



An Australian Government Initiative



Australian & New Zealand
GUIDELINES FOR
FRESH & MARINE
WATER QUALITY

Toxicant default guideline values for aquatic ecosystem protection

4-chloro-2-methylphenoxy acetic acid (MCPA) in freshwater

Technical brief

March 2024

DRAFT

Toxicant default guideline values for aquatic ecosystem protection: 4-chloro-2-methylphenoxy acetic acid (MCPA) in freshwater

© Commonwealth of Australia 2024

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 [summary of the licence terms](#) or the [full licence terms](#).

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

Cataloguing data

This publication (and any material sourced from it) should be attributed as: ANZG 2024, *Toxicant default guideline values for aquatic ecosystem protection: 4-chloro-2-methylphenoxy acetic acid (MCPA) in freshwater*. Australian and New Zealand Guidelines for Fresh and Marine Water Quality. Australian and New Zealand Governments and Australian state and territory governments, Canberra, ACT, Australia.

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

Contact

Australian Government Department of Climate Change, Energy, the Environment and Water
GPO Box 858 Canberra ACT 2601
General enquiries: 1800 920 528
Email waterquality@dcceew.gov.au

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 Naomi Cooper, Kirsten Broadgate, Clare Papaleo and Carolyn Brumley of Golder Associates, Melbourne. The DGVs were peer reviewed by two anonymous reviewers and by two

Toxicant default guideline values for aquatic ecosystem protection: 4-chloro-2-methylphenoxy acetic acid (MCPA) in freshwater

contracted technical advisors Dr Rick van Dam and Alicia Hogan.



Contents

Summary	v
1 Introduction.....	1
2 Aquatic toxicology.....	2
2.1 Mechanism of toxicity	2
2.2 Toxicity	3
3 Factors affecting toxicity	4
4 Default guideline value derivation	4
4.1 Toxicity data used in derivation	4
4.2 Species sensitivity distribution	6
4.3 Default guideline values	7
4.4 Reliability classification	8
Glossary.....	9
Appendix A: Toxicity data that passed the screening and quality assessment and were used to derive the default guideline values	11
Appendix B: Modality assessment for MCPA	13
References	15

Figures

Figure 1 Species sensitivity distribution, MCPA in freshwater.....	7
--	---

Tables

Table 1 Summary of single chronic toxicity values, all species used to derive default guideline values for MCPA in freshwater.....	6
Table 2 Default guideline values, MCPA in freshwater, moderate reliability	8

Appendix Tables

Table A 1 Summary, chronic toxicity data that passed the screening and quality assessment processes, MCPA in freshwater..... 11

Appendix Figures

Figure B 1 Histogram, raw (left) and log transformed (right) MCPA data 13

Figure B 2 Box plots, raw (left) and log transformed (right) MCPA data grouped by 'organisms considered to be taxonomically different' 14

DRAFT

Summary

4-chloro-2-methylphenoxy acetic acid (MCPA) is a post-emergence herbicide for control of broadleaf weeds in agricultural settings, predominantly on crops such as cereals and pasture (ACVM 2020, APVMA 2020). Products containing MCPA are available in a range of forms, including an aqueous concentrate, soluble concentrate, water-soluble powder, and emulsifiable concentrate (APVMA 2010).

The parent acid (MCPA) is used to produce MCPA herbicide formulations containing one or more salts (sodium and/or potassium), amine (MCPA dimethylamine salt) or ester (MCPA 2-ethylhexyl ester, MCPA butoxy ethanol ester, MCPA iso-octyl ester derivatives of MCPA) (WSSA 1989, CCME 1999, Growcom 2020).

MCPA mimics plant growth hormones (i.e. auxins), which stimulates plant growth by increasing cell extension and cell differentiation and, ultimately, results in uncoordinated growth and disruption to the plant and new seedlings (Grossman 2000, Nielsen & Dahllöf 2007, Bisewska et al. 2012). Uptake of MCPA is via the roots and leaves, with rapid translocation throughout the plant. MCPA accumulates in the meristematic tissue of plants, where growth occurs (WSSA 1989, Nielsen & Dahllöf 2007). MCPA is a selective herbicide as it is more toxic to dicots than to monocots (Von Stackelberg 2013).

In the aquatic environment, MCPA is most toxic to algae and macrophytes, slightly toxic to freshwater fish, and relatively non-toxic to aquatic invertebrates and amphibians (APVMA 2010). Compared to the acid and salt forms of MCPA, the ester form is more toxic to aquatic receptors (APVMA 2010). However, due to data availability—and because the acid form is likely to be the dominant form in freshwater—the default guideline values (DGVs) were derived from data predominantly based on the acid form of MCPA or forms that rapidly hydrolyse or dissociate to the acid form.

Moderate reliability DGVs for MCPA in freshwater were derived based on chronic toxicity values for 16 species from five taxonomic groups, with a poor fit of the distribution to the toxicity data. The DGVs are expressed in terms of the dissolved active ingredient (MCPA) rather than commercial formulations, and do not relate to any of the breakdown products of MCPA. The DGVs for 99%, 95%, 90% and 80% species protection are 3 µg/L, 7.7 µg/L, 14 µg/L, and 29 µg/L, respectively. The 95% species protection DGV of 7.7 µg/L is recommended for application to slightly-to-moderately disturbed ecosystems.

1 Introduction

4-chloro-2-methylphenoxy acetic acid (MCPA) (CASRN 94-74-6, chemical formula $C_9H_9ClO_3$, molecular mass 200.6 g/mol) is a post-emergence phenoxy acid herbicide used for the control of broadleaf weeds. In Australia and New Zealand, MCPA is approved for weed control for a range of crops, predominantly cereals (e.g. wheat, barley, oats), linseed, pasture and grass seed crops (ACVM 2020, APVMA 2020). In Australia, MCPA is also approved for use on sugar cane, field peas, sweet corn and rice (APVMA 2020, Growcom 2020). MCPA is also widely used in home garden formulations for broadleaf weed control (Growcom 2020). More than 400 products containing MCPA have been registered with the Australian Pesticides and Veterinary Medicines Authority (APVMA 2020). These products contain MCPA in a range of forms, including dimethylamine salt, dimethylammonium salt (DMAS), sodium salt, potassium salt, 2-ethylhexyl ester (2-EHE), iso-octyl ester and butoxyethanol ester (APVMA 2020). Products containing MCPA are available in a range of forms, including as an aqueous concentrate, soluble concentrate, water-soluble powder, and emulsifiable concentrate (APVMA 2010).

