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Acute copper and zinc water quality guideline values for Aotearoa

Technical report of the derivation including bioavailability model evaluation

Report prepared by **Jenni Gadd,** Hydrotoxy Research, Chris Hickey, RMA Science; and Ton Snelder, LWP

For any information regarding this report please contact:

Jenni Gadd
Hydrotoxy Research
www.hydrotoxy.co.nz
Email: jenni@hydrotoxy.co.nz

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Executive Summary

Copper and zinc are common contaminants in freshwater environments, particularly within urban areas. Stormwater inputs can increase copper and zinc substantially (e.g., more than 10-fold) during rainfall events. These rainfall events may be short-lived, causing increased concentrations for durations of minutes, hours or in some cases up to a few days. Evaluating the potential effect on aquatic organisms of these short-term exposures requires the use of acute guideline values (GVs). As copper and zinc bioavailability and toxicity to aquatic organisms is influenced by water chemistry (e.g., pH), these GVs must incorporate the use of models that consider the difference in metal bioavailability under different water chemistry conditions. Use of a single GV for each metal could result in GVs that are under-protective in some locations, but overly conservative in others.

This report details the derivation of acute GVs for copper and zinc for use in Aotearoa water management, under contract for Ministry for the Environment. This contract included:

- Toxicity testing with a native species (cladoceran) in waters with differing water chemistries
- Evaluating and selecting of bioavailability models for both copper and zinc
- Collating and reviewing toxicity data for use in the derivation
- Deriving the guideline values and evaluating their robustness
- Providing guidance on the use of the GVs for water management in NZ, including within attribute tables that could be used to assess state under the NPS-FM.

Each of these steps is reported on in this **technical report** and associated appendices. Additional details of model evaluation inputs, and results, and toxicity data are available as supporting information in **excel files**. This information is supplied to provide a transparent record of the GV derivation. This will also facilitate future revisions when new information becomes available that necessitates an update; and a methodology that can be followed for deriving other acute GVs for use in Aotearoa.

This technical report is accompanied by a **user guide** which is intended for users of the guideline values. That user guide provides the GVs, describes where and how they should be used, and includes a brief description of the derivation methods.

Copper and zinc bioavailability, models and model evaluation

The aquatic chemistry of copper and zinc toxicity is influenced by water chemistry, such as water hardness, pH, and the presence of organic matter (measured as dissolved organic carbon, DOC). Harder water, which contains higher levels of calcium and magnesium ions, can mitigate the toxic effects of these metals by competing with copper and zinc for binding sites on the gills of aquatic organisms. This reduces metal uptake into the organism, and therefore reduces toxicity. Lower pH levels increase the solubility of these metals, but also increase the levels of hydrogen ions which can compete for binding sites. The competition effect is stronger for zinc than for copper and therefore zinc can be more toxic at higher pH (whereas copper shows the opposite effect). Copper and zinc both bind to DOC, reducing the amount of "free" metal that can be taken up by an organism. The factors that influence toxicity are termed toxicity modifying factors (TMFs).

The acute toxicity of both copper and zinc was tested using a native cladocera (water flea; *Daphnia thomsoni*), which has previously been demonstrated to be sensitive to zinc under chronic exposures. Acute toxicity was tested over 48 hours, using a lethal test. The toxicity testing used five water samples collected from rivers around Aotearoa with different hardness, DOC and pH (though there was minimal variation in pH). The EC50 values (concentration that caused an effect in 50% of organisms) varied between waters by 8-fold for copper and 2-fold for zinc. Those data were used to evaluate bioavailability models, to assess their suitability for native species.

Bioavailability models have been used in deriving guideline values since the 1970s, when the hardness regression was introduced for many metals. Other factors, such as pH, DOC and other cations and anions have been considered in models developed over the last 20 years or so, including the biotic ligand model (BLM). Multiple linear regression models (MLRs) have been developed as a simple alternative to the BLM. As there is no single model that is necessarily better than all others, a set of criteria were developed to select the model for deriving acute GVs for Aotearoa, based on best practice for model selection. That criteria included qualitative factors such as the inclusion of key TMFs, data inputs required and ease of use. Based on those factors, four models for each of copper and zinc were selected for further evaluation with quantitative criteria. Those models were hardness regressions, MLRs derived by pooling toxicity data for multiple fish and invertebrate species, MLRs derived for specific trophic levels (i.e., fish vs invertebrates vs plants/algae) and acute BLMs.

Five factors were used to assess (and quantitatively score) those models: model validation with additional species; model validation with native species; the TMF range of the model compared to waters of Aotearoa; TMF range of the model compared to the toxicity dataset; the taxonomic coverage of the model. Based on those factors, the pooled fish/invertebrate model for copper had the highest score, followed by the BLM. For zinc, the pooled fish/invertebrate model and the hardness models had the highest scores, followed by the BLM. Based on the ease of use of the MLR over the BLM, and its suitability based on cross-species and native-species validation, MLRs were selected for both copper and zinc.

Collation of toxicity data and derivation of the guideline values

Toxicity data were collated from several existing compilations including guidelines used in international jurisdictions, where the quality of the study had been previously assessed. These data were supplemented with data for native species from published studies and from enquiries with local researchers. Data for algal species (a gap in the toxicity datasets) were derived from unpublished interim measurements from previously published and quality assessed studies. Although additional data were available, quality assessing those was outside the project scope and there were sufficient data from the existing compilations when supplemented as described. Collated data were restricted to EC50 values from acute (short-term) exposures to copper or zinc from tests of the ecologically relevant effects (e.g., mortality, population growth/biomass). For non-native species, data were only included if metals were measured and at least two TMFs were measured in the test waters, and the third could be reliably estimated. For native species, data where metals and TMFs were measured in the test waters were used, unless there was no other data for that species. In those cases, data with verification of the metals and estimates of TMFs were accepted.

