment (US EPA 2012).

Sulfometuron-methyl has a low potential to volatilise from soil or water, with a reported vapour pressure of 5.4 × 10-16 mm Hg and a low Henry’s Law constant of 5.17 × 10-14 atm.m3/mol (BLM and ENSR 2005; NCBI n.d.; SERA 2004; US EPA 2008). In soils, sulfometuron-methyl is broken down by microorganisms through hydrolysis and photolysis (BLM and ENSR 2005; Michael 2003), although breakdown is slower under conditions of low moisture, low organic content and alkaline pH (Lym and Swenson 1991). Biodegradation half-lives in soil range from 5 to 65 days, although are more commonly reported to be between 12 and 28 days (ATSE 2002; BLM and ENSR 2005; Kamrin 1997; Michael 2003; NCBI n.d.). A photodegradation half-life of 22.5 days has also been reported (BLM and ENSR 2005). Sulfometuron-methyl may persist longer in groundwater than in surface water and soil due to these lower rates of biodegradation and photolysis.

Sulfometuron-methyl does not sorb strongly to soils (measured *K*oc values < 100 L/kg) (Harvey et al. 1985; US EPA 2012; US EPA 2015b). It is mobile, with the potential to leach to groundwater, especially in sandy coastal plain soils (Hubbard et al. 1989). It can reach surface water during runoff events (BLM and ENSR 2005). However, *K*oc values for sulfometuron-methyl are correlated with the amount of organic matter present and pH, with the mobility of sulfometuron-methyl expected to increase with increasing pH (Harvey et al. 1985; US EPA 2008).

Sulfometuron-methyl is moderately persistent in soil, with degradation half-lives from weeks to several months in various laboratory and field studies (Harvey et al. 1985; Kamrin 1997; US EPA 2008; US EPA 2015b). Soil pH, moisture, temperature and microflora influence the persistence of sulfometuron-methyl (Lym and Swenson 1991).

In water, sulfometuron-methyl is not expected to adsorb to suspended soils and sediment, based on the estimated *K*oc. Sulfometuron-methyl is stable in water at pH 7 or 9 (hydrolysis half-life of > 30 days (BLM and ENSR 2005; Harvey et al. 1985) but hydrolyses readily (with a half-life of approximately 2 weeks) at pH 5 to methyl-2-(aminosulfonyl)benzoate and 1,2-benzisothiazol-3-one, 2,3-dihydro-1,1-dioxide (saccharin), sulphonamide and pyrimidine amine (BLM and ENSR 2005; Harvey et al. 1985; Lym and Swenson 1991; NCBI n.d.; US EPA 2012). Photolytic half-lives in water of 1 to 3 days have been reported (Harvey et al. 1985; Lym and Swenson 1991).

The major degradates of sulfometuron-methyl form by cleavage of the sulfonylurea bridge between the ring structures. Five major degradates have been identified: saccharin, pyrimidine amine, pyrimidine-ol, sulphonamide and free acid sulphonamide (US EPA 2012). Based on an assessment of chemical structure, it is unlikely that these major degradates would contribute significantly to the toxicity of sulfometuron-methyl (US EPA 2012).

Sulfometuron-methyl has a low potential to bioaccumulate (BLM and ENSR 2005; Harvey et al. 1985; US EPA 2008), although reported log *K*ow values vary, depending on pH. For example, log *K*ow values of 1.01–1.18 (at pH 5), -0.46 (at pH 7) and -1.87 (at pH 9) have been reported (BLM and ENSR 2005; Harvey et al. 1985; SERA 2004; US EPA 2012).

Sulfometuron-methyl mostly enters the aquatic environment through its use as a herbicide. This results in direct releases to soil and potential releases to water due to run-off, accidental over-spray and spray drift. Sulfometuron-methyl has been detected in watercourses adjacent to treated plantation forests. In the southern United States, in-stream concentrations of sulfometuron-methyl up to 44 µg/L were reported up to 7 days post-treatment with a pelleted form of the herbicide (no longer used) and up to 24 µg/L following treatment via spraying (Michael 2003). Sulfometuron-methyl was not detected in the sediment during this stream study. Similarly, in-stream concentrations up to 7 µg/L were reported adjacent to treated areas of plantation forest in Florida (United States) following rainfall, although these concentrations persisted for less than a week and the herbicide was not detected in sediment or groundwater (Neary and Michael 1989). In drainage ditches adjacent to forest plantations in South Carolina (United States), sulfometuron-methyl was detected after the first 5 significant rain events following herbicide application (during a 3-month period), with a maximum concentration of 24 µg/L following the first storm, decreasing to 0.1 µg/L following the fifth storm (Michael et al. 2006). No negative effects of sulfometuron-methyl treatment on aquatic faunal communities in the ditches were observed (Michael et al. 2006).

