ACUTE COPPER AND ZINC WATER QUALITY GUIDELINE VALUES FOR AOTEAROA: USER GUIDE

The metals copper (Cu) and zinc (Zn) are among the most ubiquitous contaminants in freshwater aquatic environments, due to their widespread use for many purposes. Although both metals are essential trace elements, when they are present in high concentrations, they can become toxic to fish, micro- and macroinvertebrates, plants and algae living in water. Excessive copper and zinc can harm aquatic organisms by disrupting their normal biological functions, affecting growth, reproduction, and survival. These effects can happen within hours or over a few days, depending on the metal concentration, the organism's sensitivity, and the water chemistry.

Acute GVs are expected to be useful in managing effects of intermittent or short-term discharges such as stormwater, short-term dewatering discharges, spills, or runoff from fungicide/pesticide spraying operations. They could also be useful in assessing risks within mixing zones of continuous discharges, such as industrial and municipal wastewaters.

The acute guideline values

The acute GVs for copper and zinc have been developed specifically for Aotearoa New Zealand to assist in managing the effects of metals in aquatic environments. The GVs have been derived generally following the process used for Australian New Zealand Guidelines for Fresh & Marine Water Quality[2, 3].

The bioavailability and toxicity of copper and zinc are affected by pH, water hardness and dissolved organic carbon (DOC) concentrations (collectively termed toxicity modifying factors (TMFs)) and these factors are accounted for in bioavailability models. This means **the acute GVs are not a single number** (or set of numbers) but differ with water chemistry and are best expressed as equations. These copper acute GVs increase (i.e., copper becomes less toxic) with *increasing* pH, water hardness and DOC concentrations. The zinc acute GVs increase (i.e., zinc becomes less toxic) with *decreasing* pH and *increasing* water hardness and DOC concentrations.

Copper (bioavailability-adjusted GV) for 95% species protection:

$$Copper\ acute\ GV_{95} = \exp(-6.6 + 0.78 \times \mathrm{pH} + 0.58 \times \ln Hardness + 0.70 \times \ln DOC)$$

Zinc (bioavailability-adjusted GV) for 95% species protection:

$$Zinc\ acute\ GV_{95} = \exp(2.3 - 0.12 \times \mathrm{pH} + 0.60 \times \ln Hardness + 0.13 \times \ln DOC)$$

where guideline values shown are for 95% species protection, dissolved copper or zinc concentrations are in µg/L, hardness is measured in mg/L as $CaCO_3$ and DOC is measured in mg/L. Ln refers to natural logarithm. Equations for other levels of species protection are provided on page 4.

Key terminology

Acute toxicity	A lethal or adverse sub-lethal effect that occurs after exposure to a chemical for a short period relative to the organism's life span
Bioavailability	A measure of the rate and extent to which a substance (such as a metal) is taken up by an organism and reaches the site of action where toxicity can occur
Calculated acute GV	Acute GV calculated for a combination of water chemistry (pH, hardness or DOC)
DGV	Default guideline value; a term used by ANZG [4] to describe guideline values (GVs) for generic application (different to site-specific or local GVs)
DOC	Dissolved organic carbon; measurement of organic matter in solution, based on the carbon content (using a carbon analyser), after passing through a 0.45 µm filter
mg/L	A unit of concentration, equivalent to parts per million
µg/L	A unit of concentration, equivalent to parts per billion

This document should be referred to as:

Gadd J; Hickey C; Snelder T. 2024. Acute copper and zinc water quality guideline values for Aotearoa. Acute copper and zinc water quality guideline values for Aotearoa: User guide. Report for Ministry for the Environment, 8 November 2024. 12 p. https://environment.govt.nz/publications/acute-copper-and-zinc-water-quality-guideline-values-for-aotearoa-user-guide

For further details on the derivation of these acute guideline values see:

Gadd J; Hickey C; Snelder T. 2024. Acute copper and zinc water quality guideline values for Aotearoa. Technical report of the derivation including bioavailability model selection. Report for Ministry for the Environment, 8 November 2024. 260 p. https://environment.govt.nz/publications/acute-copper-and-zinc-water-quality-guideline-values-for-aotearoa-technical-report-of-the-derivation-including-bioavailability-model-evaluation

Also see: https://www.waterquality.gov.au/anz-guidelines/guideline-values/default/water-quality-toxicants for details of the chronic guideline values

Toxicity of copper and zinc and effects of water chemistry

The acute toxicity of copper primarily stems from its ability to disrupt cellular ion regulation. Copper ions (Cu^{2+}) interfere with the function of sodium (Na^{+}) channels in the gills of fish and other aquatic organisms, leading to an imbalance in sodium homeostasis. This disruption can cause a loss of cellular integrity, leading to cell death, impaired respiratory function, and eventually, organism mortality. Depending on the species, length of exposure and the water chemistry (see below/inset box), mortality thresholds (death of a small proportion of organisms) can occur at concentrations of 1-12,000 µg/L (0.001-12 mg/L).

The main mechanism for zinc toxicity is by reducing uptake of calcium (an essential element), though zinc also interferes with transport of other ions. This interference can result in an inability to maintain proper ionic balance and acid-base equilibrium. Other mechanisms can lead to oxidative stress and impairment of enzyme and protein functions. Overall, at higher concentrations zinc exposures can lead to metabolic failure, lethargy, loss of equilibrium, and death. The thresholds for these effects occur at concentrations of 20-24,000 µg/L (0.02-24 mg/L), depending on the species, length of exposure, and the water chemistry.

Water chemistry conditions influence how toxic copper and zinc are to aquatic organisms by affecting their environmental fate, speciation and bioavailability. Metals are distributed between:

- particulate fraction: adsorbed to particulate matter (included when measuring "total" copper or zinc), and
- dissolved fraction: found in solution (measured when filtering a sample prior to analysis).

Particulate forms are not readily bioavailable. Although they may be important for some species exposed via their diet, this exposure route is not considered for water quality guidelines.

Not all of the dissolved fraction is bioavailable; this depends on the water chemistry. In most natural waters, a high proportion of copper and a smaller proportion of zinc will be bound to dissolved organic matter (DOM, measured in water as dissolved organic carbon, DOC), and not readily available for uptake by aquatic organisms. The hardness of the water (concentration of calcium and magnesium ions) also influences the bioavailability. Calcium and magnesium compete with both metals for the binding and uptake sites (such as fish gills) on aquatic organisms, reducing metal uptake and therefore toxicity. The pH of water affects copper and zinc toxicity in opposite ways. Copper toxicity is higher at low pH, as a greater proportion is present in more bioavailable forms. At higher pH, copper hydroxides and carbonates become more prevalent, and these forms are less soluble and of lower bioavailability. Although zinc is also more soluble at lower pH, the concentration of hydrogen ions (H^{+}) is higher. These hydrogen ions compete with zinc for binding sites on biological organisms (just like calcium and magnesium), such as fish gills. This competition effect is stronger for zinc than for copper and outweighs the increased solubility of zinc.