For each metal, all accepted data were normalised to a single index (standard) water chemistry using the pooled MLR model. The EC50 values were then converted to EC10 values (representing a low effect concentration) using conversion factors for each metal and taxonomic group calculated from reported EC50 and EC10 data. Those ratios were 1.6 to 2.5 depending on the metal and taxonomic groups, and considerably lower than the default value of 5 recommended for that conversion. Converted, normalised EC10 values were selected for each species from the most sensitive endpoint, using a geometric mean where multiple values were available. These single species values were modelled in a species sensitivity distribution, with multiple statistical distributions fitted to the data. A weighted-average approach was used to calculate acute GVs at differing levels of species protection (99%, 95%, 90% and 80%).

The acute GVs differ depending on the pH, hardness and DOC of the waters and are therefore provided as a set of equations (different equations for different levels of species protection). For both copper and zinc, GVs are higher at higher concentrations of DOC and hardness. For copper, the GVs are higher at higher pH. By contrast, for zinc the GVs are lower at higher pH, though the difference is relatively minor compared to the effect of hardness.

Evaluation of the guideline values

The data used to derive these acute GVs was generally high ranked data, where metals and TMFs were measured in the test waters (and tests otherwise met acceptability standards). Lower ranked data were only included for species native to Aotearoa.

The acute GVs are each based on large toxicity datasets, covering 90 and 69 species for copper and zinc respectively. Despite the abundance of species, there were few plant and algal species included,. Species were from 7 (copper) and 8 (zinc) different taxonomic groups. The species included are not necessarily representative of freshwater ecosystems in Aotearoa, though this is a frequent weakness for toxicity guideline values, as not all species present in an ecosystem can be used in toxicity testing. Lack of freshwater algae data for copper and plant data for zinc means that when these GVs are applied, they may not be protective of whole ecosystems. Although the GVs are largely derived from data for species that are not present in Aotearoa, they are expected to protect native species, based on the available data for native species.

Sensitivity tests with slightly different datasets, such as excluding lower ranked data where TMFs were estimated, or different assumptions for estimating TMFs, showed minimal differences in the acute GVs. This is likely due to the large toxicity datasets used in their derivation. Use of a default ratio of five to convert from EC50 to EC10 values did result in significantly lower acute GVs than the GVs based on a data based EC50 to EC10 conversion factor.

Based on the TMF ranges of the bioavailability models and the toxicity datasets, the acute GVs will be applicable to >90% of waters in Aotearoa. However, they are not applicable to low pH waters (e.g., <5) or very high pH waters (>8.5 or >9). A possible limitation of the GVs is the applicable range of the zinc GVs – these cannot be applied to low hardness waters (<14 mg/L as $CaCO_3$), and zinc may have high bioavailability in those waters (depending on the pH and DOC).

Application of the acute GVs

A tiered approach to implementation is recommended for use of the acute GVs. That is, dissolved copper and zinc concentrations are first compared to Tier 1 GVs (based on a water chemistry combination with high bioavailability). If these are exceeded, then bioavailability-adjusted GVs can be calculated (Tier 2), based on pH, hardness and DOC appropriate for that sample. This tiered approach allows for screening of sites and samples where acute toxicity risks are low and those where further investigation is needed. Tier 1 acute GVs should represent conditions where bioavailability is high and should be based on data for Aotearoa. Interim Tier 1 acute GVs are provided in this report (Table 1) but these should be updated when the Tier 1 chronic DGVs are published, following the same methodology as used for the chronic DGVs.

Table 1: Interim Tier 1 acute GVs for **copper** and **zinc** (µg/L). Copper GVs at pH 7.0, hardness 17 mg $CaCO_3$/L and DOC 0.7 mg/L; zinc GVs at pH 8.2, hardness 17 mg $CaCO_3$/L and DOC 0.7 mg/L. The pH values are different because of the different effect of pH on copper toxicity and zinc toxicity.

	Level of protection			
	99%	95%	90%	80%
Copper interim tier 1 acute GV	0.7	1.3	1.7	2.9
Zinc interim tier 1 acute GV	11	24	36	59

Guidance is provided for the use of these acute GVs where TMF data are not available, based on guidance previously provided for chronic default guideline values (DGVs) for copper and zinc. That provides differing levels of the assessments, with the most robust level (high confidence in the assessment of toxicity risk) where TMFs are measured in the samples being assessed. When TMF data are estimated from other samples, there is less certainty in the toxicity assessment.

Guidance is also provided for samples that are outside the applicable range of the models. At high hardness and DOC, upper limits can be used to calculate GVs that will be conservative. At low DOC and hardness, lower limits can be used but only with caution as these may not be protective. For pH the implications for copper and zinc are different as the effect of pH on copper toxicity (more toxic at low pH) is the reverse of that for zinc (more toxic at high pH).

Acute GVs are used to assess risks of short-term exposure to higher concentrations of metals. Generally this exposure period can be considered around 48 hours but may be 24-96 hours. The acute GVs would be expected to be conservative if used for assessing exposures that occur for minutes or hours, and would likely under-estimate toxicity if used for assessing exposures of a week or more.

Use of the acute GVs in attribute tables

Copper and zinc attributes generally meet the requirements for NPS-FM attributes. Both metals are linked to compulsory values listed in the NPS-FM, including ecosystem health and mahinga kai as they can cause acute and chronic toxicity to freshwater organisms. There are established methods for sampling and measuring these metals (and the TMFs required to assess bioavailable concentrations). However, developing tables with appropriate band thresholds is difficult when aiming to protect from both acute and chronic exposures. This is a particular challenge for urban waters where concentrations can change rapidly. The attributes can be linked to catchment limits and to management actions, with models (simple or complicated) available for that assessment. There are existing data available to assess the current state of the attribute in some locations, or this could be modelled, though both those assessments would be most appropriate for an attribute table based largely on chronic DGVs, not acute GVs. The economic costs of meeting target attribute states where currently non-compliant can be expected to be significant. This could be evaluated if an attribute table is developed.

Further work to develop copper and zinc attributes should focus on how an attribute table can best combine both short-term and long-term exposures. A draft table should then be tested with existing data to identify whether there are issues with the use of different bioavailability models for acute GVs and chronic GVs. If based on percentiles, the thresholds in the table should be compared to percentiles of time. This would require discretion in assessing current state from monitoring data, as metals cannot be measured on a continuous basis. There would be low confidence in assessments associated with infrequent (monthly) sampling if acute GVs are included in the attribute table.