## Aquatic toxicology

### Mechanism of toxicity

As with other SU herbicides, sulfometuron-methyl acts by inhibiting the activity of the ALS enzyme (also known as acetohydroxyacid synthase [AHAS]). ALS is a catalyst for production of the amino acids valine, leucine and isoleucine, all of which are required for cell growth in plants, fungi and bacteria (ATSE 2002; BLM and ENSR 2005; Chipman et al. 2005; US EPA 2008; US EPA 2012; US EPA 2015a, 2015b). Based on this inhibitory mode of action, sulfometuron-methyl is classified as a Group B herbicide (HRAC 2015). Relatively low concentrations of sulfometuron-methyl affect plants, as evidenced by the generally low range (< 500 g/ha) of labelled application rates (BLM and ENSR 2005).

Although the mechanism of phytotoxic action of SU herbicides, including sulfometuron-methyl, is fairly well characterised, the mechanism of toxicity of sulfometuron-methyl in higher organisms is not well known. Sulfometuron-methyl is less toxic to mammals, birds, amphibians and fish due to their absence of ALS, the enzyme that sulfometuron-methyl acts on in plants and microorganisms (BLM and ENSR 2005; Zhou et al. 2007; US EPA 2012).

### Acute and chronic toxicity

A literature review of the effects of sulfometuron-methyl on freshwater organisms found toxicity data for acute and chronic exposures to both plant and animal species (a total of 43 toxicity values for 17 species, consisting of 21 chronic values for 8 species from 6 taxonomic groups and 22 acute values for 11 species from 3 taxonomic groups). Some toxicity studies assessed formulations containing sulfometuron-methyl as the active ingredient with other ingredients (e.g. a carrier solvent), for which the combined toxicity may not be well understood. Accordingly, such studies are typically not used in the derivation of guideline values and are not discussed further.

Seventeen of the 21 chronic toxicity values were for plants (cyanobacteria, diatoms, green algae and macrophytes), with effects ranging from 0.12 µg/L to 370 µg/L for growth endpoints. The remaining 4 chronic toxicity values were for 2 animals (a crustacean and an amphibian), with no such data available for other taxa. Chronic growth-effect concentrations varied for the plant species. The macrophyte *Myriophyllum sibricum* was the most sensitive, with a 14-day IC50 of 0.12 µg/L (root dry mass) (Roshon et al. 1999). The next-most sensitive species was another macrophyte (*Lemna gibba*), with a 14-day NOEC (shoot growth) of 0.207 µg/L (Kannuck and Sloman 1995; US EPA 2019), followed by a green alga (*Raphidocelis subcapitata*), with a 5-day NOEC of 0.63 µg/L for growth (abundance) (Hoberg 1990; US EPA 2019). Another macrophyte (*Hydrilla verticillata*) had a 7-day NOEC of 0.75 µg/L for growth (abundance) (Byl et al. 1994). A diatom (*Navicula pelliculosa*) was the least sensitive plant species, with a 5-day NOEC of 370 µg/L for growth (abundance) (Thompson 1994; US EPA 2019). Based on limited available data, sulfometuron-methyl appears to be less toxic to animals than it is to plants. For the amphibian *Xenopus laevis*, 30-day NOEC and lowest-observed-effects concentration (LOEC) (development) of 1,000 µg/L and 5,000 µg/L, respectively, have been reported (Fort et al. 1999). For the crustacean *Daphnia magna*, 21-day NOEC and LOEC (reproduction) values of 6,100 µg/L and 24,000 µg/L, respectively, have been reported (US EPA 2019).