The parent acid (MCPA) is formulated into esters, salts, and amine derivatives, all of which have varying solubilities in water. USEPA (2004) reported MCPA to be '*practically insoluble*', the 2-EHE form to be '*slightly soluble in water*' and the sodium salt form to be '*water soluble*'. However, more recently, the solubility of the MCPA acid and MCPA salt forms has been reported as high—at 825 mg/L (WHO 2003) and 866 mg/L (Morton et al. 2019), respectively—and the 2-EHE form reported as low—at approximately 5 mg/L (Morton et al. 2019). The solubility of MCPA is pH-dependent, and it is generally considered to be highly soluble except under very acidic conditions (Morton et al. 2019).

MCPA can enter the aquatic environment via surface water runoff following application to land, via spray drift, leaching, or accidental spills. A surface water monitoring study in an agricultural area of the Anglian Water region in the United Kingdom reported concentrations of MCPA up to 0.12 µg/L (NCBI 2020). Other reported concentrations of MCPA in the environment include a groundwater concentration of 0.53 µg/L in Saskatchewan, Canada (NCBI 2020), and a river water concentration of 1.3 µg/L in Quebec, Canada (Maathuis et al. 1988). A 1975–1977 Canadian study of surface water concentrations of MCPA in 11 agricultural watersheds reported concentrations ranging from <0.1 µg/L to 1.7 µg/L (Giroux et al. 1997). A later Canadian study (1981–1985) of the Grand, Saugeen and Thames rivers in Ontario detected MCPA in one out of 100 Grand River samples (0.1 µg/L), four out of 200 Thames River samples (1.8 µg/L mean), and no reported concentrations of MCPA in Saugeen River samples (NCBI 2020). In Australia, MCPA was detected in over 50% of samples taken in a study of urban stormwater, although concentrations were generally below 0.1 µg/L, with median concentrations lower than those reported for the United States, Canada and Europe (Rippy et al. 2017).

The ester, salt, and amine derivatives of MCPA hydrolyse or dissociate to MCPA acid in alkaline water (Frank & Logan 1988). MCPA acid was reported to not readily dissociate in sterile water at pH 5 (Chau & Thomson 1978, MCPA Task Force II. 1993a). Photolysis half-lives of MCPA and derivatives are reported to range between 1 h (Soderquist & Crosby 1975, MCPA Task Force II. 1993b) and 20 d

Toxicant default guideline values for aquatic ecosystem protection: 4-chloro-2-methylphenoxy acetic acid (MCPA) in freshwater

(NCBI 2020). The by-products of photolysis include 4-chloro-2-methylphenol, o-cresol and 4-chloro-2-formylphenol (NCBI 2020).

Half-lives of MCPA acid in soil ranged 7–41 d, with an average of approximately 2–3 weeks (NCBI 2020). Data on the aerobic and anaerobic degradation of MCPA and derivatives in water include:

- half-lives of 76 d at pH 7, and 117 d at pH 9 for the 2-EHE derivative of MCPA (MCPA Task Force II. 1993c)
- 95% degradation of MCPA in water within 13 d (MCPA Task Force II. 1993b)
- rapid ozonolysis in the dark, with half-lives reported between 4.2 h and 11.5 h (MCPA Task Force II. 1993d).

K_{oc} values ranging from 50 L/kg to 62 L/kg (NCBI 2020) indicate that MCPA is unlikely to adsorb to suspended solids and sediment.

A log K_{ow} value of 2.8 was reported for MCPA (Benoit-Guyod et al. 1986, APVMA 2010), while MCPA DMAS has a reported log K_{ow} value of 1.415 (USEPA 2004). Consistent with the low log K_{ow} values, bioconcentration factors (BCFs) of <1 (CCME 1999) have been reported for MCPA for the freshwater fish *Cyprinus carassius* and snail *Lymnea stagnalis*, indicating that MCPA does not bioaccumulate in aquatic fauna. However, in terrestrial plants, MCPA accumulates in meristematic tissue, where growth occurs (WSSA 1989, Mierzejewska et al. 2022). Uptake of MCPA in terrestrial and aquatic plants is via the roots and leaves, with rapid translocation throughout the plant. Metabolism of MCPA in plants appears to be via oxidation of the phenyl methyl, and the resulting 2-hydroxy-4-chlorophenoxyacetic acid (HMCPA) forms conjugates, including a glucose conjugate (FAO 2013).

2 Aquatic toxicology

2.1 Mechanism of toxicity

MCPA is an artificial mimic of plant auxin-hormones that stimulates cell growth (elongation and differentiation of cells) (Nielsen & Dahllöf 2007, Bisewska et al. 2012). MCPA is typically applied at doses 1 000 times higher than the natural auxin level in plants, which stimulates rapid and uncoordinated cell growth, resulting in plant death (Nielsen & Dahllöf 2007). In plants, MCPA acts as a selective, systemic, hormone-type herbicide that, at a molecular level, influences levels of RNA and DNA polymerase and levels of enzymes involved in normal growth and development processes. There is limited information on the mechanism of toxicity of MCPA in animals. Studies on terrestrial mammals indicate the potential for effects on developmental processes, although this is at doses generally >50 mg/kg body weight per day (FAO 2013, O'Mullane & Moretto 2013). Reports of MCPA poisoning in humans indicated that uncoupled oxidative phosphorylation was the cause of death (Roberts et al. 2005). Although at least one study has suggested a teratogenic mode of action for MCPA (Lindquist 1974), WHO (2003) concluded that MCPA was not teratogenic in rats or rabbits, and Bernardini et al. (1996) found that MCPA did not present a high teratogenic risk to embryos of the amphibian *Xenopus laevis*.

2.2 Toxicity

A literature review of the effects of MCPA on freshwater organisms indicated the majority of studies relate to plants. According to APVMA (2010), the ester form of MCPA exhibits higher toxicity than the acid or salt forms to all aquatic trophic levels. Similarly, the Canadian interim guidelines for MCPA reported that 2-EHE and the iso-octyl ester forms of MCPA were most toxic to fish and invertebrates (CCME 1999).

The majority of studies considered for the default guideline value (DGV) derivation were based on the acid derivative of MCPA. Few studies conducted using the salt, amine, ester, potassium or sodium salts were available. The differences in the chemical form of MCPA (i.e. acid, salt, amine, ester, potassium or sodium salts) may not materially affect the DGVs as the ester, salt, and amine derivatives of MCPA rapidly convert to MCPA acid (CCME 1999, USEPA 2004, Morton et al. 2019), thereby limiting the duration of aquatic exposure to the more toxic ester form. The APVMA (2010) noted that most of the aquatic toxicity values were within one order of magnitude when comparing the MCPA acid, sodium salt and DMAS forms of MCPA. When comparing the toxicity of acid and the salts to 2-EHE, the toxicity of 2-EHE was two to three orders of magnitude greater for fish and invertebrates and one to two orders of magnitude greater for aquatic plants (APVMA 2010).