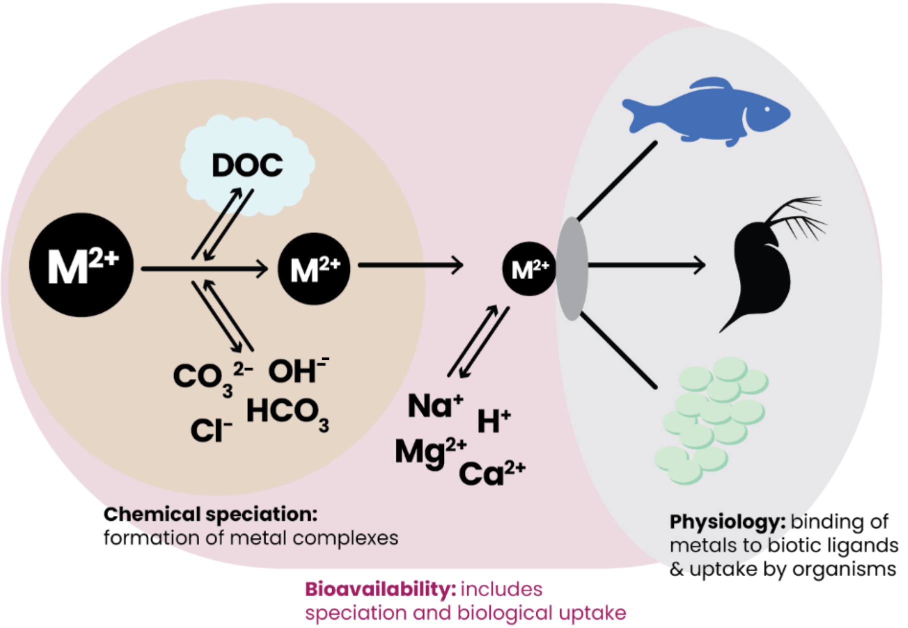


Figure 1: Schematic of metals speciation and bioavailability. M^{2+} represents metals, size of circle represents concentration, which is reduced by interactions with DOC and inorganic species, and by competition for biotic ligands.

Where and how to use the acute guideline values

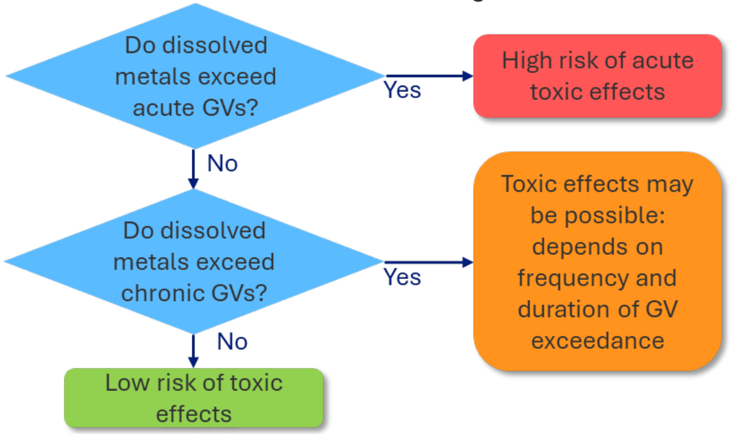
Acute water quality guideline values (GVs) are designed to assist in understanding and managing the **short-term** exposures to copper and zinc. The acute GVs are most appropriate for a timeframe of up to 96 hours (acute GVs would be conservative when used for very short exposures, minutes to hours).

The acute GVs can be used as a screening assessment for exposures of minutes to hours (for example, sampling during storm events). If the metal concentrations do not exceed the acute GVs, there would be high confidence the ecosystem is protected from acute effects. If those concentrations exceed the acute GVs, this indicates a high likelihood for acute toxicity. An adverse effect may or may not occur - this depends on the magnitude and duration of that exceedance.

Acute GVs may under-estimate toxicity risks when used to assess exposures of a week or more. **Chronic DGVs are appropriate for that timeframe**. If, samples from monthly monitoring programmes exceed acute GVs, this indicates potential for acute toxicity. In that case, further action should be taken. That action could include more frequent sampling to assess the duration of an exceedance, and/or targeted sampling that investigates whether acute GVs are regularly exceeded (e.g., during high flows).

Multiple short-term exposures may result in harmful effects even if concentrations are below these acute GVs because of the repeated nature of the exposures [1]. Toxicity assessments are particularly challenging when exposure concentrations vary over time as risks depend on the frequency, duration and concentrations. A framework for assessments of intermittent discharges is provided here.

Flow chart for considering acute and chronic toxicity risks from short-duration and intermittent discharges:



The GVs are only applicable within the water chemistry range shown below and in waters with salinity <1 ppt. The applicability ranges relate to the validated range of the bioavailability models that were used to derive and adjust the guideline values.

Toxicity modifying factors included for these guideline values	Measure-ment	Applicable range	
		Copper	Zinc
pH influences metal solubility and speciation but also provides hydrogen ions that compete with zinc (and to a lesser extent copper) for uptake into biological organisms.	Measure in field or lab	5.0-9.0	5.4-8.5
Water **hardness** (calcium and magnesium content) decreases metal bioavailability. Ca^{2+} and Mg^{2+} bind to uptake sites on aquatic organisms (like gills), blocking the channels for metal uptake.	Calculate from calcium & magnesium	3-898 mg $CaCO_3$/L	14-826 mg $CaCO_3$/L
Dissolved organic carbon (DOC) from leaves and humic material binds dissolved copper and zinc reducing the amount able to be absorbed by living organisms.	Measure as DNPOC	0.1-33 mg/L	0.1-22 mg/L

These GVs are for **dissolved** copper and zinc. Water samples should be filtered (0.45 µm filter) before analysis. Total copper and zinc can be compared to the GVs, and this will provide a conservative indication of the risk (likely over-estimating the risk). NEMS[8] provides standards for sampling and analysis of dissolved metals and all three TMFs.