Most aquatic toxicity studies for sulfometuron-methyl on animals represent acute exposures where only mortality was measured. Of these studies, a crustacean and a fish were the most sensitive, with 48-hour and 96-hour LC50s of 200 µg/L for *Ceriodaphnia dubia* (crustacean; Tatum et al. 2012) and *Pimephales promelas* fry (fish; Tatum et al. 2012), respectively. However, crustaceans appear to be generally less sensitive than fish and frogs, with effects following 48-hour exposure ranging from 12,500 µg/L (*D. magna*, immobilisation EC50; US EPA 2019) to 12,174 mg/L (12,174,000 µg/L) (*Procambarus clarkii*, LC50; Naqvi et al. 1987). Acute toxicity to the frog *X. laevis* ranged from 4,200 µg/L (4-day EC50, malformation) to 24,300 µg/L (4-day LC50), although toxicity was further reduced when the purity of the test compound was increased from 98.5% to 99.5% (Fort et al. 1999). Reported acute toxicity to fish ranged from the above-mentioned 96-hour LC50 of 200 µg/L for *P. promelas* (Tatum et al. 2012) to 150,000 µg/L for a 4-day survival LC50 for *Lepomis macrochirus* (US EPA 2019), with most within this range representing ‘>’ values. The data for fish are highly variable and, in some cases, there was no difference in toxicity values for LC50 and NOEC for tests conducted using the same species and for the same exposure duration. No acute toxicity data for plants were found in the literature review.

Consistent with the above summary, an ecological risk assessment for the registration review of 22 SU herbicides in the United States found that SU herbicides are virtually non-toxic to freshwater invertebrates and fish on an acute basis, with the risks of concern relating to terrestrial and aquatic plants (US EPA 2015a).

## Factors affecting toxicity

Sulfometuron-methyl is a weak acid, so changes in pH will affect physico-chemical properties of the herbicide, such as its solubility, partitioning and rate of hydrolysis. This indicates that chronic toxicity may differ depending on pH (US EPA 2012). However, the preparation of this technical brief did not identify any studies that indicated differences in the toxicity of sulfometuron-methyl with changes in pH. The absence of this information introduces some additional uncertainty to the default guideline values.

## Default guideline value derivation

The DGVs were derived in accordance with the method described in Warne et al. (2018). Due to insufficient data to meet the minimum data requirements of the SSD method, the AF method was used to derive the current DGV, in accordance with ANZECC and ARMCANZ (2000) and Warne (1998, 2001) guidance.

### Toxicity data used in derivation

A summary of the toxicity data and conversions applied to the data that passed the quality assessment and screening processes are provided in Table 1, with more details presented in Appendix A.

Toxicity data that represented exposures of acceptable quality (i.e. the studies passed quality assessment and did not use a formulation as the test substance, and the test substance was of > 80% purity) were considered for derivation of the DGV.

As noted in Section 2, toxicity data for exposure using formulations are generally excluded from derivation of DGVs due to the potential for toxicity from the carrier solvent (and other ingredients). For sulfometuron-methyl, many of the available studies used formulations and, therefore, were excluded from the current derivation, because the toxicity attributable to the active ingredient alone was not known. Toxicity data that were excluded because the studies used sulfometuron-methyl formulations included 2 macrophyte species (*Myriophyllum sibricum* [estimated 14-day IC50 of 0.12 µg active ingredient/L for growth; Roshon et al. 1999] and *Hydrilla ventricillata* [estimated 7-day NOEC of 0.75 µg/L for growth; Byl et al. 1994]), 6 invertebrate species (the cladoceran *Alonella* sp. [2-day LC50 of 802 mg/L; Naqvi and Hawkins 1989], the ostracod *Cypria* sp. [2-day LC50 of 2,241 mg/L; Naqvi and Hawkins 1989], the calanoid copepod *Diaptomus* sp. [2-day LC50 of 1,315 mg/L; Naqvi and Hawkins 1989], the cyclopoid copepod *Eucyclops* sp. [2-day LC50 of 1,320 mg/L; Naqvi and Hawkins 1989], the cladoceran *Ceriodaphnia dubia* [2-day LC50 of 200 µg/L; Tatum et al. 2012] and the crayfish *P. clarkii* [4-day LC50 of 12,174 mg/L; Naqvi et al. 1987]) and one fish species (*P. promelas* [4-day LC50 of 200 µg/L; Tatum et al. 2012]).