The literature review for MCPA identified toxicity data for 26 species from seven taxonomic groups (green alga, diatom, blue–green alga, macrophyte, crustacean, fish, amphibian), consisting of 35 chronic values for 20 species and 13 acute values for seven species. The data are predominantly for plant species, with only very limited data for invertebrates (one species) and vertebrates (five species). Some toxicity studies assessed formulations containing MCPA as the active ingredient with other ingredients (e.g. a carrier solvent), for which the combined toxicity may not be well understood. Such studies are typically not used to derive DGVs and are not discussed further.

Chronic toxicity studies for MCPA indicate that diatoms are generally the most sensitive taxonomic group, with green algae generally the least sensitive plant group. No chronic toxicity data for fish and amphibians were found. The most sensitive diatom species was *Navicula pelliculosa* (OPP 2019), with a 5 d NOEC for growth of 7.7 µg/L, followed by *Gomphonema* spp., *Encyonema gracilis* and *Ulnaria ulna*, with 2 d LOECs for growth of 50 µg/L (Wood et al. 2016). Chronic toxicity data for green algae included EC50s of 86 100 µg/L (4 d growth) and 85 100 µg/L (20 d growth) for *Scenedesmus quadricauda* (Fargosova 1994, Ma et al. 2003) and an EC10 of 142 700 µg/L (30 d growth) for *Desmodesmus subspicatus* (Bisewska et al. 2012). One species of green alga (*Raphidocelis subcapitata*) showed a range of sensitivities to MCPA, with a chronic NOEC for 4 d growth of 32 µg/L (OPP 2019) and a chronic NOEC for 2 d growth of 100 000 µg/L (Cedergreen & Streibig 2005). Toxicity data for other species of green algae included 4 d growth EC50s for *Chlorella pyrenoidosa* of 21 670 µg/L and 21 960 µg/L (Ma et al. 2001, 2002), *Scenedesmus obliquus* of 35 490 µg/L (Ma 2002) and *Scenedesmus acutus* of 200 620 µg/L (Grossman et al. 1992). NOECs for 5 d growth were also reported for the blue–green alga *Anabaena flos-aqua* at concentrations of 470 µg/L and 10 200 µg/L (OPP 2019). Data were also available for three macrophytes: *Lemna gibba* 14 d growth NOEC of <14 µg/L (OPP 2019); *Lemna minor* 7 d growth EC10s of 248 µg/L and 800 µg/L (Cedergreen & Streibig 2005, Bisewska et al. 2012) and 7 d growth EC50 of 4 240 µg/L (Cedergreen & Streibig 2005); and *Lemna paucicostata* 8 d growth IC50 of 1 605 µg/L (Grossman et al. 1992). For the crustacean *Daphnia magna*, a 21 d immobilisation NOEC of 13 000 µg/L was reported (OPP 2019).

Acute toxicity studies included effects reported for fish, including a 2 d LC50 of 1 500 µg/L for *Lepomis macrochirus* (Hughes & Davis 1964) and 4 d LC50s ranging 3 200–1 647 000 µg/L for *Oncorhynchus mykiss* (Fochtman et al. 2000, OPP 2019). Acute toxicity to the green alga *Scenedesmus vacuolatus* was lower than for the fish, with a 1 d growth EC50 of 160 095 µg/L (Junghans et al. 2006). The amphibian *X. laevis* was the least sensitive species, with 5 d LC50s of >3 000 000 µg/L (Bernardini et al. 1996).

3 Factors affecting toxicity

To date, there is no evidence of abiotic factors affecting the toxicity of MCPA to freshwater aquatic organisms.

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.

4.1 Toxicity data used in derivation

A summary of the toxicity data and conversions used to calculate the DGVs for MCPA in freshwater is in Table 1. Further details on the data that passed the screening and quality assessment processes are in Appendix A: Toxicity data that passed the screening and quality assessment and were used to derive the default guideline values.

Results for toxicity testing using herbicide formulations containing MCPA as the active ingredient were excluded from the DGV derivation because the toxicity of the carrier solvent (as well as other ingredients) was not known. As mentioned in Section 2, formulations include a carrier solvent and, in some cases, other proprietary ingredients, of which the combined toxicity is not well understood. Additionally, results from studies where the MCPA purity was not known or was <80% were excluded from the derivation. For example, the following toxicity data were excluded from the derivation because the test purity was not stated or because a formulation was used.

- Green alga: *C. pyrenoidosa* (4 d EC50s of 21 670 µg/L and 21 960 µg/L), *R. subcapitata* (4 d EC50 of 13 713 µg/L), *S. acutus* (1 d EC50 of 200 620 µg/L), *S. obliquus* (4 d EC50 of 35 490 µg/L), and *S. quadricauda* (3 d EC50 of 1 000 000 µg/L) (Grossmann et al. 1992, Fochtman et al. 2000, Ma 2002, Ma et al. 2001, 2002, 2006).
- Macrophyte: *L. paucicostata* (8 d IC50 of 1 605 µg/L (Grossmann et al. 1992).
- Fish: *Oreochromis mossambicus* (2 d LC50s of 486 407 µg/L and 620 870 µg/L), *O. mykiss* (4 d LC50 of 1 647 000 µg/L), and *Cyprinus carpio* (4 d LC50 of 2 833 000 µg/L) (Shafiei & Costa 1990, Fochtman et al. 2000).

All the excluded data were either within or above the range of the toxicity values in the final dataset used to derive the DGVs.

The quality assessment and screening processes identified data of acceptable quality (i.e. the data passed quality assessment (quality score >50%), were not assessed using a formulation, and the test

Toxicant default guideline values for aquatic ecosystem protection: 4-chloro-2-methylphenoxy acetic acid (MCPA) in freshwater

substance was of MCPA >80% purity) for seven acute values for four species from three taxonomic groups (green algae, fish and amphibians) and 26 chronic values for 16 species from five taxonomic groups (diatoms, blue-green algae, green algae, macrophytes and crustaceans).