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Report limitations

This document sets out a process and derives acute guideline values for copper and zinc for use in Aotearoa New Zealand fresh waters. This is based on the bioavailability models and toxicity data currently available. Guideline values can (and should) be updated and improved as new knowledge is obtained and new toxicity data become available. Any updates could follow the process described in this report or may follow an updated process.

Although these guideline values may be of interest for locations outside of Aotearoa, that use has not been assessed and the guideline values may not be protective in those locations.

While the methodology and the guideline values have been reviewed by international experts, those reviewers are not responsible for the content or accuracy of this report and shall not be responsible for any decisions made based on such information.

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1 Introduction

1.1 Copper, zinc and the need for acute guideline values

The metals copper and zinc are among the most ubiquitous contaminants in aquatic environments, due to their widespread use for diverse purposes. Many urban waterbodies have consistently elevated copper and zinc concentrations due to stormwater inputs, which can contain high levels of zinc from vehicle tyre wear and zinc-based roofing materials, and elevated copper from copper-based brake pads and copper building materials.[1] Chronic guideline values (for long-term exposures) are provided for use in Aotearoa New Zealand (hereafter Aotearoa[2]) under the framework of the Australian and New Zealand guidelines (ANZG) for fresh and marine water quality.[3] These chronic guideline values (termed default guideline values or DGVs) are widely used throughout Aotearoa for water management, particularly in urban water management. Use of these DGVs with monitoring data can indicate locations where there are high risks of chronic toxicity to aquatic organisms.

However, copper and zinc concentrations in urban streams can vary considerably over time, and increase substantially during rainfall events from the concentrations measured at baseflow. Those conditions may represent only a short-term exposure, and chronic DGVs would likely provide a very conservative estimate of toxicity risk. Acute guideline values (GVs) would be more appropriate for these short-term exposures, but are not provided by ANZG. Guideline values or criteria derived in other jurisdictions (e.g., US or Canada) may not be protective of native species, may be out of date (e.g., US zinc guidelines) or may not be consistent with Aotearoa legislation and management (e.g., Canadian short-term guidelines do not relate to narrative terminology used in RMA such as “no significant adverse effects”).

A project team led by Hydrotoxy Research were therefore contracted by New Zealand Government’s Ministry for the Environment (MfE) to derive acute water quality guideline values for use in Aotearoa.

These are expected to have multiple applications in water management. This includes resource consenting for industrial and municipal wastewaters, mining discharges and stormwater network discharge consents. In those contexts, the guideline values may be used to assess potential effects (e.g., in a consent application assessment of environmental effects), where they would act as guidelines. Alternatively, they may be adopted as consent limits, to be met within receiving waters downstream of a discharge or discharges, where the exceedance of that limit carries regulatory implications.

Acute GVs could also be used for freshwater planning, within the National Policy Statement for Freshwater Management (NPS-FM[4]), with the possibility of their use within numeric attributes (water quality standards) that may be adopted regionally or nationally. Their use in attributes would likely be in combination with the chronic guideline values provided by ANZG and may be as a minimum acceptable state (a national “bottom-line”). If used in attributes, the acute guideline values are effectively “standards” rather than “guidelines”. That is, they must be adhered to and would have regulatory implications if not met.

These multiple uses require that the acute GVs are as reliable as possible and follow international best practice for deriving guideline values, including taking into account the effects of water chemistry on metal toxicity.

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[1] Tyres contain around 1-2% zinc by weight.
[2] Where the Australian and New Zealand Guidelines for Fresh & Marine Water Quality are referred to, the name “New Zealand” will be used; as in “Australian and New Zealand Guidelines”.
[3] "Australian and New Zealand guidelines for fresh and marine water quality," Australian and New Zealand Governments, 2018, https://www.waterquality.gov.au/anz-guidelines/.
[4] New Zealand Government, 2024. *National Policy Statement for Freshwater Management 2020* (Wellington, New Zealand: Minister for the Environment, January 2024), https://environment.govt.nz/publications/national-policy-statement-for-freshwater-management-2020-amended-january-2024/.

1.2 Overview of the process to derive guideline values

The overall process used for the deriving the acute copper and zinc GVs generally follows that used for chronic DGVs used in Australia and New Zealand[3], with reference to aspects from other jurisdictions for best practice (Figure 1.1). The process requires the collation and quality assessment of toxicity data and, where sufficient data are available, uses the statistical extrapolation method based on species sensitivity distributions (SSDs).[5] This is the preferred method used in many jurisdictions internationally (e.g., United States, Canada, Europe, Japan, China) for developing water quality guidelines for toxic contaminants. The SSD approach aims to extrapolate to an ecosystem the results from toxicity testing of an individual chemical on a limited number of test species (restricted to those that are amendable to culturing and testing in a laboratory setting). This is undertaken by plotting the toxicity data as a cumulative distribution, fitting a statistical model, and then calculating the lower 5th percentile from that model for use as a guideline value.