Toxicity values representing acute NOECs/LOECs were also excluded, as they are unacceptable for derivation of DGVs (Warne et al. 2018). These included values for the fish *Oncoryhynchus mykiss* (Muska and Trivits 1980; US EPA 2019) and *L. macrochirus* (Muska and Hall 1980; US EPA 2019), the frog *X. laevis* (Fort et al. 1999) and the cladoceran *D. magna* (Muska and Trivits 1980). Acute LC50s for *O. mykiss* (US EPA 2019), *L. macrochirus* (US EPA 2019) and *D. magna* (US EPA 2019) reported as ‘>’ values were also excluded, as they did not meet the inclusion recommendations specified in Warne et al. (2018).

The acceptable data available for the DGV derivation represented 6 species from 6 taxonomic groups, comprising 4 phototroph species from 4 taxonomic groups (one macrophyte, one green alga, one diatom and one cyanobacterium) and 2 animal species from 2 taxonomic groups (one crustacean and one amphibian) (Table 1). Of the toxicity data available for these 6 species, 10 were chronic NOEC/NOEL values, 2 were chronic LOEC values, 3 were chronic EC50 values and one was an acute LC50. Where acceptable toxicity data are available for sufficient species and taxonomic groups (i.e. ≥ 5 species from ≥ 4 taxonomic groups), DGVs can be derived using the SSD method.

Modality checks on the 6 species from 6 taxonomic groups presented in Table 1 were performed according to the 4 questions stipulated in Warneet al. 2018, with the details of the assessment provided in Appendix B. The weight-of-evidence assessment concluded that organisms that possess ALS (the enzyme that sulfometuron-methyl acts upon) – in this case the phototrophs (i.e. plant, alga, diatom and cyanobacterium) – were more sensitive than those that do not (i.e. the animal species), and that the toxicity of sulfometuron-methyl was, therefore, likely to exhibit a bimodal relationship. Consequently, it was concluded that the DGV should be determined based on the phototroph data only. Thus, the final acceptable dataset for the DGV derivation consisted of toxicity data for 4 phototroph species from 4 taxonomic groups. Notably, however, this dataset is insufficient to enable the use of the SSD method for deriving DGVs (see sections 4.2 and 0).

Table 1 Summary of acceptable chronic toxicity data values available for deriving the default guideline values for sulfometuron-methyl. Toxicity values are reported to no more than 3 significant figures.

| **Taxonomic group** | **Species** | **Life stage** | **Duration (h)** | **Toxicity measurea (test endpoint)** | **Reported toxicity value (µg/L)** | **Final toxicity value (µg/L)** |
| --- | --- | --- | --- | --- | --- | --- |
| Green alga | *Raphidocelis subcapitata*b | — | 120 | NOEC (growth) | 0.63 | 0.63 |
| Cyanobacterium | *Anabaena flosaqua* | — | 120 | NOEC (growth) | 14 | 14 |
| Diatom | *Naviculla pelliculosa* | — | 120 | NOEC (growth) | 370 | 370 |
| Macrophyte | *Lemna gibba* | — | 336 | NOEC (growth) | 0.207 | 0.207  |
| Crustacean | *Daphnia magna* | Neonates | 504 | NOEC (reproduction) | 6,100 | 6,100 |
| Amphibian | *Xenopus laevis* | Embryos | 720 | NOEC (development) | 1,000 | 1,000 |

a The measure of toxicity being estimated/determined. NOEC: no-observed-effect concentration.

b Formerly known as *Selenastrum capricornutum* and *Pseudokirchneriella subcapitata.*

### Species sensitivity distribution

Where acceptable toxicity data are available for sufficient species and taxonomic groups (i.e. ≥ 5 species from ≥ 4 taxonomic groups), DGVs are derived using the SSD method. Given that the final acceptable dataset for sulfometuron-methyl (Table 1) did not meet this minimum requirement to use the SSD method, the AF method was used to derive a DGV for sulfometuron-methyl. However, an SSD was prepared using the phototroph and animal data (6 species from 6 taxonomic groups) as a means of comparison against the DGV derived using the AF method. This is presented in

Appendix C.

### Default guideline values

It is important that the DGV 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*](http://www.waterquality.gov.au/anz-guidelines) (ANZG 2018).

The AF method was adopted due to there being insufficient acceptable data to meet the minimum requirements of the SSD method. This method is outlined in ANZECC and ARMCANZ (2000) and described further in Warne (1998, 2001).

The AF method divides the lowest available acceptable toxicity value by an AF, the magnitude of which is based on the number, type (e.g. acute or chronic, representation of taxonomic groups) and quality of the available toxicity data. Typical Afs used are 10, 100 and 1,000, with the aim to protect all species from lifetime exposures to toxicants.