Particular attention should be given to the recommended methods for DOC – this should be analysed as DNPOC when requesting this analysis from a laboratory. An alternative method for DOC, based on measuring total carbon then total inorganic carbon and subtracting these to give organic carbon, can result in poor resolution for the DOC measurement.[a]

The acute GVs are designed to be applied within freshwater receiving environments including streams, rivers and lakes. They can be used in assessing the potential for toxicity for fish migrating through a mixing zone downstream of a point source discharge. They are not intended as discharge limits, to be applied at the end-of-pipe (though if applied there they would be conservative).

[a] This method does remove volatile organics such as some light hydrocarbons but these are not relevant to the measurement of DOC for adjustment of metal guideline values. For further details on this method see: https://www.hill-labs.co.nz/media/pwlfsvse/4073v5_technical-note-total-organic-carbon-toc-water.pdf

Guideline values at different water chemistry combinations

The hardness, pH and DOC of a sample are used to calculate adjusted acute GVs for each metal using the equations below for each level of protection:

$$\text{Copper GV}_{99} = \exp\left(-7.2 + 0.78\,pH + 0.58 \times \ln(hard.) + 0.70 \times \ln(DOC)\right)$$

$$\text{Copper GV}_{95} = \exp\left(-6.6 + 0.78\,pH + 0.58 \times \ln(hard.) + 0.70 \times \ln(DOC)\right)$$

$$\text{Copper GV}_{90} = \exp\left(-6.3 + 0.78\,pH + 0.58 \times \ln(hard.) + 0.70 \times \ln(DOC)\right)$$

$$\text{Copper GV}_{80} = \exp\left(-5.8 + 0.78\,pH + 0.58 \times \ln(hard.) + 0.70 \times \ln(DOC)\right)$$

$$\text{Zinc GV}_{99} = \exp\left(1.75 - 0.12 \times pH + 0.6 \times \ln(hard.) + 0.13 \times \ln(DOC)\right)$$

$$\text{Zinc GV}_{95} = \exp\left(2.5 - 0.12 \times pH + 0.6 \times \ln(hard.) + 0.13 \times \ln(DOC)\right)$$

$$\text{Zinc GV}_{90} = \exp\left(2.9 - 0.12 \times pH + 0.6 \times \ln(hard.) + 0.13 \times \ln(DOC)\right)$$

$$\text{Zinc GV}_{80} = \exp\left(3.4 - 0.12 \times pH + 0.6 \times \ln(hard.) + 0.13 \times \ln(DOC)\right)$$

where guideline values (GVs) are as dissolved copper or zinc concentration (µg/L) for the level of species protection shown in subscript; hard. Is hardness is measured in mg/L as $CaCO_3$ and DOC is measured in mg/L. Ln refers to natural logarithm.

Bioavailability-adjusted acute GVs are shown in Tables 1 (copper) and 2 (zinc) for different pH, hardness and DOC concentrations. These are calculated using the equations above. Adjusted acute GVs can be used where dissolved copper or zinc concentrations exceed the interim Tier 1 GVs (see page 5).

Table 1: **Copper** acute GVs (µg/L) for 95% species protection at different pH, hardness and DOC concentrations. Interim tier 1 acute GV for 95% species protection is 1.3 µg/L.

Copper acute GV_{95} for 95% species protection						
pH	**DOC (mg/L)**	**Hardness (mg $CaCO_3$/L)**				
		15	**30**	**60**	**120**	**240**
6.5	**0.5**	0.6	0.9	1.4	2.0	3.1
7.5	**0.5**	1.3	2.0	3.0	4.4	6.6
8.5	**0.5**	2.9	4.3	6.5	9.7	14
6.5	**1.5**	1.3	2.0	2.9	4.4	6.6
7.5	**1.5**	2.9	4.3	6.4	9.6	14
8.5	**1.5**	6.3	9.3	14	21	31
6.5	**6**	3.5	5.2	7.8	12	17
7.5	**6**	7.6	11	17	25	38
8.5	**6**	17	25	37	55	82

Table 2: **Zinc** acute GVs (µg/L) for 95% species protection at different pH, hardness and DOC concentrations. Interim tier 1 acute GV for 95% species protection is 24 µg/L.

Zinc acute GVs for 95% species protection						
pH	**DOC (mg/L)**	**Hardness (mg $CaCO_3$/L)**				
		15	**30**	**60**	**120**	**240**
6.5	**0.5**	26	39	60	91	137
7.5	**0.5**	23	35	53	80	122
8.5	**0.5**	20	31	47	71	108
6.5	**1.5**	30	45	68	103	157
7.5	**1.5**	26	40	60	92	139
8.5	**1.5**	23	35	54	81	123
6.5	**6**	35	54	81	123	187
7.5	**6**	31	48	72	109	166
8.5	**6**	28	42	64	97	147