Where only one endpoint was available for a species, that endpoint was included in the dataset for the DGV derivation. For species with more than one toxicity value available, data were selected in accordance with Warne et al. (2018). Acute data were not required for the DGV derivation because the chronic toxicity dataset met the minimum species and taxonomic group requirements (at least five species from at least four taxonomic groups (Warne et al. 2018)). Thus, the chronic toxicity data for 16 species from five taxonomic groups were used to derive the DGVs. These species included: three green algae, one blue-green alga, nine diatoms, two macrophytes, and one crustacean. The toxicity values represented exposures to MCPA acid (12 species), MCPA dimethylamine salt (one species: *D. magna*), MCPA 2-ethylhexyl ester (two species: *R. subcapitata* and *N. pelliculosa*) and an unspecified form (*L. minor*). Although the two species for which the ester form was used were amongst the most sensitive species, they were grouped with four other sensitive species for which the acid form had been used. Hence, there was no strong indication that the non-acid forms of MCPA were more or less toxic than the acid form. Of the toxicity data used for the 16 species, 10 were NOEC values, two were EC10 values, three were LOEC values and one was an EC50 value. The EC10 values did not require conversion. The LOEC and EC50 values were converted to 'no or low effect' equivalents using the default factors of 2.5 and 5, respectively.

The toxicity values reported for eight of the nine diatom species were generated from a multispecies laboratory study by Wood et al. (2016), where the effects of MCPA on individual diatom species were measured in a diatom community collected from the field. Warne et al. (2018) permits the use of data from multispecies tests as long as they meet the quality requirements, which these data did. Notably, five of the nine diatom species assessed did not exhibit any adverse effects up to and including the highest MCPA concentration of 500 µg/L. The 500 µg/L concentration was considered acceptable to use as a NOEC for each of the five species because it was located approximately in the middle of the effects range for the whole dataset (i.e. 7.7 µg/L to 143 000 µg/L) and the inclusion of these data did not have a large influence on the final DGVs (i.e. there was less than a two-fold difference in DGVs when the data were included or excluded). The remaining three diatom species exhibited significant effects at the lowest concentration of 50 µg/L. These data were considered acceptable for use in the derivation because there were no other data for these species and they were at the more sensitive end of the distribution of species' sensitivities. However, rather than using the lowest concentration as the value for the final dataset (as recommended by Warne et al. 2018), they were treated as LOECs and divided by the default conversion factor of 2.5, because the effects observed at this concentration ranged from 25% to 75% relative to the carrier controls (Wood et al. 2016).

Modality checks were performed according to the method stipulated in Warne et al. (2018) (see Appendix B: Modality assessment for MCPA for details). The weight of evidence assessment concluded that the dataset did not exhibit bimodality or multimodality and, thus, supported use of the dataset for the DGV derivation.

Table 1 Summary of single chronic toxicity values, all species used to derive default guideline values for MCPA in freshwater

Taxonomic group	Species	Life stage	Duration (h)	Toxicity measure ^e (test endpoint)	Reported toxicity value (µg/L)	Estimated chronic value (µg/L) ^a
Green alga	<i>Raphidocelis subcapitata</i> ^f	–	96	NOEC (growth)	32	32 ^b
	<i>Scenedesmus quadricauda</i>	–	480	EC50 (growth)	85 100	17 020 ^c
	<i>Desmodesmus subspicatus</i>	–	72	EC10 (growth)	142 700	143 000 ^b
Blue–green alga	<i>Anabaena flos-aqua</i>	–	120	NOEC (growth)	470	470 ^b
Macrophyte	<i>Lemna gibba</i>	–	336	NOEC (growth)	14	14 ^b
	<i>Lemna minor</i>	–	168	EC10 (growth)	248	248 ^b
Diatom	<i>Navicula pelliculosa</i>	–	120	NOEC (growth)	7.7	7.7 ^b
	<i>Gomphonema</i> spp.	–	48	LOEC (growth)	50	20 ^d
	<i>Encyonema gracilis</i>	–	48	LOEC (growth)	50	20 ^d
	<i>Ulnaria ulna</i>	–	48	LOEC (growth)	50	20 ^d
	<i>Gomphonema gracile</i>	–	48	NOEC (growth)	≥500	500 ^b
	<i>Cymbella</i> sp.	–	48	NOEC (growth)	≥500	500 ^b
	<i>Achnantheidium minutissimum</i>	–	48	NOEC (growth)	≥500	500 ^b
	<i>Eunotia</i> cf. <i>incisa</i>	–	48	NOEC (growth)	≥500	500 ^b
	<i>Navicula cryptotenella</i>	–	48	NOEC (growth)	≥500	500 ^b
Crustacean	<i>Daphnia magna</i>	Neonate	504	NOEC (immobilisation)	13 000	13 000 ^b

a Values rounded to a maximum of 3 significant figures.

b Actual chronic NOEC/EC10.

c Default conversion from chronic EC50 to chronic NOEC: chronic EC50 ÷ 5 = chronic NOEC.

d Default conversion from chronic LOEC to chronic NOEC: chronic LOEC ÷ 2.5 = chronic NOEC.

e The measure of toxicity being estimated/determined: NOEC: no observed effect concentration; EC50: median effective concentration; EC10: 10% effect concentration; LOEC: lowest observed effect concentration.

f Formerly *Selenastrum capricornutum* and *Pseudokirchneriella subcapitata*.

– : Data not available / not stated.

4.2 Species sensitivity distribution

The cumulative frequency (species sensitivity) distribution (SSD) of the 16 chronic MCPA toxicity values reported in Table 1 is shown in Figure 1. The SSD was plotted using Burrlioz 2.0 software. The model was judged to provide a poor (visual) fit to the data, largely because of the multiple occurrences of the 20 µg/L and 500 µg/L toxicity values based on the diatom study of Wood et al. (2016) (see Section 4.1) and two large gaps in the dataset, each spanning approximately an order of magnitude in concentration.

Toxicant default guideline values for aquatic ecosystem protection: 4-chloro-2-methylphenoxy acetic acid (MCPA) in freshwater