The AF method for sulfometuron-methyl considered the final acceptable chronic NOEC data for the 3 plant species and one cyanobacterial species, in conjunction with supporting acceptable chronic NOEC data for the amphibian and crustacean (Table 1). Warne (2001) provides specific recommendations for the size of the AF depending on the number and type of available data, including the range of taxonomic groups that are represented (e.g. fish, invertebrates, microalgae, macrophytes). However, the recommendations for the minimum range of taxonomic groups do not consider the case of bimodal datasets for toxicants that are highly specific in their mode of action. This includes sulfometuron-methyl, a herbicide that is highly specific to plants and microorganisms and that acts upon an enzyme (ALS) that is not produced by higher organisms. In such a case, a requirement for data from fish and invertebrates is less relevant, and greater weight should be given to the availability of phototroph data. Thus, a degree of professional judgement was required to determine the appropriate AF for sulfometuron-methyl. The available acceptable dataset included toxicity data for 6 species from 6 taxonomic groups. Four of the species are phototrophs and so are targeted by sulfometuron-methyl’s mode of action. A vertebrate and invertebrate are also represented. Given the nature of the toxicant, this dataset was deemed to be consistent with the requirements in Warne (2001) for the selection of an AF of 10. Thus, the lowest acceptable toxicity value of 0.207 µg/L (5-day NOEC, growth) for the macrophyte *L. Gibba* was divided by an AF of 10 to derive the DGV. The DGV is provided in Table 2 and relates to sulfometuron-methyl only and not any of its breakdown products.

Table 2 Toxicant default guideline value (DGV) for sulfometuron-methyl in freshwater, with unknown reliability

| Level of species protection (%) | DGV for sulfometuron-methyl in freshwater (µg/L)**a** |
| --- | --- |
| Unknownb | 0.02 |

**a** The DGV was derived using the assessment factor method and has been rounded to one significant figure given the high uncertainty associated with the method.

b It is not possible to specify the level of species protection when using the assessment factor method to derive a DGV.

It is important to note that the DGV may be below routine analytical limits of reporting. ANZG (2018; see [*Accounting for local conditions*](https://www.waterquality.gov.au/anz-guidelines/guideline-values/default/water-quality-toxicants/local-conditions#default-guideline-values-and-analytical-detection-limits)) provides guidance on what to do in the event that guideline values are below analytical detection limits.

Guideline values derived using the AF method do not need to undergo the reliability check procedure. This is because the DGV is the most sensitive toxicity value divided by an AF and, therefore, the DGV provides protection to all species for which there is toxicity data (Warne et al. 2018). Although not a benchmarking exercise as such, the DGV based on the AF method was compared with the 95% species-protection concentration estimated from an SSD of the 6 acceptable toxicity values in Table 2 (

Appendix C). The 2 values were within a factor of 2 of each other, with the AF-derived DGV being the lower of the 2 values. This provides an additional degree of conservatism for the protection of aquatic ecosystems, which is considered appropriate given the high uncertainty associated with the DGV derivation.

### Reliability classification

The sulfometuron-methyl freshwater DGV has an ‘unknown’ reliability classification based on using the AF method for the DGV derivation (Warne et al. 2018). Updating these DGVs and improving their reliability will require more toxicity data.

## Glossary and acronyms

| 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. |
| AF | Assessment factor |
| AHAS | Acetohydroxyacid synthase enzyme |
| ALS | Acetolactate synthase enzyme |
| BC | Bimodality coefficient |
| CASRN | Chemical Abstracts Service Registry Number |
| Chronic toxicity | A lethal or sub-lethal adverse effect that occurs after exposure to a chemical for a period 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. a site-specific guideline value) in the *Australian and New Zealand Guidelines for Fresh and Marine Water Quality.* Formerly known as ‘trigger values’. |
| 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). |
| 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 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](https://www.waterquality.gov.au/anz-guidelines/resources/glossary#default-guideline-value) and [site-specific guideline value](https://www.waterquality.gov.au/anz-guidelines/resources/glossary#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 (unexposed) response, under specified conditions. |
| IUPAC | International Union of Pure and Applied Chemistry |
| *K*oc | Adsorption coefficient normalised to the organic carbon content of the soil |
| *K*ow or *P*ow | The ratio of a chemical's solubilities in *n*-octanol and water at equilibrium. The logarithm of *P*OW is used as an indication of a chemical's propensity for bioaccumulation by aquatic organisms. |
| LCx | The concentration of a substance in water or sediment that is estimated to be lethal to x% of a group of test organisms, relative to the control response, under specified conditions. |
| LOEC (lowest-observed-effect concentration) | 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 with the controls. |
| NOEC (no-observed-effect concentration) | 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. |
| pKa | The acid dissociation constant. A quantitative measure of the strength of an acid in solution, and the equilibrium constant for the acid–base dissociation reaction.  |
| 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. |
| SU | sulfonylurea |
| 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 considered in the derivation of the default guideline value