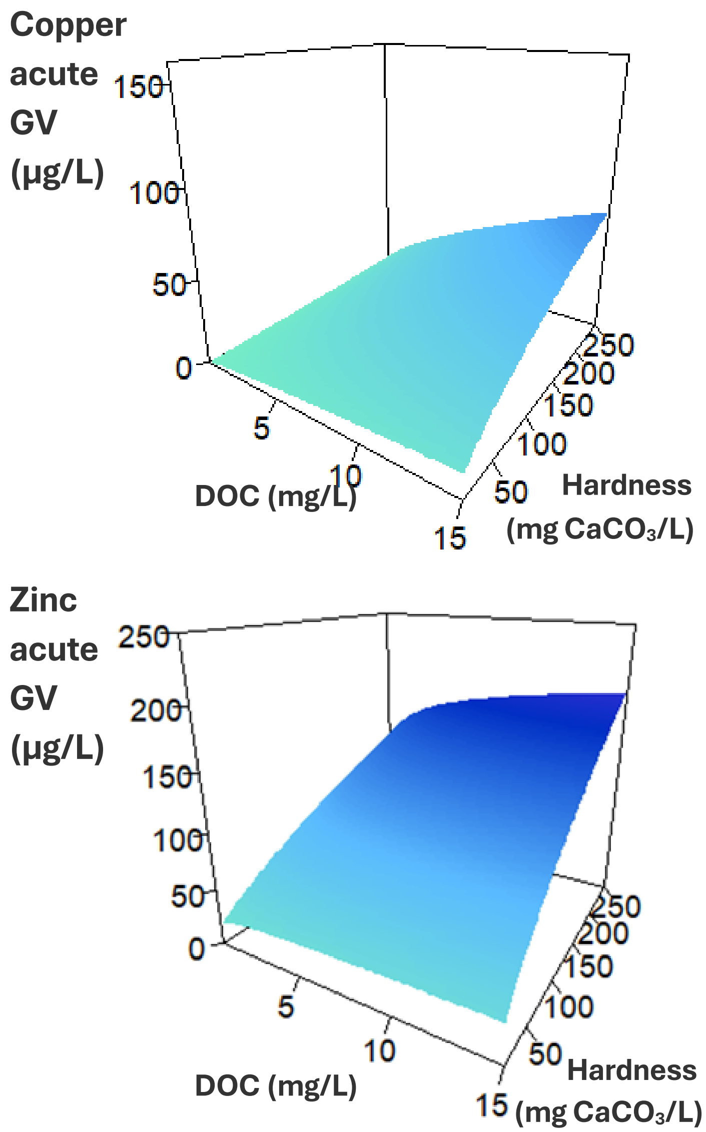
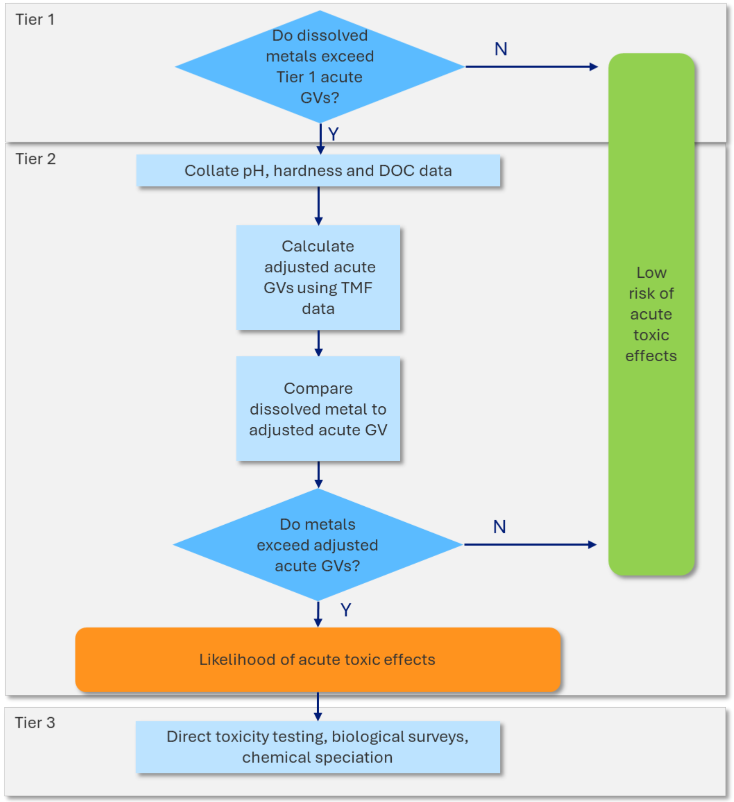


Figure 2: Illustration of **copper** (top) and **zinc** (bottom) acute GVs (for 95% species protection) as a function of hardness and DOC. Acute GVs calculated at pH 7.5 for these two plots, illustrations at different pH values are shown in technical report[5].

A tiered approach is recommended for implementing these acute GVs, analogous to advice for the Australian and New Zealand chronic DGVs.

Tiered approach to risk assessment



In **Tier 1** of this approach measurements of dissolved copper and zinc are first compared to Tier 1 acute GVs. These acute GVs represent conditions where bioavailability is high, aiming to protect 95% of locations that would be monitored. This approach aims to minimise instances where there is a risk of toxicity, but the assessment finds there is low risk. If metal concentrations exceed those acute GVs, then the assessment progresses to tier 2.

The **interim Tier 1 GVs** provided are based on the 10th percentile values for hardness, DOC and pH (90th percentile of pH for zinc) of measured waters in Aotearoa. However, these may not be protective in all environments, especially pristine waters, where pH, hardness and/or DOC are below the 10th percentile, and the GVs should be calculated for those waters based on the site-specific water chemistry. These interim Tier 1 GVs are intended for use only until definitive values can be developed using a more robust process, to replace those provided in Table 3. Note that the pH used for these interim Tier 1 GVs differs between copper (pH 7.0) and zinc (pH 8.2).

Table 3: Interim Tier 1 (bioavailability-adjusted) dissolved copper and zinc acute guideline values (GVs)* and chronic guideline values (DGVs) for the protection of aquatic life in freshwater.

Level of species protection	Dissolved copper		Dissolved zinc	
	Acute GVs † (µg/L)	Chronic DGV‡ (µg/L)	Acute GVs # (µg/L)	Chronic DGV § (µg/L)
99% (most protective ¶)	0.7	0.2	11	0.51
95% (applicable to most human-modified environments)	1.3	0.5	24	1.9
90% (applicable to highly disturbed systems)	1.7	0.7	36	3.4
80% (least protective)	2.9	1.3	59	6.6

*These GVs recommended for initial screening of dissolved copper and zinc concentrations. These are calculated at the pH, hardness and DOC specified. For greater certainty in assessing risks of acute toxicity, GVs should be recalculated for sample-specific pH, DOC and hardness using equations on page 4. Note that acute GVs are only applicable within a specified range of water chemistry – see page 3.

¶See https://www.waterquality.gov.au/anz-guidelines/resources/key-concepts/level-of-protection

† Calculated acute guideline values at pH 7.0, hardness 17 mg $CaCO_3$/L, DOC 0.7 mg/L from equations provided on page 4.

‡ Draft chronic default guideline values, as published by ANZG[6], for DOC ≤0.5 mg/L (pH and hardness not included in adjustment of chronic copper DGVs).

Calculated acute guideline values at pH 8.2, hardness 17 mg $CaCO_3$/L, DOC 0.7 mg/L from equations provided on page 4.

§ Draft chronic default guideline values, as published by ANZG[7], for pH 8.2, hardness 17 mg $CaCO_3$/L, DOC 0.7 mg/L.