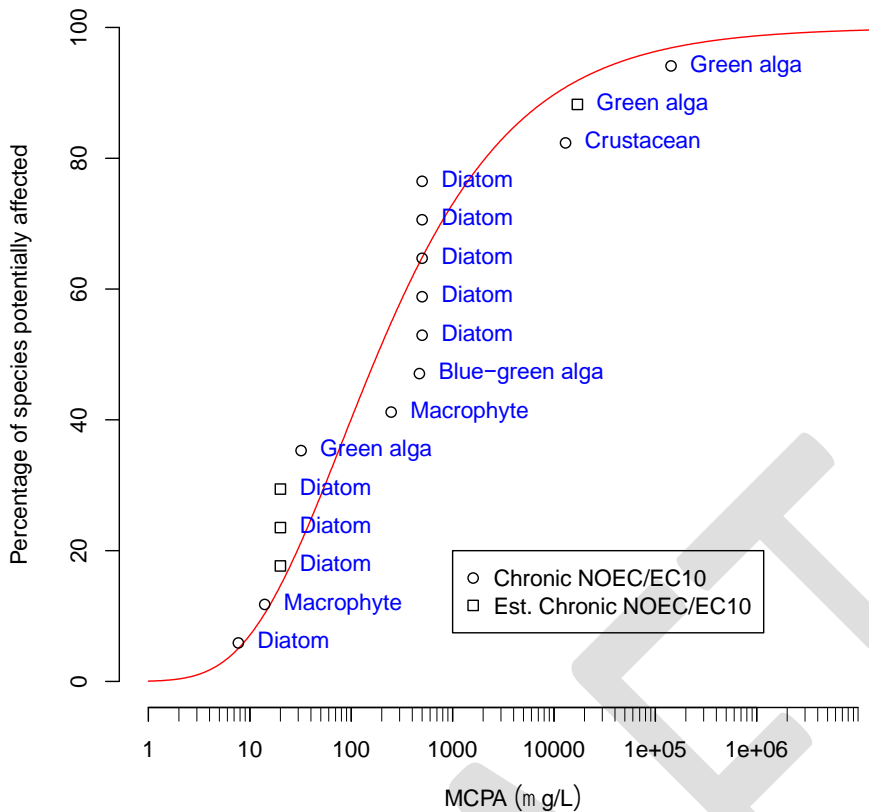


Figure 1 Species sensitivity distribution, MCPA in freshwater

4.3 Default guideline values

It is important that the DGVs (Table 2) 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 [website](#) (ANZG 2018).

The DGVs are expressed in terms of the dissolved active ingredient (MCPA) rather than commercial formulations, and do not relate to any of the breakdown products of MCPA. Although some of the MCPA toxicity data used to derive the DGVs may have included some toxicity due to MCPA metabolites, this has not been quantified; therefore, only MCPA (and not its metabolites) should be measured for comparison with the DGVs.

The MCPA DGVs for 99%, 95%, 90% and 80% species protection are shown in Table 2. The 95% species protection DGV is recommended for application to slightly-to-moderately disturbed ecosystems.

The DGVs were compared to the chronic and acute toxicity data (converted to chronic LOEC/NOEC data where necessary) that passed the quality assessment (i.e. 26 chronic values for 16 species and seven acute values for four species). The theoretical protection offered by the DGVs for 99%, 95%, 90% and 80% species protection is considered to be adequate.

Table 2 Default guideline values, MCPA in freshwater, moderate reliability

Level of species protection (%)	DGV for MCPA in freshwater ($\mu\text{g/L}$)
99	3
95	7.7
90	14
80	29

4.4 Reliability classification

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

- sample size—16 (preferred)
- type of toxicity data—chronic
- SSD model fit—poor (Inverse Weibull model).

It is important to recognise that several factors related to the nature of the dataset—specifically the >4 orders of magnitude data range, and the inclusion of '<' values as LOECs for three diatom species, a NOEC for one blue-green alga species and '≥' values as NOECs for five diatom species—introduce additional uncertainty to the DGVs that is not reflected in the moderate reliability classification.

Glossary

Term	Definition
acute toxicity	A lethal or adverse sublethal effect that occurs as the result of a short exposure period to a chemical relative to the organism's life span.
BCF (bioconcentration factor)	The ratio of the concentration of a contaminant in an organism to its concentration in the ambient water (or sediment) at a steady state. It can be expressed on a wet weight, dry weight or lipid weight basis.
CASRN	Chemical Abstracts Service Registry Number.
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.
DGV (default guideline value)	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'.
EC10	The concentration of a substance in water or sediment that is estimated to produce a 10% change in the response being measured or a certain effect in 10% of the test organisms relative to the control response, under specified conditions.
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.
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 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.
K_{oc}	Organic carbon-water partition coefficient. It is a measure of the mobility of a substance in soil.
K_{ow} / P_{ow}	Octanol-water partition coefficient. The ratio of a chemical's solubilities in n-octanol and water at equilibrium. The logarithm of K_{ow}/P_{ow} is used as an indication of a chemical's propensity for bioconcentration by aquatic organisms.
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.
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.
macrophyte	A member of the macroscopic plant life of an area, especially of a body of water; large aquatic plant.
MCPA	4-chloro-2-methylphenoxy acetic acid.
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.
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.

Toxicant default guideline values for aquatic ecosystem protection: 4-chloro-2-methylphenoxy acetic acid (MCPA) in freshwater

Term	Definition
SSD (species sensitivity distribution)	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.

DRAFT

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 assessment processes, MCPA in freshwater

Taxonomic group	Species	Life stage	Exposure duration (h)	Toxicity measure ^a (test endpoint)	Test medium	Temp. (°C)	Salinity (µS/cm)	pH	Concentration (µg/L)	Reference
Green alga	<i>Raphidocelis subcapitata</i> ^f	–	96	NOEC (growth)	–	–	–	–	32 ^b	OPP 2019
	<i>Scenedesmus quadricauda</i>	–	480	EC50 (growth)	HB-4 medium	25	–	–	85 100 ^c	Fargasova 1994
	<i>Desmodesmus subspicatus</i>	–	72	EC10 (growth)	Algal medium	21–25	–	7.9–8.3	142 700 ^b	Bisewska et al. 2012
Blue–green alga	<i>Anabaena flos-aqua</i>	–	120	NOEC (growth)	–	–	–	–	470 ^b	OPP 2019
Macrophyte	<i>Lemna gibba</i>	–	336	NOEC (growth)	–	–	–	–	14 ^b	OPP 2019
	<i>Lemna minor</i>	–	168	EC10 (growth)	K-medium	24	–	–	248 ^b	Cedergreen & Streibig 2005
Diatom	<i>Navicula pelliculosa</i>	–	120	NOEC (growth)	–	–	–	–	7.7 ^b	OPP 2019
	<i>Gomphonema</i> spp.	–	48	LOEC (growth)	River water	22–26	–	–	50 ^d	Wood et al. 2016
	<i>Encyonema gracilis</i>	–	48	LOEC (growth)	River water	22–26	–	–	50 ^d	Wood et al. 2016
	<i>Ulnaria ulna</i>	–	48	LOEC (growth)	River water	22–26	–	–	50 ^d	Wood et al. 2016
	<i>Gomphonema gracile</i>	–	48	NOEC (growth)	River water	22–26	–	–	≥500 ^e	Wood et al. 2016

Toxicant default guideline values for aquatic ecosystem protection: 4-chloro-2-methylphenoxy acetic acid (MCPA) in freshwater