Table A1 Summary of chronic toxicity data that passed the screening and quality assurance processes for sulfometuron-methyl in freshwater

| **Taxonomic group** | **Species** | **Life stage** | **Exposure duration (h)** | **Toxicity measurea****(test endpoint)** | **Test medium** | **Temp. (°C)** | **Salinity (‰)** | **pH** | **Conc. (µg/L)** | **Reference** |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Green alga | *Raphidocelis subcapitata*b | – | 120 | NOEC (growth) | Nutrient medium | – | – | – | 0.63c | US EPA 2019 |
| Cyanobacterium | *Anabaena flosaqua* | – | 120 | NOEC (growth) | Nutrient medium | – | – | – | 14c | US EPA 2019 |
| Diatom | *Naviculla pelliculosa* | – | 120 | NOEC (growth) | Nutrient medium | – | – | – | 370c | US EPA 2019 |
| Macrophyte | *Lemna gibba* | – | 336 | NOEC (growth) | Nutrient medium | – | – | – | 0.207c | US EPA 2019 |
| Crustacean | *Daphnia magna* | Neonates | 504 | NOEC (reproduction) | – | – | – | – | 6,100c | US EPA 2019 |
| Amphibian | *Xenopus laevis* | Embryos | 720 | NOEC (development) | FETAX solution | 23.5–24.5 °C | – | 7.8­–8.0 | 1000c | Fort et al. 1999 |

a The measure of toxicity being estimated/determined. NOEC: no-observed-effect concentration; IC50: inhibition concentration for 50% of test organisms.

b formerly known as *Selenastrum capricornutum* and *Pseudokirchneriella subcapitata.*

c Value included in the dataset to derive the default guideline values, as reported.

## Appendix B: modality assessment for sulfometuron-methyl

A modality assessment was undertaken for sulfometuron-methyl according to the 4 questions stipulated in Warneet al. (2018). These questions and their answers are listed below.

**Is there a specific mode of action that could result in taxa-specific sensitivity?**

Sulfometuron-methyl inhibits activity of the enzyme acetolactate synthase (ALS, also known as acetohydroxyacid synthase [AHAS]). ALS catalyses production of the amino acids valine, leucine and isoleucine, all of which are required for cell growth in phototrophs, fungi and bacteria. Higher organisms do not produce ALS. Therefore, sulfometuron-methyl’s mode of action would be expected to result in taxa-specific sensitivity, with higher organisms such as invertebrates and vertebrates being less sensitive.

**Does the dataset suggest bimodality?**

The modality assessment was undertaken on the lowest toxicity value for each species that passed the screening and quality assessment stipulated in Warne et al. (2018).

Table B1 summarises the data considered for the SSD.

Table B1 Lowest chronic toxicity value for each species that passed the screening and quality assessment stipulated in Warne et al. (2018)

| **Taxonomic group** | **Species** | **Toxicity measurea** | **Toxicity value (µg/L)** |
| --- | --- | --- | --- |
| Green alga | *Raphidocelis subcapitata*b | NOEC  | 0.63 |
| Cyanobacterium | *Anabaena flosaqua* | NOEC  | 14 |
| Diatom | *Naviculla pelliculosa* | NOEC | 370 |
| Macrophyte | *Lemna gibba* | NOEC  | 0.207 |
| Crustacean | *Daphnia magna* | NOEC  | 6,100 |
| Amphibian | *Xenopus laevis* | NOEC  | 1,000 |

a The measure of toxicity being estimated/determined. NOEC: no-observed-effect concentration.

b formerly known as *Selenastrum capricornutum* and *Pseudokirchneriella subcapitata.*

The data were visualised, the bimodality coefficient (BC) was calculated, and the range in the effect concentrations was considered. These factors are recommended lines of evidence in evaluating whether the dataset is bimodal or multimodal. This is discussed below.