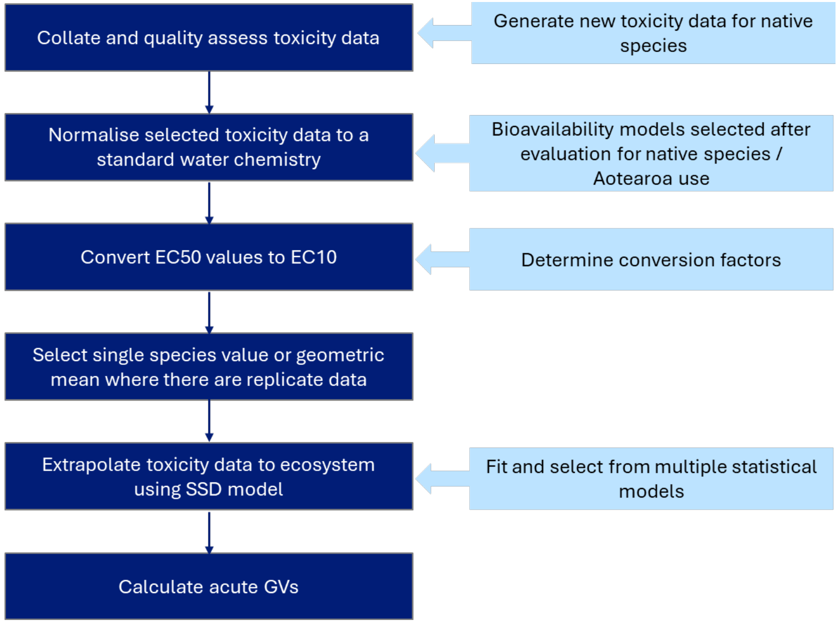
In **Tier 2**, pH, hardness and DOC (TMF) data are required to provide a sample-specific assessment. Dissolved metal concentrations can be compared to adjusted acute GVs, calculated for each sample using the TMF measurements. Conversely, if Tier 1 GVs are established (replacing the interim Tier 1 GVs) the TMFs can be used to estimate the bioavailable metal concentrations, which can then be compared to the tier 1 GV. If dissolved metals exceed the adjusted acute GVs, or the estimated bioavailable metal concentrations exceed the tier 1 GVs, then there is a **high likelihood for acute toxicity** to occur. Adverse effects may not always occur – this depends on factors such as the duration of exceedance and the sensitivity of the organisms present in the ecosystem.

A **tier 3** step could be added, which could include acute toxicity testing of water samples and/or looking at other lines of evidence such as biological surveys.

If there is no information for the TMFs, the assessment can stop at tier 1, however this would be a highly precautionary and conservative assessment of toxicity risk.

How the guideline values were derived

The process outlined by Warne et al. [2] for Australia and New Zealand water quality guidelines for toxicants was generally followed for these acute guideline values.

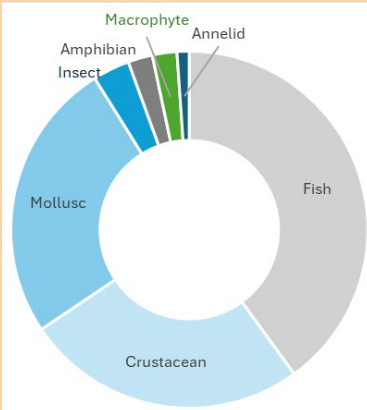
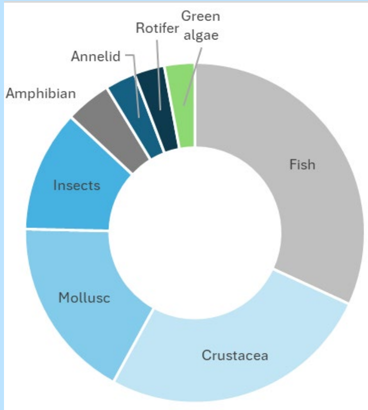


First toxicity data were collated from existing guidelines, collations and peer-reviewed sources; and from New Zealand researchers (for native species). New data were also generated through toxicity testing with one species (in a range of water chemistries). Only data from short-term toxicity tests were included – generally 96 hours for fish/amphibians; 48 hours for invertebrates and 24 hours for algae. Although low effect concentrations (e.g., EC10) are recommended for developing guideline values (see Batley et al. [3]) few short-term studies report this statistic. Most report EC50 data (the concentration at which 50% of test organisms show an effect, such as mortality) and so these were used to increase the breadth of data and the number of species included when deriving the GVs.

All data were screened and ranked based on their quality and reporting of the data required (including pH, hardness and DOC). Primary ranked data (metals, pH, hardness and DOC measured in test solutions) were used where possible, followed by secondary (metals measured in solutions or stock solutions; two of pH, hardness and DOC reported, the third could be estimated with high certainty). Tertiary-ranked data (metals measured in solutions or stock solutions; one of pH, hardness and DOC reported, the other two could be estimated with high certainty) were only accepted for native species.

All accepted data were normalised to a standard water chemistry (pH 7.5, hardness 30 mg/L and DOC 0.5 mg/L) to account for the different water chemistry used in each test. This ensures that the toxicity values are comparable within and between species, and that differences in values relate to differences in species sensitivity, not water chemistry. This normalisation used multiple linear regression (MLR) equations[9]. Those models were developed as alternatives to the more mechanistic biotic ligand models (BLM) that are used to account for metal bioavailability. The MLR models were evaluated for both native species and a range of other fish/invertebrate/algal species and compared favourably to the BLM[5]. For both copper and zinc, the MLRs included pH, hardness and DOC, the key modifiers of toxicity for these metals.

Summary of toxicity data included

Copper	Zinc
90 species	69 species
7 Native species	11 Native species
7 taxonomic groups	8 taxonomic groups
	
75% data primary-ranked pH reported for 99.7% data DOC reported for 91% data Hardness reported for 72% data	32% data primary ranked pH reported for 100% data DOC reported for 65% data Hardness reported for 100% data

Guideline value derivation continued

All normalised data were converted from EC50 values to estimates of low effect concentration (EC10) to ensure that the final GVs are protective of aquatic ecosystems. This conversion used different factors for vertebrates, invertebrates and algae, based on reported EC50 to EC10 ratios for each metal. The resulting toxicity data (converted EC10 values) used to derive the GVs ranged from 0.9 to 12,400 µg/L for copper, and 16 to 23,800 µg/L for zinc.

The converted EC10s were then summarised to single values representing the toxicity to each species. Those values were used in species sensitivity distribution models to extrapolate the toxicity data to the ecosystems requiring protection. This involves ranking the toxicity data according to sensitivity (lowest value to highest value, Figures 1 and 2).

Multiple different statistical distributions were fitted to the data using the ssdtools package in R[10] based on the recommendations for deriving toxicant guideline values in Australia and New Zealand[11]. Goodness of fit statistics were used to indicate the best fitting model and for zinc, where multiple models fitted almost as well, the ssdtools package was used to estimate the average fit. Guideline values were calculated from the fitted models for various levels of species protection (99%, 95%, 90% and 80%).

Native species were generally not the most sensitive species of those included to determine the guideline values. However, some of the most sensitive species are found in Aotearoa either naturally (such as the ubiquitous algae *Raphidocelis subcapitata,* which is not considered a unique native species) or as introduced species (such as rainbow trout and other salmonids).