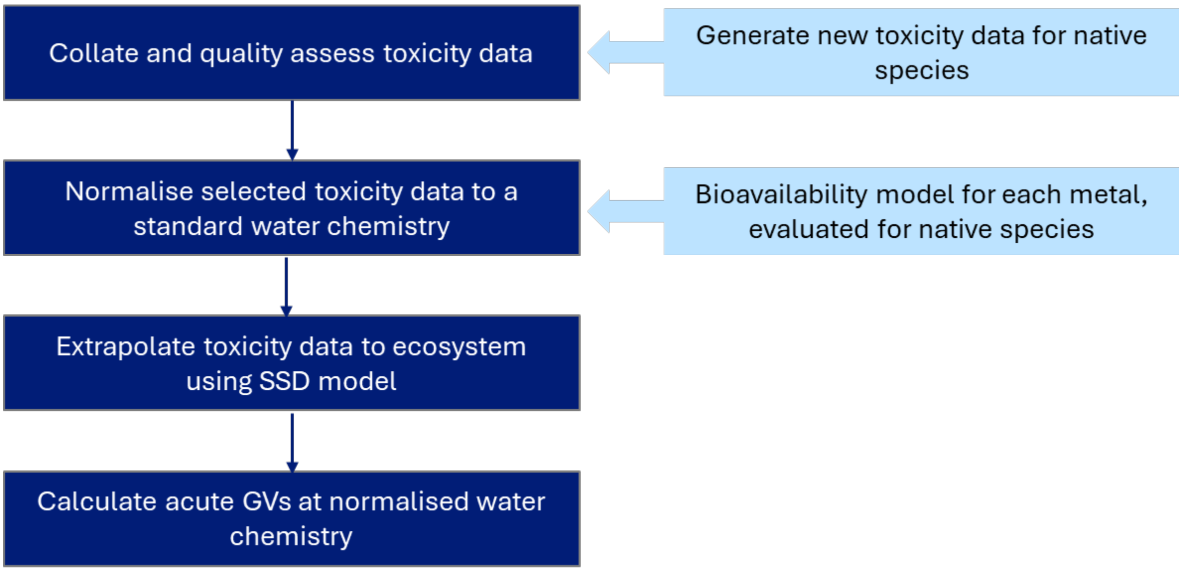

Figure 1.1: Simplification of the process for deriving bioavailability-based metal guideline values (dark blue boxes) with indication of additional work required to ensure acute GVs are relevant for Aotearoa (light blue boxes).

The toxicity of both copper and zinc to aquatic organisms is affected by the water chemistry – as this influences the amount of metal the organisms can take up (i.e., the bioavailability of the metal). Metal bioavailability must therefore be considered, both in deriving metal GVs and when applying those GVs to environments with different water chemistry. This requires the use of a bioavailability-model to first normalise (or standardise) toxicity test data to a common and comparable water chemistry, and then to adjust GVs for different environments. Although it is widely accepted that bioavailability models are needed in developing GVs, there are multiple models available for this purpose and different models can be appropriate in different situations.[6] This means that the available models must be evaluated for their suitability in deriving acute GVs for Aotearoa.

As the available bioavailability models have been developed with species that are not native to Aotearoa (and in some cases, not present in Aotearoa), the models should be evaluated to ensure that they can predict bioavailability to native species. This step requires toxicity data for native species, conducted under conditions with differing water chemistry.

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[5] MS Warne et al., 2018. *Revised method for deriving Australian and New Zealand water quality guideline values for toxicants - update of 2015 version*, Prepared for the Australian and New Zealand Guidelines for Fresh and Marine Water Quality. Australian and New Zealand Governments and Australian state and territory governments (Canberra, August 2015 - updated October 2018). The SSD approach is recommended over an Assessment Factor (AF) approach which typically uses the lowest toxicity data point divided by an arbitrary safety factor.
[6] W Adams et al., 2020. Bioavailability assessment of metals in freshwater environments: A historical review. *Environmental Toxicology and Chemistry* 39, 1: 48-59.

1.3 Contents of this report

This technical document details the process for the derivation of the acute GVs for copper and zinc in Aotearoa. Each of the steps outlined in the previous section (and shown in Figure 1.1) requires numerous decisions regarding data quality, missing data, model evaluation and selection, and statistical methods. To ensure transparency in the derivation, these decisions are described in this report. Figure 1.2 outlines the contents of this report and which aspects are also included in the user guide.

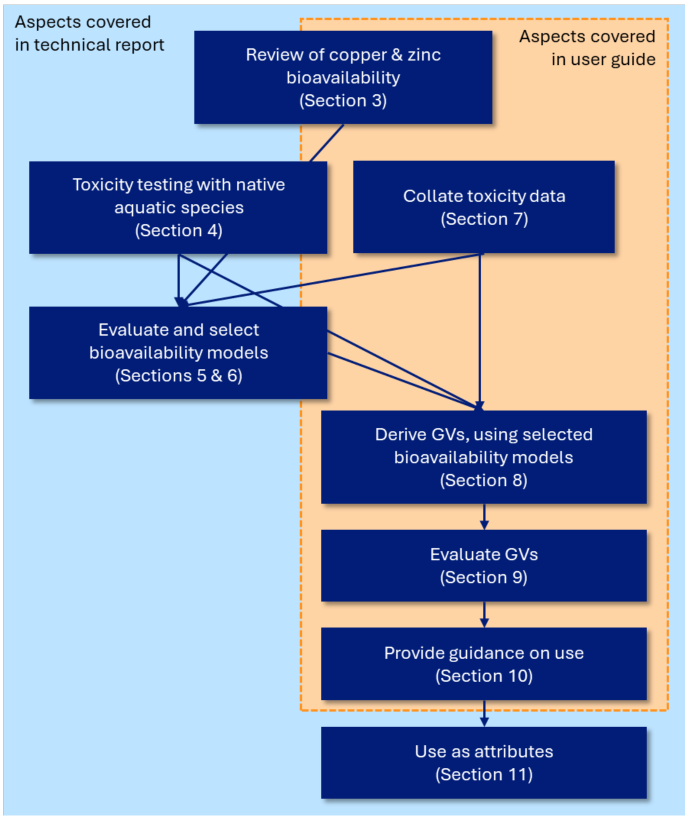

Figure 1.2: Outline of the derivation strategy and reporting.

This report begins with some introductory information copper and zinc occurrence and fate (section 2). Section 3 reviews copper and zinc toxicity and how this is modified by water chemistry. Section 4 includes a description of acute toxicity testing with a native species undertaken for this project, for evaluating bioavailability models and for inclusion in deriving the GVs. The report also sets out the method used to evaluate metal bioavailability models to select the models most suitable for the deriving acute GVs for copper and zinc (sections 5 and 6). This considers factors including suitability for native species, relevance for waters in Aotearoa and use by end-users.

The acute GVs derived (section 8) are evaluated in terms of the quality and breadth of toxicity data used, the inclusion of native species and the relevance for Aotearoa freshwater ecosystems (section 9). For transparency, sensitivity tests have been undertaken to assess the effect of different decisions on the GVs.