Bimodal or multimodal distributions are not evident in the histograms of the raw effect-concentration SSD data and the log-transformed data (

* Figure B1).
* Data that span large ranges (> 4 orders of magnitude) indicate potential for underlying bimodality or multimodality (Warne et al. 2018). The sulfometuron-methyl data span 4 orders of magnitude.
* A BC greater than 0.555 indicates that the dataset may be bimodal (Warne et al. 2018). The BC for the log-transformed data is 0.243, indicating that the dataset is not bimodal.

While a bimodal distribution was expected based on the lines of evidence described above, the distribution of the log-transformed dataset is generally in accordance with a unimodal distribution. However, the small dataset hampers the ability to detect a bimodal distribution.



Figure B1 Histograms of raw data (left) and log-transformed data (right)

**Do data show taxa-specific sensitivity (i.e. through distinct groupings of different taxa types)?**

Sulfometuron-methyl is expected to show taxa-specific sensitivity, given its mode of action (as discussed in response to question 1). Boxplots of the data visualise the differences between effect concentrations in different major types of organisms.

When grouped by phylum or clade (Figure B2), there is a slight trend for the Chlorophyta and Tracheophyta to be most sensitive to sulfometuron-methyl, with Ochrophyta and Cyanophyta slightly less sensitive. The animal phyla Arthropoda and Chordata were even less sensitive. However, this observation is based on very small sample sizes (i.e. only one datum per phylum) and, as such, it is difficult to draw conclusions with any confidence.



Figure B2 Boxplots of data grouped by phylum or clade, showing raw data (left) and log-transformed data (right)

Even with the limited sample size, Figure B3 shows a general trend for major types of organisms, with plants and cyanobacteria being more sensitive to sulfometuron-methyl than invertebrates and vertebrates (plants: n = 3; invertebrates: n = 1; vertebrates: n = 1 and cyanobacteria: n = 1).



Figure B3 Boxplots of data grouped by major types of organism, showing raw data (left) and log-transformed data (right)

**Is it likely that indications of bimodality or multimodality or distinct clustering of taxa groups are not due to artefacts of data selection, small sample size, test procedures or other reasons unrelated to a specific mode of action?**

The sulfometuron-methyl dataset has a small sample size, making it difficult to determine whether any apparent trends in the dataset are real or an artefact. However, it was considered appropriate to derive the DGV using only the phototroph data, given that the mode of action for sulfometuron-methyl is specifically targeted at phototrophs and microorganisms over heterotrophic organisms, and the dataset supported the associated likelihood of the herbicide exhibiting a bimodal toxicity relationship.

## Appendix C: species sensitivity distribution for sulfometuron-methyl

An SSD of the 6 chronic sulfometuron-methyl toxicity data reported in Table 1 was constructed to compare with the DGV derived using the AF method (Figure C1). The model appears to provide a poor fit to the data, specifically at both the lower and upper tails of the distribution.



Figure C1 Cumulative frequency distribution (from Burrlioz 2.0) for sulfometuron-methyl freshwater chronic toxicity (NOEC).

Using the SSD method, the 99%, 95%, 90% and 80% species-protection concentrations for sulfometuron-methyl in freshwater are shown in Table C1. If they were adopted as DGVs, they would be assigned a ‘low’ reliability rating (i.e. less than 8 chronic data with a poor fit of the SSD model). The 95% species-protection concentration of 0.042 µg/L using the SSD method is only a factor of 2 different than the DGV of 0.02 µg/L derived using the AF method. Being lower than the SSD-derived 95% species-protection concentration, the AF-derived DGV provides an additional degree of conservatism for the protection of aquatic ecosystems, which is considered appropriate given the high uncertainty associated with the DGV derivation.

Table C1 Species-protection concentrations for sulfometuron-methyl in freshwater

| Level of species protection (%) | Concentration of sulfometuron-methyl in freshwater (µg/L)a |
| --- | --- |
| 99 | 0.00085 |
| 95 | 0.042 |
| 90 | 0.25 |
| 80 | 1.7 |

**a** The concentrations were derived using the Burrlioz 2.0 software and rounded to 2 significant figures.

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