Copper and zinc species sensitivity distributions

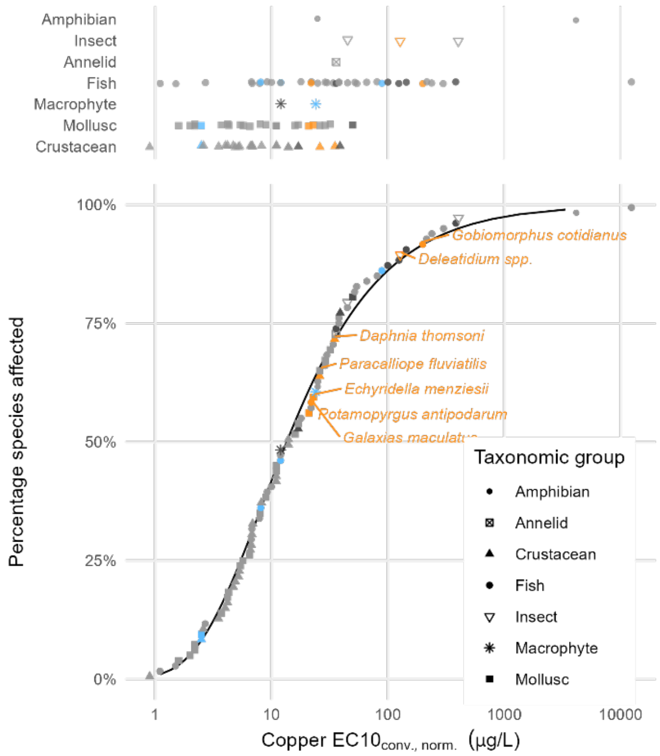


Figure 3: Species sensitivity distribution (SSD) for acute toxicity to dissolved **copper** in freshwater. Native species shown in orange and labelled; other species present in Aotearoa shown in blue. Black line indicates average fit of statistical distribution models fitted using the ssdtools package in R. Toxicity data were normalised to pH 7.5, hardness 30 mg/L as $CaCO_3$ and DOC 0.5 mg/L as described on page 6.

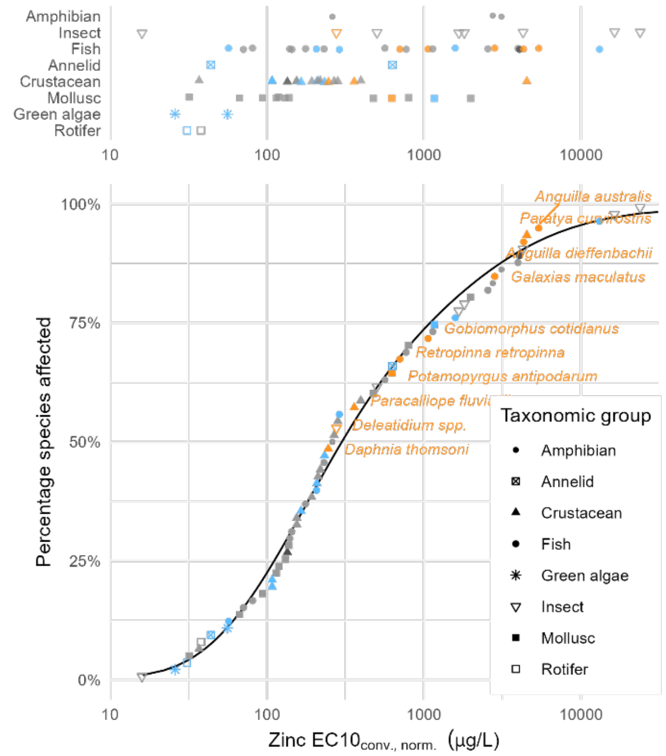


Figure 4: Species sensitivity distribution (SSD) for acute toxicity to dissolved **zinc** in freshwater. Native species shown in orange and labelled; other species present in Aotearoa shown in blue. Black line indicates average fit of statistical distribution models fitted using the ssdtools package in R. Toxicity data were normalised to pH 7.5, hardness 30 mg/L as $CaCO_3$ and DOC 0.5 mg/L as described on page 6.

Table 4: Toxicity data used to determine acute (short-term) **copper** guideline values (*in order of effect concentration*). Rows in bold are species native to Aotearoa.

Acute copper GV: ranked species data				
Rank	**Species**	**Taxonomic group**	**Effect and duration**	**Normalised, converted EC10 value (µg/L)**
1	*Scapholeberis mucronata* (water flea)	Crustacean	48-h mortality	0.9
2	*Acipenser transmontanus* (White sturgeon)	Fish	96-h growth	1.1
3	*Prosopium williamsoni* (Mountain whitefish)	Fish	96-h mortality	1.5
4	*Venustaconcha ellipsiformis* (Ellipse mussel)	Mollusc	24-h mortality	1.6
5	*Epioblasma capsaeformis* (Oyster mussel)	Mollusc	48-h mortality	2.0
6	*Villosa iris* (Rainbow mussel)	Mollusc	24-h mortality	2.2
7	*Potamilus ohiensis* (Pink papershell)	Mollusc	24-h mortality	2.2
8	*Lymnaea stagnalis* (Great pond snail)	Mollusc	96-h mortality	2.5
9	*Ceriodaphnia dubia* (Cladoceran)	Crustacean	48-h mortality	2.5
10	*Alona quadrangularis* (water flea)	Crustacean	48-h mortality	2.6
11	*Cottus bairdii* (Mottled sculpin)	Fish	96-h mortality	2.7
12	*Daphnia longispina* (water flea)	Crustacean	48-h mortality	3.5
13	*Lampsilis siliquoidea* (Lamp-mussel)	Mollusc	24-h mortality	3.9
14	*Alona* sp. (water flea)	Crustacean	48-h mortality	4.0
15	*Daphnia pulex* (water flea)	Crustacean	48-h mortality	4.2
16	*Leptodea leptodon* (Scaleshell)	Mollusc	48-h mortality	4.2
17	*Lithoglyphus virens* (Giant Columbia River spire shell)	Mollusc	96-h mortality	4.3
18	*Simocephalus exspinosus* (cladoceran)	Crustacean	48-h mortality	4.7
19	*Daphnia galeata* (water flea)	Crustacean	48-h mortality	4.9
20	*Ceriodaphnia reticulata* (water flea)	Crustacean	48-h mortality	5.3
21	*Daphnia magna* (water flea)	Crustacean	48-h mortality	5.4
22	*Lampsilis abrupta* (Pink mucket)	Mollusc	24-h mortality	5.4
23	*Villosa fabalis* (Rayed bean)	Mollusc	24-h mortality	5.7
24	*Lampsilis rafinesqueana* (Neosho mucket)	Mollusc	24-h mortality	6.5
25	*Disparalona rostrata* (water flea)	Crustacean	48-h mortality	6.6
26	*Ptychocheilus oregonensis* (Northern pikeminnow)	Fish	96-h mortality	6.7
27	*Daphnia obtusa* (water flea)	Crustacean	48-h mortality	6.7
28	*Simocephalus vetulus* (water flea)	Crustacean	48-h mortality	6.8
29	*Etheostoma rubrum* (Bayou darter)	Fish	96-h mortality	6.8
30	*Hyalella azteca* (Amphipod)	Crustacean	96-h mortality	6.9
31	*Oncorhynchus clarkii* (Cutthroat trout)	Fish	96-h mortality	7.9
32	*Juga plicifera* (Snail)	Mollusc	96-h mortality	8.0
33	*Eurycercus lamellatus* (water flea)	Crustacean	48-h mortality	8.2
34	*Oncorhynchus mykiss* (Rainbow trout)	Fish	96-h mortality	8.4
35	*Epioblasma triquetra* (Snuffbox)	Mollusc	24-h mortality	9.0
36	*Oncorhynchus apache* (Apache trout)	Fish	96-h mortality	9.2
37	*Pleuroxus truncatus* (water flea)	Crustacean	48-h mortality	11
38	*Acroperus harpae* (water flea)	Crustacean	48-h mortality	11
39	*Obovaria subrotunda* (Round hickorynut)	Mollusc	24-h mortality	11
40	*Epioblasma rangiana* (Northern riffleshell)	Mollusc	24-h mortality	11
41	*Oncorhynchus tshawytscha* (Chinook salmon)	Fish	96-h mortality	12
42	*Ceratophyllum demersum* (Rigid hornwort)	Macrophyte	96-h biomass	12
43	*Oncorhynchus kisutch* (Coho salmon)	Fish	96-h mortality	12
44	*Pimephales promelas* (Fathead minnow)	Fish	96-h mortality	13
45	*Chydorus sphaericus* (water flea)	Crustacean	48-h mortality	14
46	*Caridina* sp. (Shrimp)	Crustacean	48-h mortality	14
47	*Lampsilis fasciola* (Wavy-rayed lampmussel)	Mollusc	24-h mortality	16
48	*Daphnia carinata* (water flea)	Crustacean	48-h mortality	17
49	*Pomacea paludosa* (Florida applesnail)	Mollusc	96-h mortality	17
50	*Perca flavescens* (Yellow perch)	Fish	96-h mortality	18
51	*Poeciliopsis occidentalis* (Gila topminnow)	Fish	96-h mortality	21