Taxonomic group	Species	Life stage	Exposure duration (h)	Toxicity measure ^a (test endpoint)	Test medium	Temp. (°C)	Salinity (µS/cm)	pH	Concentration (µg/L)	Reference
	<i>Cymbella</i> sp.	–	48	NOEC (growth)	River water	22–26	–	–	≥500 ^e	Wood et al. 2016
	<i>Achnanthydium minutissimum</i>	–	48	NOEC (growth)	River water	22–26	–	–	≥500 ^e	Wood et al. 2016
	<i>Eunotia</i> cf. <i>incisa</i>	–	48	NOEC (growth)	River water	22–26	–	–	≥500 ^e	Wood et al. 2016
	<i>Navicula cryptotenella</i>	–	48	NOEC (growth)	River water	22–26	–	–	≥500 ^e	Wood et al. 2016
Crustacean	<i>Daphnia magna</i>	Neonate	504	NOEC (immobilisation)	–	–	–	–	13 000 ^b	OPP 2019

a The measure of toxicity being estimated/determined: NOEC: no observed effect concentration; EC50: median effective concentration; EC10: 10% effect concentration; LOEC: lowest observed effect concentration.

b Value used without adjustment.

c Default conversion from chronic EC50 to chronic NOEC used for DGV derivation: chronic EC50 ÷ 5 = chronic NOEC.

d Default conversion from chronic LOEC to chronic NOEC used for DGV derivation: chronic LOEC ÷ 2.5 = chronic NOEC.

e Value represents the highest MCPA concentration tested; thus reported as '≥' value, but used as 500 µg/L for the DGV derivation.

f Formerly *Selenastrum capricornutum* and *Pseudokirchneriella subcapitata*.

Appendix B: Modality assessment for MCPA

A modality assessment was undertaken for MCPA according to the four questions stipulated in Warne *et al.* (2018). These questions and their answers are listed below.

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

The mode of action for MCPA is to stimulate plant auxin hormones, which stimulates growth by increasing cell extension and cell differentiation and, ultimately, causes uncoordinated growth. Therefore, MCPA appears to be more toxic to plants than to other aquatic receptors.

Does the dataset suggest bimodality?

Visual representation of the data, calculation of the bimodality coefficient (BC), and the range of the effect concentrations are the recommended lines of evidence for evaluating whether the dataset is bimodal or multimodal. This is discussed as follows.

- The histogram of the raw effect concentration species sensitivity distribution (SSD) data (Figure B 1) could be interpreted as positively right-skewed, which is typical of concentration-based data (Warne *et al.* 2018). The log transformed histogram appears to follow a normal distribution, suggestive of the data being unimodal (Figure B 1).
- Data that span large ranges (>4 orders of magnitude) indicate potential for underlying bimodality or multimodality (Warne *et al.* 2018). The MCPA data span >4 orders of magnitude.
- When the BC is >0.555, it indicates that the data do not follow a normal distribution and may be bimodal. The BC of the log transformed data is 0.41 and does not support bimodality.

Based on these lines of evidence, the distribution of the log transformed dataset is generally in accordance with a unimodal normal distribution.

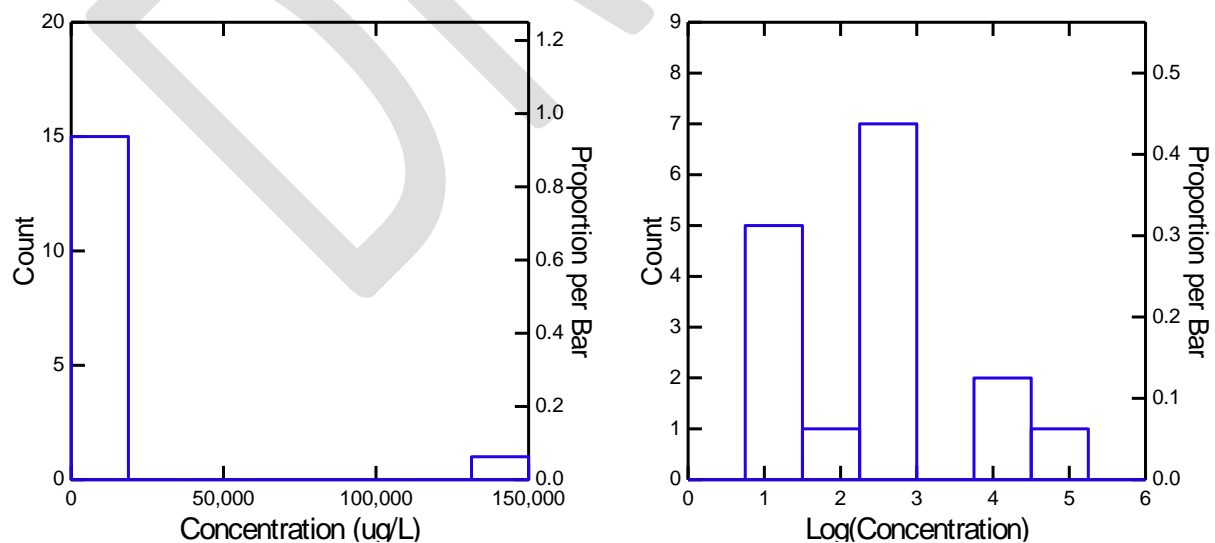


Figure B 1 Histogram, raw (left) and log transformed (right) MCPA data

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

The mode of action for MCPA affects organisms that respond to auxin hormones. Different organisms categorised as ‘plants’ in Table 6 of Warne et al. (2018) may have different levels of sensitivity to this toxicant. Therefore, the potential for taxa-specific sensitivity in the data was examined using box plots of the SSD data with the grouping variable ‘organisms considered to be taxonomically different’ in accordance with Table 6 of Warne et al. (2018).

As shown in Figure B 2, there does not appear to be any distinct groupings in the sensitivities of the organisms included in the SSD. The range in exposure concentrations for diatoms, green algae and macrophytes overlap and include the toxicity values for the crustacean and blue–green alga. The LOEC/NOECs for the diatoms and macrophytes are at the lower end of the concentration range for the green algae; however, it is unclear if this is representative of a true trend in the data or an artefact of sample size.

The low and uneven sample sizes (green algae (n=3), blue–green algae (n=1), crustaceans (n=1) and macrophytes (n=2) and diatoms (n=9) hinder the ability to detect bimodality or multimodality.