GVs that vary with water chemistry are not expressed as a single numeric value like traditional GVs. Depending on the bioavailability model used to derive the GVs, they may be expressed as an equation (like the Canadian zinc GVs), or a model (like the US EPA copper GVs).[7] This report therefore also provides guidance around the application of these acute GVs and how to account for bioavailability in their use (section 10). This application guidance includes where and when they should be used. Section 11 discusses

[7] CCME, 2018. Canadian water quality guidelines for the protection of aquatic life: zinc, in *Canadian environmental quality guidelines, 1999* (Winnipeg, MB: Canadian Council of Ministers for the Environment, National Guidelines and Standards Office, Water Policy and Coordination Directorate, Environment Canada; reprint); US EPA, 2007. *Aquatic life ambient freshwater quality criteria - copper. 2007 Revision*, United States Environmental Protection Agency, Criteria and Standards Division (Washington D.C.), https://www.epa.gov/sites/default/files/2019-02/documents/al-freshwater-copper-2007-revision.pdf.

the potential use of acute GVs within attribute tables for use within numeric attributes used in implementing the NPS-FM.

This report is accompanied by:

- multiple appendices, provided as a separate document
- excel files for the model evaluation that include inputs (including validation data) and outputs of model validation
- an excel file with the toxicity data used (and not included) in the GV derivation.

This technical report is accompanied by a user guide, which is expected to be the key document for users of the acute GVs. That user guide provides the recommended acute GVs, an overview of the derivation process, and describes how to use the GVs in water management.

1.4 Terminology

This report includes many acronyms and scientific terms, which are defined in the glossary (section 13). The key terms used most often in the document are defined here.

Acute GV	An acute guideline value, developed to assist in managing effects of short-term exposures to toxicants.
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 (see Appendix A for details for different species types).
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.
DGV	Default guideline value; a term used by ANZG (2018) to describe the guideline values (GVs) developed for generic application. These are differentiated from site-specific or local GVs.
DOC	Dissolved organic carbon; a measurement of organic matter in solution, based on the carbon content (using a carbon analyser), after passing through a 0.45 µm filter.
EC10	The concentration of a substance in water or sediment that is estimated to produce a 10% change in the response being measured (such as biomass) or a certain effect in 10% of the test organisms (such as mortality) relative to the control response, under specified conditions. This is considered a low effect concentration and so is used for deriving GVs that will be protective of toxic effects.
EC50	The concentration of a substance in water or sediment that is estimated to produce a 50% change in the response being measured (such as biomass) or a certain effect in 50% of the test organisms (such as mortality) relative to the control response, under specified conditions.
TMFs	Toxicity modifying factors; aspects of water chemistry that affect the bioavailability of a substance. For copper and zinc, the key TMFs are generally considered to by pH, hardness and DOC.

2 Environmental occurrence and fate

2.1 Physical and chemical properties

Copper, with an atomic mass of 63.55 u, is a reddish-brown metal. As a transition metal, it exhibits a variety of oxidation states, the most common being +1 and +2, although +3 is also known in certain compounds. Copper is typically found in mineral ores such as chalcopyrite, bornite (copper iron sulfides) and malachite (copper carbonate hydroxide).

Copper has a melting point of 1,080°C and a boiling point of 2,560°C. It is known for its high thermal and electrical conductivity, and is malleable and ductile, making it ideal for applications like wiring and plumbing. Chemically, copper is relatively unreactive and resists corrosion in dry air. However, it slowly reacts with atmospheric oxygen, forming a greenish layer of copper carbonate over time. This patina serves as a protective barrier against further corrosion, giving aged copper surfaces their distinctive green appearance.

Zinc, with an atomic mass of 65.38 u, is a bluish-white metal and also a transition metal. It exhibits oxidation states of +2, with +1 and +3 being rare and less stable. Zinc has a lower melting point of 420°C and a boiling point of 907°C. It is less dense and more brittle compared to copper. The most important mineral ores of zinc are sphalerite (zinc sulfide) and smithsonite (zinc carbonate).

Zinc's primary chemical property is its ability to form protective coatings through galvanization. In this process, zinc reacts with atmospheric oxygen and carbon dioxide to create a layer of zinc carbonate, providing robust protection against rust and corrosion. This property makes zinc essential in steel protection and is a major use of zinc. Additionally, zinc is an effective alloying element, for example, combined with copper to create brass, which enhances strength and ductility.

2.2 Environmental occurrence

Copper and zinc are naturally occurring elements found in all freshwater environments, though their concentrations can vary based on geological and anthropogenic factors. Natural sources of copper include the weathering of copper-bearing rocks, volcanic activity, and the decomposition of organic matter, all of which release copper into rivers, lakes, and streams. Similarly, zinc is naturally introduced into freshwater systems through the weathering of zinc-containing minerals and soils, as well as volcanic eruptions. In pristine freshwaters of Aotearoa, copper concentrations are reportedly less than 0.5 µg/L, while zinc concentrations are less than 2 µg/L.[8] These levels are low by global standards but are presumably sufficient for biological function for the organisms present.

Anthropogenic sources, however, significantly contribute to elevated concentrations of copper and zinc in freshwater environments. Industrial activities, such as mining, smelting, and manufacturing, can release substantial amounts of these metals into water bodies through point-source discharges. Urban stormwater runoff is a key contributor to elevated copper and zinc in Aotearoa. Stormwater transports copper from brake linings, roofing and guttering materials; and zinc from tyre wear, roofing and other surfaces with galvanised steel. Wastewater treatment plants are also sources of copper and zinc. Agricultural practices also play a major role, as copper is used in fungicides, and zinc is a key treatment for facial eczema in sheep. These anthropogenic inputs can raise copper and zinc levels well above natural background concentrations. For example, dissolved copper concentrations in urban streams are regularly

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[8] W Ahlers, J Kim, and K Hunter, 1991. Dissolved trace metals and their relationship to major elements in the Manuherikia River, a pristine subalpine catchment in central Otago, New Zealand. *Marine and Freshwater Research* 42, 4: 409-22; SG Sander et al., 2013. Trace metal chemistry in the pristine freshwater Lake Hauroko, Fiordland, New Zealand. *Microchemical Journal* 111: 74-81; MJ Ellwood, KA Hunter, and JP Kim, 2001. Zinc speciation in Lakes Manapouri and Hayes, New Zealand. *Marine and Freshwater Research* 52, 2: 217-22; MR Reid, JP Kim, and KA Hunter, 1999. Trace metal and major ion concentrations in Lakes Hayes and Manapouri. *Journal of the Royal Society of New Zealand* 29, 3: 245-55.