Acute copper GV: ranked species data				
Rank	**Species**	**Taxonomic group**	**Effect and duration**	**Normalised, converted EC10 value (µg/L)**
52	***Potamopyrgus antipodarum* (Mud snail)**	**Mollusc**	**96-h mobility**	**21**
53	***Galaxias maculatus* (Inanga)**	**Fish**	**96-h mortality**	**22**
54	***Echyridella menziesii* (Freshwater mussel)**	**Mollusc**	**48-h mortality**	**23**
55	*Lemna aequinoctialis* (duckweed)	Macrophyte	96-h growth	24
56	*Gila elegans* (Bonytail chub)	Fish	96-h mortality	25
57	*Lithobates clamitans* (green frog)	Amphibian	96-h mortality	25
58	*Actinonaias ligamentina* (mucket)	Mollusc	24-h mortality	26
59	***Paracalliope fluviatilis* (Amphipod)**	**Crustacean**	**48-h mortality**	**26**
60	*Ptychobranchus fasciolaris* (Kidneyshell)	Mollusc	24-h mortality	29
61	*Salvelinus confluentus* (Bull Trout)	Fish	96-h mortality	29
62	*Scaphirhynchus platorynchus* (Shovelnose sturgeon)	Fish	96-h mortality	29
63	*Ligumia recta* (Black sandshell)	Mollusc	24-h mortality	32
64	*Etheostoma lepidum* (Darter)	Fish	96-h mortality	34
65	***Daphnia thomsoni* (water flea)**	**Crustacean**	**48-h mortality**	**35**
66	*Macquaria ambigua* (Golden perch)	Fish	96-h mortality	36
67	*Acrocheilus alutaceus* (Chiselmouth)	Fish	96-h mortality	38
68	*Entosphenus tridentatus* (Pacific lamprey)	Fish	96-h mortality	38
69	*Paratya australiensis* (shrimp)	Crustacean	96-h mortality	39
70	*Lumbriculus variegatus* (blackworm)	Annelid	48-h mortality	39
71	*Gasterosteus aculeatus* (Three-spined stickleback)	Fish	96-h mortality	45
72	*Rhithrogena hageni* (mayfly)	Insect	96-h mortality	45
73	*Hyridella depressa* (freshwater mussel)	Mollusc	48-h valve opening	50
74	*Pseudomugil tenellus* (Blue eye)	Fish	96-h mortality	52
75	*Etheostoma flabellare* (Darter)	Fish	96-h mortality	54
76	*Ptychocheilus lucius* (Colorado pikeminnow)	Fish	96-h mortality	66
77	*Etheostoma nigrum* (Darter)	Fish	96-h mortality	81
78	*Cyprinus carpio* (Common carp)	Fish	96-h mortality	89
79	*Melanotaenia nigrans* (Australian redtailed rainbowfish)	Fish	96-h mortality	100
80	*Mogurnda mogurnda* (Purple spotted gudgeon)	Fish	96-h mortality	130
81	***Deleatidium* spp. (Mayfly)**	**Insect**	**48-h mortality**	**130**
82	*Hypseleostris compressus* (Carp gudgeon)	Fish	96-h mortality	140
83	*Denariusa bandata* (Penny fish)	Fish	96-h mortality	220
84	***Gobiomorphus cotidianus* (Bully)**	**Fish**	**96-h mortality**	**220**
85	*Porochilus rendahli* (Eel-tailed catfish)	Fish	72-h mortality	240
86	*Lepomis macrochirus* (Bluegill)	Fish	96-h mortality	330
87	*Melanotaenia splendida inornata* (Chequered rainbowfish)	Fish	96-h mortality	380
88	*Chironomus decorus* (midge)	Insect	48-h mortality	390
89	*Lithobates catesbeianus* (American bullfrog)	Amphibian	96-h mortality	4200
90	*Notemigonus crysoleucas* (Golden shiner)	Fish	96-h mortality	12000

Table 5: Toxicity data used to determine acute (short-term) **zinc** guideline values (*in order of threshold effect concentration*). Rows in bold are species native to Aotearoa.