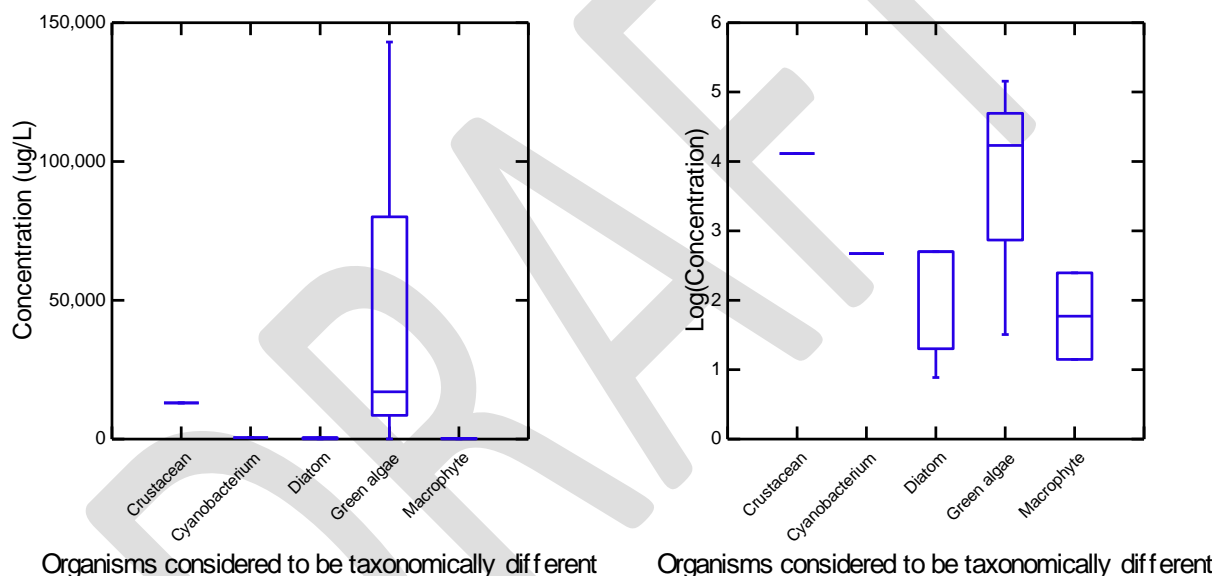


Figure B 2 Box plots, raw (left) and log transformed (right) MCPA data grouped by ‘organisms considered to be taxonomically different’

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 data are considered unlikely to be bimodal or multimodal. Although plants were generally more sensitive, the chronic data for the other organism (crustacean) was within the range of data for the macrophytes, diatoms, green algae, and blue–green alga. The weight of evidence supports use of the 16 chronic species included in the SSD.

References

- ACVM 2020. [Agricultural Compounds and Veterinary Medicines Register](#). Ministry for Primary Industries, New Zealand.
- ANZG 2018. Australian and New Zealand Guidelines for Fresh and Marine Water Quality. Australian and New Zealand Governments and Australian state and territory governments, Canberra, Australia. <https://www.waterquality.gov.au/anz-guidelines>.
- APVMA 2010. The reconsideration of registrations of products containing MCPA and the approvals of their labels, Spray Drift Review, Scope Document, dated April 2010. Australian Pesticides and Veterinary Medicines Authority.
- APVMA 2020. [Public Chemical Registration Information System Search](#). Australian Pesticides and Veterinary Medicines Authority.
- Benoit-Guyod, JL, Crosby, DG & Bowers, JB 1986. Degradation of MCPA by ozone and light. *Water Research*, 20, 67–72.
- Bernardini, G, Spinelli, O, Presutti, C, Vismara, C, Bolzacchini, E, Orlandi, M & Settimi, R 1996. Evaluation of the developmental toxicity of the pesticide MCPA and its contaminants phenol and chlorocresol. *Environmental Toxicology and Chemistry*, 15, 754–760.
- Bisewska, J, Sarnowska, EI & Tukaj, ZH 2012. Phytotoxicity and antioxidative enzymes of green microalga (*Desmodesmus subspicatus*) and duckweed (*Lemna minor*) exposed to herbicides MCPA, chloridazon and their mixtures. *Journal of Environmental Science and Health, Part B*, 47, 814–822.
- CCME 1999. Canadian water quality guidelines for the protection of aquatic life: MCPA. Canadian Environmental Quality Guidelines, 1999. Canadian Council of Ministers of the Environment, Winnipeg.
- Cedergreen, N & Streibig, JC 2005. The toxicity of herbicides to non-target aquatic plants and algae: assessment of predictive factors and hazard. *Pest Management Science*, 61, 1152–1160.
- Chau, ASY & Thomson, K 1978. Investigations of the integrity of seven herbicide acids in water samples. *Journal of Association of Official Analytical Chemists*, 61, 1481–1485.
- FAO 2013. Pesticide residues in food 2012. Joint FAO/WHO Meeting on Pesticide Residues. FAO Plant Production and Protection Paper 215. Report of the Joint Meeting of the FAO Panel of Experts on Pesticide Residues in Food and the Environment and the WHO Core Assessment Group on Pesticide Residues Rome, Italy, 11-20 September 2012. World Health Organization, Food and Agriculture Organization of the United Nations.
- Fargasova, A 1994. Toxicity determination of plant growth hormones on aquatic alga – *Scenedesmus quadricauda*. *Bulletin of Environmental Contamination and Toxicology*, 52, 706–711.

Toxicant default guideline values for aquatic ecosystem protection: 4-chloro-2-methylphenoxy acetic acid (MCPA) in freshwater

- Fochtman, P, Raszka, A & Nierzedzka, E 2000. The use of conventional bioassays, microbiotests, and some 'rapid' methods in the selection of an optimal test battery for the assessment of pesticides toxicity. *Environmental Toxicology. Special Issue: Ninth International Symposium on Toxicity Assessment*, 15, 5, 376–384.
- Frank, R & Logan, L 1988. Pesticide and industrial chemical residues at the mouth of the Grand, Saugeen and Thames rivers, Ontario, Canada 1981–85. *Archives of Environmental Contamination and Toxicology*, 17, 741–754.
- Giroux, I, Duchemin, M & Roy, M 1997. Conamination de l'eau par les pesticides dans les regions de culture intensive du maïs au Quebec. Campagnes d'échantillonnage de 1994 et 1995. Ministère de l'Environnement et de la Faune, Direction des écosystèmes aquatiques, Quebec, Canada.
- Grossmann, K 2000. Mode of action of auxin herbicides: A new ending to a long, drawn out story. *Trends in Plant Science*, 2000, 5, 506–508.
- Grossmann, K, Berghaus, R & Retzlaff, G 1992. Heterotrophic plant cell suspension cultures for monitoring biological activity in agrochemical research. Comparison with screens using algae, germinating seeds and whole plants. *Pest Management Science*, 35, 283–289.
- Growcom 2020. [Infopest](#). Growcom Australia Pty Ltd.
- Hughes, JS & Davis, JT 1964. Effects of selected herbicides on bluegill sunfish. Proceedings of Southeastern Fish and Wildlife Conference, 18, 480–482.
- Junghans, M, Backhaus, T, Faust, M, Scholze, M & Grimme, LH 2006. Application and validation of approaches for the predictive hazard assessment of realistic pesticide mixtures. *Aquatic Toxicology*, 76, 93–110.
- Linquist, NG 1974. An autoradiographic study on the distribution of the herbicide 4-chloro-2-methylphenoxyacetic acid in pregnant mice. *Toxicology and Applied Pharmacology*, 30, 227–236.
- Ma, J 2002. Differential sensitivity to 30 herbicides among populations of two green algae *Scenedesmus obliquus* and *Chlorella pyrenoidosa*. *Bulletin of Environmental Contamination and Toxicology*, 68, 275–281.
- Ma, J, Liang, W, Xu, L, Wang, S, Wei, Y & Lu, J 2001. Acute toxicity of 33 herbicides to the green alga *Chlorella pyrenoidosa*. *Bulletin of Environmental Contamination and Toxicology*, 66, 536–541.
- Ma, J, Lin, F, Wang, S & Xu, L 2003. Toxicity of 21 herbicides to the green alga *Scenedesmus quadricauda*. *Bulletin of Environmental Contamination and Toxicology*, 71, 594–601.
- Ma, J, Wang, S, Wang, P, Ma, L, Chen, X & Xu, R 2006. Toxicity assessment of 40 herbicides to the green alga *Raphidocelis subcapitata*. *Ecotoxicology and Environmental Safety*, 63, 456–462.
- Ma, J, Xu, L & Wang, S 2002. A quick, simple, and accurate method of screening herbicide activity using green algae cell suspension cultures. *Weed Science*, 50: 555–559.