1-3 µg/L and dissolved zinc concentrations are regularly 10-100 µg/L. During storm events, concentrations of copper can measure in the 10s of µg/L while zinc can even exceed 1 mg/L in some locations.[9]

2.3 Partitioning & speciation

In aquatic environments, the partitioning and speciation of copper and zinc—meaning the various chemical forms these metals can take—is critical to understanding their bioavailability and toxicity.

Partitioning describes the distribution of copper and zinc between different environmental compartments—such as water, particulate matter, and biota. In the water column, a portion of copper and zinc may remain dissolved (either as free ions or complexed metal species–termed speciation, see following paragraphs), while another fraction can adsorb onto particulate matter. The former is measured when filtering a sample prior to analysis; and the latter is included when measuring "total copper" or "total zinc".

That partitioning depends on the source of the metals as well as processes that occur when released into aquatic environments. For example, zinc is found predominantly in dissolved form in runoff from galvanised roofing. However, when that runoff reaches a stream, some of the dissolved metals may partition onto suspended sediments present there. In contrast, zinc from road runoff is generated as very fine particles (e.g., of tyre rubber), and although a portion of this dissolves when washed off during a rain event, much of it remains insoluble.

Dissolved copper and zinc can exist in different forms (different chemical species) depending on factors such as pH, redox potential, and the presence of complexing agents. Dissolved copper primarily occurs as either free Cu^{2+} ions, which are highly reactive and toxic, or as complexed forms bound to organic and inorganic ligands like dissolved organic matter (DOM), carbonates, and hydroxides (Figure 2.1). Similarly, dissolved zinc can exist as free Zn^{2+} ions, but it often forms complexes with hydroxides, carbonates, and sulfides, and organic ligands. The form in which these metals are present determines their mobility and the extent to which they can interact with aquatic organisms. It is generally accepted that the free ionic forms (Cu^{2+} and Zn^{2+}) and some hydroxide forms are the most bioavailable and toxic, while generally organic complexes[10] and those bound to sediments are less so.

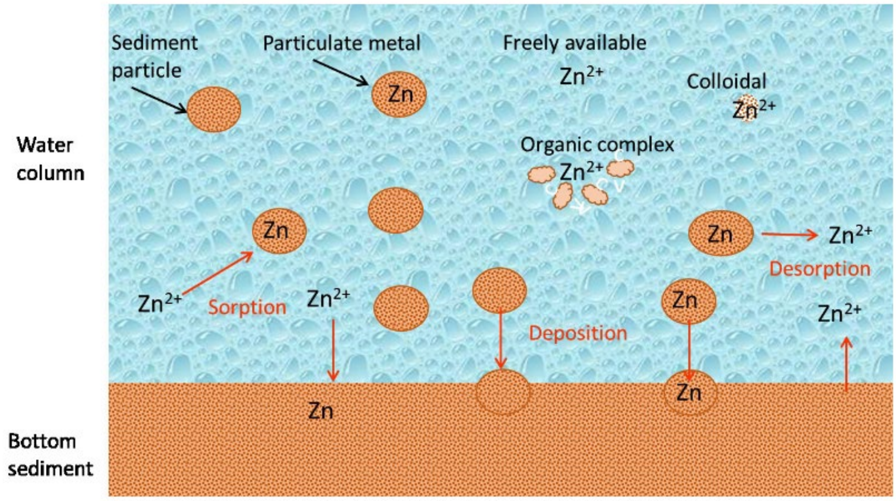

Figure 2.1: Simplified conceptual outline for metal partitioning and speciation. .

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[9] J Gadd et al., 2024. *Heavy metals state and trends in New Zealand rivers. Analyses of national data ending in 2022*, National Institute of Water & Atmospheric Research Ltd (Auckland, New Zealand, March 2024), https://doi.org/10.1080/00288330.2020.1753787; J Gadd et al., 2019. *Developing Auckland-Specific Ecosystem Health Attributes for Copper and Zinc: Summary of work to date and identification of future tasks*, Auckland Council (Auckland); C Appleton et al., 2023. *Comprehensive Stormwater Network Discharge Consent Annual Report – June 2023. Prepared to meet the requirements of CRC231955*, Christchurch City Council (Christchurch, New Zealand).

[10] There can be exceptions; lipid-soluble copper complexes are extremely toxic compared to the free ion as these are readily transported across cell membranes. TM Florence and JL Stauber, 1986. Toxicity of copper complexes to the marine diatom *Nitzschia closterium*. *Aquatic Toxicology* 8, 1: 11-26.

3 Effects of water chemistry on acute copper and zinc toxicity

3.1 Introduction

This section provides an overview of the mechanisms by which copper and zinc cause toxicity to aquatic organisms, and the way that this is affected by water chemistry.

3.2 Mechanisms of copper and zinc toxicity

Copper and zinc are essential trace metals for aquatic organisms, but at elevated concentrations, they become toxic. 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 aquatic invertebrates, leading to an imbalance in sodium homeostasis.[11] This disruption can cause a loss of cellular integrity, leading to cell death, impaired respiratory function, and eventually, organism mortality. The mechanism of copper toxicity in unicellular algae is through changes in membrane potential and permeability, competition with essential metals for binding and uptake, and oxidation of thiol groups, inhibiting cell division.[12] These acute effects are generally observed as reductions in population growth or biomass. In plants, excess copper accumulates in the roots affecting root growth and structure, which leads to reductions in plant growth.[13]