Acute Zinc GV: ranked species data				
Rank	**Species**	**Taxonomic group**	**Effect and duration**	**Normalised, converted EC10 value (µg/L)**
1	*Neocloeon triangulifer* (mayfly)	Insect	96-h mortality	16
2	*Raphidocelis subcapitata* (green algae)	Green algae	24-h population growth	26
3	*Euchlanis dilatata* (rotifer)	Rotifer	24-h mortality	31
4	*Leptoxis ampla* (round rocksnail)	Mollusc	96-h mortality	32
5	*Hyalella azteca* (amphipod)	Crustacean	96-h mortality	37
6	*Lecane quadridentata* (rotifer)	Rotifer	48-h mortality	38
7	*Limnodrilus hoffmeisteri* (red worm)	Annelid	96-h mortality	44
8	*Chlorella* sp. (PNG isolate) (green algae)	Green algae	24-h population growth	56
9	*Oncorhynchus mykiss* (Rainbow trout)	Fish	96-h mortality	57
10	*Lampsilis rafinesqueana* (Neosho mucket)	Mollusc	48-h mortality	67
11	*Cottus bairdi* (mottled sculpin)	Fish	96-h mortality	71
12	*Oncorhynchus clarkii* (Westslope Cutthroat trout)	Fish	96-h mortality	81
13	*Villosa vibex* (Southern rainbow mussel)	Mollusc	96-h mortality	94
14	*Ceriodaphnia dubia* (water flea)	Crustacean	48-h mortality	110
15	*Daphnia carinata* (water flea)	Crustacean	48-h mortality	110
16	*Pomacea paludosa* (applesnail)	Mollusc	96-h mortality	120
17	*Actinonaias pectorosa* (pheasant shell)	Mollusc	96-h mortality	120
18	*Epioblasma capsaeformis* (oyster mussel)	Mollusc	96-h mortality	130
19	*Paratya australiensis* (amphipod)	Crustacean	48-h mortality	130
20	*Lampsilis straminea claiborten* (rough fatmucket)	Mollusc	96-h mortality	140
21	*Prosopium williamsoni* (Mountain Whitefish)	Fish	96-h mortality	140
22	*Cottus confusus* (Shorthead Sculpin)	Fish	96-h mortality	140
23	*Ceriodaphnia reticulata* (water flea)	Crustacean	48-h mortality	150
24	*Simocephalus vetulus* (cladoceran)	Crustacean	48-h mortality	160
25	*Daphnia galeata* (cladoceran)	Crustacean	48-h mortality	170
26	*Acipenser transmontanus* (White sturgeon)	Fish	96-h mortality	180
27	*Simocephalus exspinosus* (cladoceran)	Crustacean	48-h mortality	190
28	*Salmo trutta* (brown trout)	Fish	96-h mortality	210
29	*Ceriodaphnia pulchella* (water flea)	Crustacean	48-h mortality	210
30	*Daphnia magna* (water flea)	Crustacean	48-h mortality	210
31	*Chydorus sphaericus* (water flea)	Crustacean	48-h mortality	220
32	*Pimephales promelas* (fathead minnow)	Fish	96-h mortality	230
33	*Daphnia pulex* (water flea)	Crustacean	48-h mortality	230
34	***Daphnia thomsoni* (water flea)**	**Crustacean**	**48-h mortality**	**250**
35	*Bufo boreas* (western toad)	Amphibian	96-h mortality	260
36	*Chydorus ovalis* (cladoceran)	Crustacean	48-h mortality	270
37	***Deleatidium* spp. (mayfly)**	**Insect**	**96-h mortality**	**280**
38	*Daphnia longispina* (water flea)	Crustacean	48-h mortality	280
39	*Salvelinus fontinalis* (brook trout)	Fish	96-h mortality	290
40	***Paracalliope fluviatilis* (amphipod)**	**Crustacean**	**48-h mortality**	**360**
41	*Macrobrachium nipponense* (East Asian river prawn)	Crustacean	96-h mortality	400
42	*Cipangopaludina cathayensis* (freshwater snail)	Mollusc	96-h mortality	480
43	*Rhithrogena* sp. (mayfly)	Insect	96-h mortality	500
44	*Rhinichthys cataractae* (longnose dace)	Fish	96-h mortality	560
45	***Potamopyrgus antipodarum* (pond snail)**	**Mollusc**	**96-h mortality**	**630**
46	*Nais elinguis* (annelid)	Annelid	96-h mortality	630
47	***Retropinna retropinna* (Smelt)**	**Fish**	**96-h mortality**	**700**
48	*Platygobio gracilis* (flathead chub)	Fish	96-h mortality	770
49	*Lampsilis siliquoidea* (fatmucket clam)	Mollusc	96-h mortality	800

Acute Zinc GV: ranked species data				
Rank	**Species**	**Taxonomic group**	**Effect and duration**	**Normalised, converted EC10 value (µg/L)**
50	***Gobiomorphus cotidianus* (Bully)**	**Fish**	**96-h mortality**	**1100**
51	*Lepomis macrochirus* (bluegill)	Fish	96-h mortality	1100
52	*Gyraulus* sp. (Gastropod)	Mollusc	96-h mortality	1200
53	*Cyprinus carpio* (common carp)	Fish	96-h mortality	1600
54	*Chironomus riparius* (midge)	Insect	96-h mortality	1700
55	*Capnia* sp. (stonefly)	Insect	96-h mortality	1800
56	*Lymnaea luteola* (snail)	Mollusc	48-h mortality	2000
57	*Pseudorasbora parva* (Stone moroko)	Fish	96-h mortality	2600
58	*Bufo gargarizans* (Asiatic toad)	Amphibian	96-h mortality	2700
59	***Galaxias maculatus* (inanga)**	**Fish**	**96-h mortality**	**2800**
60	*Duttaphrynus melanostictus* (Asian common toad)	Amphibian	96-h mortality	3100
61	*Misgurnus anguillicaudatus* (pond loach)	Fish	96-h mortality	4000
62	*Macquaria ambigua* (Golden perch)	Fish	96-h mortality	4100
63	*Baetis tricaudatus* (mayfly)	Insect	96-h mortality	4300
64	***Anguilla dieffenbachii* (Longfin eel)**	**Fish**	**96-h mortality**	**4300**
65	*Paratya curvirostris* (amphipod)	Crustacean	96-h mortality	4500
66	***Anguilla australis* (Shortfin eel)**	**Fish**	**96-h mortality**	**5400**
67	*Gambusia affinis* (mosquitofish)	Fish	96-h mortality	13000
68	*Rhithrogena hageni* (mayfly)	Insect	96-h mortality	16000
69	*Cinygmula* sp. (mayfly)	Insect	96-h mortality	24000

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