Toxicant default guideline values for aquatic ecosystem protection: 4-chloro-2-methylphenoxy acetic acid (MCPA) in freshwater

Maathuis, H, Wasiuta, V, Nicholaichuk, W & Grover, R 1988. Study of herbicides in shallow groundwater beneath three irrigated sites in Outlook Irrigation District, Saskatchewan: Results of 1987 field investigations. SRC Publication Number R0844-13-E-88. Saskatchewan Research Council, Regina, Canada.

MCPA Task Force II 1993a. Special study: Dissociation of MCPA DMAS in water. Industry Task Force II on MCPA Research Data, Research Triangle Park, NC.

MCPA Task Force II 1993b. Hydrolysis of 14C-MCPA buffered aqueous solutions. Industry Task Force II on MCPA Research Data, Research Triangle Park, NC.

MCPA Task Force II 1993c. MCPA acid: Toxicity to the marine diatom, *Skeletonema costatum*. Industry Task Force II on MCPA Research Data, Springborn Laboratories Inc., Research Triangle Park, NC.

MCPA Task Force II 1993d. Hydrolysis of 14C-MCPA-2-EHE in buffered aqueous solutions. Industry Task Force II on MCPA Research Data, Research Triangle Park, NC.

Mierzejewska, E, Urbaniak, M, Zagibajło, K, Vangronsveld, J & Thijs, S 2022. [The effect of syringic acid and phenoxy herbicide 4-chloro-2-methylphenoxyacetic acid \(MCPA\) on soil, rhizosphere, and plant endosphere microbiome](#). *Frontiers in Plant Science*, 13.

Morton, PA, Fennell, C, Cassidy, R, Doody, D, Fenton, O, Mellander, PE & Jordan, P 2019. [A review of the pesticide MCPA in the land-water environment and emerging research needs](#). *WIREs Water*, 7, 1, e1402.

NCBI 2020. [PubChem Database. \(4-Chloro-2-methylphenoxy\)acetic acid, CID=7204](#). National Center for Biotechnology Information, National Library of Medicine, USA.

Nielsen, LW & Dahllöf, I 2007. Direct and indirect effects of the herbicides glyphosate, bentazone and MCPA on eelgrass (*Zostera marina*). *Aquatic Toxicology*, 82, 47–54.

O'Mullane, M & Moretto, A 2013. MCPA. In: Pesticide residues in food – 2012. Toxicological evaluations. Joint meeting of the FAO Panel of Experts on Pesticide Residues in Food and the Environment and the WHO Core Assessment Group on Pesticide Residues, Rome, Italy, 11–20 September 2012. World Health Organization, Food and Agriculture Organization of the United Nations, 653–724.

OPP 2019. [Office of Pesticide Programs Pesticide Ecotoxicity Database](#). United States Environmental Protection Agency, Southern Integrated Pest Management Center.

Rippy, MA, Deletic, A, Black, J, Aryal, R, Lampard, JL, Tang, JY, McCarthy, D, Kolotelo, P, Sidhu, J & Gernjak, W 2017. Pesticide occurrence and spatio-temporal variability in urban run-off across Australia. *Water Research*, 115, 245–255

Roberts, DM, Seneviratne, R, Mohammed, F, Patel, R, Senarathna, L, Hittarage, A & Eddleston, M 2005. Intentional self-poisoning with the chlorophenoxy herbicide 4-chloro-2-methylphenoxyacetic acid (MCPA). *Annals of Emergency Medicine*, 46, 3, 275–284.

Toxicant default guideline values for aquatic ecosystem protection: 4-chloro-2-methylphenoxy acetic acid (MCPA) in freshwater

Shafiei, TM & Costa, HH 1990. The susceptibility and resistance of fry and fingerlings of *Oreochromis mossambicus* Peters to some pesticides commonly used in Sri Lanka. *Journal of Applied Ichthyology*, 6, 73–80.

Soderquist, CJ & Crosby, DG 1975. Dissipation of 4-chloro-2-methylphenoxyacetic acid (MCPA) in a rice field. *Pest Management Science*, 6, 17–33.

USEPA 2004. Reregistration Eligibility Decision (RED) for MCPA (2-methyl-4-chlorophenoxyacetic acid) List A Case 0017, 30 September 2004. Office of Prevention, Pesticides and Toxic Substances, United States Environmental Protection Agency, Washington, DC.

Von Stackelberg, K 2013. [A systematic review of carcinogenic outcomes and potential mechanisms from exposure to 2,4-D and MCPA in the environment](#). *Journal of Toxicology*, 10.1155/2013/371610.

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.

WHO 2003. MCPA in drinking-water: Background document for development of WHO Guidelines for Drinking-water Quality. WHO/SDE/WSH/03.04/38. World Health Organisation, Geneva, Switzerland.

Wood, RJ, Mitrovic, SM, Lim, RP & Kefford, BJ 2016. How benthic diatoms within natural communities respond to eight common herbicides with different modes of action. *Science of The Total Environment*, 557–558, 636–643.

WSSA 1989. Herbicide Handbook. 6th edition. Weed Science Society of America, Champaign, Illinois, US.