Zinc toxicity in aquatic organisms shares some similarities with copper but operates through slightly different mechanisms. Zinc ions (Zn^{2+}) also disrupt ion regulation, particularly affecting the sodium-potassium ATPase pump in the gills.[14] This interference can result in an inability to maintain proper ionic balance and acid-base equilibrium, leading to osmoregulatory stress. In addition, zinc can impair the functioning of enzymes and proteins by binding to their active sites, displacing other essential metals, or disrupting the protein structure itself.[15] This enzymatic disruption can lead to a cascade of metabolic failures, ultimately causing acute toxicity symptoms such as lethargy, loss of equilibrium, and death in severe cases. In algae, and in plants, zinc first accumulates (in roots for plants), then affects photosynthesis and at high concentrations causes chlorosis and necrosis.[16]

3.3 Review of water chemistry effects on acute copper toxicity

Both copper and zinc toxicity are influenced by water chemistry, such as pH, cations and anions and the presence of organic matter which modify the chemical speciation of the metals and affect metal uptake. There are multiple studies that have assessed the effect of pH, hardness and/or organic matter (generally measured as dissolved organic carbon (DOC); referred to as DOC from here on) on acute copper toxicity, including different species and different trophic levels[17] (algae, plants, invertebrates and fish). Not all studies have investigated each of the toxicity modifying factors (TMFs). The effect of each TMF is summarised in Table 3.1.

There is sufficient evidence to suggest that increased pH reduces copper toxicity for some species but not all, and the effect is not consistent across or within trophic levels (e.g., differences between invertebrates).

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[11] M Grosell and CM Wood, 2002. Copper uptake across rainbow trout gills: mechanisms of apical entry. *Journal of Experimental Biology* 205, 8: 1179-88.

[12] JL Stauber and CM Davies, 2000. Use and limitations of microbial bioassays for assessing copper bioavailability in the aquatic environment. *Environmental Reviews* 8, 4: 255-301; P Van Sprang et al., 2008. Chapter 3.2: Environmental effects., in *Voluntary risk assessment of copper, copper II sulphate pentahydrate, copper(I) oxide, copper(II) oxide, dicopper chloride trihydroxide* (Brussels, Belgium: European Copper Institute; reprint).

[13] V Kumar et al., 2021. Copper bioavailability, uptake, toxicity and tolerance in plants: A comprehensive review. *Chemosphere* 262: 127810.

[14] C Hogstrand, SD Reid, and CM Wood, 1995. Ca^{2+} versus Zn^{2+} transport in the gills of freshwater rainbow trout and the cost of adaptation to waterborne Zn^{2+}. *Journal of Experimental Biology* 198: 337-48; VL Loro and CM Wood, 2022. The roles of calcium and salinity in protecting against physiological symptoms of waterborne zinc toxicity in the euryhaline killifish (Fundulus heteroclitus). *Comparative Biochemistry and Physiology Part C: Toxicology & Pharmacology* 261: 109422.

[15] C Hogstrand, 2012. Zinc, in *Homeostasis and Toxicology of Essential Metals*, ed. CM Wood, AP Farrell, and CJ Brauner, Fish Physiology (London, UK: Elsevier Inc.; Academic Press; reprint).

[16] H Balafrej et al., 2020. Zinc hyperaccumulation in plants: A review. *Plants (Basel)* 9, 5.

[17] Trophic levels refer to the position of the organism within a food web; in this document three levels are used, differentiating fish from invertebrates, and from plants and algae.

Hardness appears to affect acute copper toxicity to fish, but rarely to invertebrates, except for some crustaceans (*Daphnia*) species and an oligochaete worm (*Lumbriculus variegatus*). Where tested, DOC has affected all species by decreasing acute copper toxicity as DOC increases. Overall, this suggests that there are some differences between trophic levels, and/or species in the way TMFs influence copper toxicity.

In waters with higher alkalinity, copper toxicity can be decreased–partly due to changes in pH and partly due to changes in metal speciation (e.g., formation of copper-carbonates). This effect has been demonstrated in laboratory waters with low DOC,[18] however, alkalinity is not widely considered to be an important TMF for copper.[19]

Temperature affects chemical reactions, and metabolic rates and therefore has potential to influence metal speciation and bioavailability. Meyer et al. concluded from meta-analysis that the acute toxicity of copper generally increases as temperature increases.[20] Despite that temperature is not generally considered an important modifying factor,[19] though this may be at least partly due to lack of research.[21]

There can be differences in the effect of TMFs on acute copper toxicity compared to chronic toxicity, depending on taxa. While hardness affects copper toxicity for fish and some invertebrates in acute exposures (Table 3.1), there is less evidence for this effect in chronic exposures.[22] Differences in the effects of TMFs on acute and chronic toxicity mean that different TMFs may need to be measured in water samples when comparing to acute or chronic guideline values.

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[18] RV Hyne et al., 2005. Influence of water chemistry on the acute toxicity of copper and zinc to the cladoceran *Ceriodaphnia* cf *dubia*. *Environmental Toxicology and Chemistry* 24, 7: 1667-75.

[19] US EPA, 2022. *Metals Cooperative Research and Development Agreement (CRADA) Phase I Report: Development of an overarching bioavailability modeling approach to support US EPA's Aquatic Life Water Quality Criteria for metals*, Developed by the US Environmental Protection Agency in collaboration with the Metals CRADA Partners (Office of Water, US EPA, March 2022).;

[20] JS Meyer et al., 2007. *Effects of water chemistry on bioavailablity and toxicity of waterborne cadmium, copper, nickel, lead and zinc to freshwater organisms*, Metals and the Environment Series, (Pensacola, FL.: The Society of Environmental Toxicology and Chemistry (SETAC)). https://www.setac.org/resource/setac-water-chemistry-cadmium-copper-pdf.html.

[21] CA Mebane et al., 2020. Metal bioavailability models: Current status, lessons learned, considerations for regulatory use, and the path forward. *Environmental Toxicology and Chemistry* 39, 1: 60-84.

[22] See for example KAC De Schamphelaere and CR Janssen, 2004. Development and field validation of a biotic ligand model predicting chronic copper toxicity to *Daphnia magna*. *Environmental Toxicology and Chemistry* 23, 6: 1365-75.;

Table 3.1: Effect of key TMFs on **acute copper** toxicity across different species. Downwards arrow indicates toxicity decreases as TMF increases. Sideways arrow indicates toxicity does not change substantially with increases in TMF.

	Effect of:				
Species	**pH**	**Hardness**	**DOC**	**Alkalinity**	**Temperature**
Fish					
Fathead minnow (*Pimephales promelas*) [23]	↓↓	↓	↓↓	Not tested	Not tested
Rainbow trout (*Oncorhynchus mykiss*) [24]	↔	↓↓	↓↓	Not tested	Not tested
Australian fish (*Ambassis* sp.) [25]	Not tested	Not tested	Not tested	Not tested	↔
Invertebrates					
Crustacean (*Daphnia magna*) [26]	↔↓	↓	Not tested	Not tested	Not tested
Crustacean (*D. magna*) [27]	Not tested	↔	↓	Not tested	Not tested
Crustacean (*D. pulex*) [28]	Not tested	↔	↓	Not tested	Not tested
Crustacean **(***Ceriodaphnia dubia*) [29]	↔↓	↔	↓	↓	Not tested
Crustacean (*Macrobrachium* sp.) [30]	Not tested	Not tested	Not tested	Not tested	↑
Amphipod (*Hyalella azteca*) [31]	↓	Not tested	↓	Not tested	Not tested
Snail (*Pomacea paludosa*) [32]	↔↓	↔	↓	Not tested	Not tested
Mussel (*Hyridella depressa*) [33]	↓	Not tested	↓	Not tested	Not tested
Fatmucket clam (*Lampsilis siliquoidea*) [34]	Not tested	↔	↓	Not tested	Not tested
Black worm (*Lumbriculus variegatus*) [35]	↔↓	↓	Not tested	Not tested	Not tested
Sludge worm (*Tubifex tubifex*) [36]	Not tested	Not tested	Not tested	Not tested	↑
Green hydra (*Hydra viridissima*) [37]	Not tested	↔	Not tested	Not tested	Not tested
Plants & algae					
Green alga (*Chlorella* sp.) [11]	↔↓	↔	↓	Not tested	Not tested
Hornwort (*Ceratophyllum demersum*) [38]	Not tested	↔	Not tested	Not tested	Not tested

[23] RJ Erickson et al., 1996. The Effects of water chemistry on the toxicity of copper to fathead minnows. *Environmental Toxicology and Chemistry* 15, 2: 181-93.
[24] A Crémazy et al., 2017. Experimentally derived acute and chronic copper Biotic Ligand Models for rainbow trout. *Aquatic Toxicology* 192: 224-40.
[25] JF Skidmore and IC Firth, 1983. *Acute sensitivity of selected Australian freshwater animals to copper and zinc*, ed. C Australian Water Resources, Research project (Australian Water Resources Council) ; no. 78/102., (Canberra: Australian Government Publishing Service).
[26] KAC De Schamphelaere and CR Janssen, 2002. A biotic ligand model predicting acute copper toxicity for *Daphnia magna*: The effects of calcium, magnesium, sodium, potassium, and pH. *Environmental Science & Technology* 36, 1: 48-54.
[27] RW Winner, 1985. Bioaccumulation and toxicity of copper as affected by interactions between humic-acid and water hardness. *Water Research* 19, 4: 449-55; RW Winner and JD Gauss, 1986. Relationship between chronic toxicity and bioaccumulation of copper, cadmium and zinc as affected by water hardness and humic-acid. *Aquatic Toxicology* 8, 3: 149-61.
[28] Winner, 1985; Winner and Gauss, 1986.
[29] Hyne et al., 2005. SJ Markich et al., 2005. Hardness corrections for copper are inappropriate for protecting sensitive freshwater biota. *Chemosphere* 60: 1-8.
[30] Skidmore and Firth, 1983.
[31] MK Schubauer-Berigan et al., 1993. pH-dependent toxicity of Cd, Cu, Ni, Pb and Zn to *Ceriodaphnia dubia*, *Pimephales promelas*, *Hyalella azteca* and *Lumbriculus variegatus*. *Environmental Toxicology and Chemistry* 12, 7: 1261-66; PG Welsh et al., 1996. Estimating acute copper toxicity to larval fathead minnow (*Pimephales promelas*) in soft water from measurements of dissolved organic carbon, calcium, and pH. *Can. J. Fish. Aquat. Sci.* 53, NA: 1263-71; PG Welsh et al., 1993. Effect of pH and dissolved organic carbon on the toxicity of copper to larval fathead minnow (*Pimephales promelas*) in natural lake waters of low alkalinity. *Canadian Journal of Fisheries and Aquatic Sciences* 50, 7: 1356-62.
[32] EC Rogevich, TC Hoang, and GM Rand, 2008. The effects of water quality and age on the acute toxicity of copper to the florida apple snail, *Pomacea paludosa*. *Archives of Environmental Contamination and Toxicology* 54, 4: 690-96.
[33] SJ Markich et al., 2003. The effects of pH and dissolved organic carbon on the toxicity of cadmium and copper to a freshwater bivalve: Further support for the extended free ion activity model. *Archives of Environmental Contamination and Toxicology* 45, 4: 479-91.
[34] N Wang et al., 2009. Evaluation of acute copper toxicity to juvenile freshwater mussels (fatmucket, *Lampsilis siliquoidea*) in natural and reconstituted waters. *Environmental Toxicology and Chemistry* 28, 11: 2367-77.
[35] JS Meyer, CJ Boese, and SA Collyard, 2002. Whole-body accumulation of copper predicts acute toxicity to an aquatic oligochaete (*Lumbriculus variegatus*) as pH and calcium are varied. *Comparative Biochemistry and Physiology C-Toxicology & Pharmacology* 133, 1-2: 99-109. Schubauer-Berigan et al., 1993.
[36] RS Rathore and BS Khangarot, 2002. Effects of temperature on the sensitivity of sludge worm *Tubifex tubifex* Muller to selected heavy metals. *Ecotoxicology and Environmental Safety* 53, 1: 27-36.
[37] N Reithmuller et al., 2000. *The effect of true water hardness and alkalinity on the toxicity of copper and uranium to two tropical Australian freshwater organisms*, Supervising Scientist (Canberra, Australia).
[38] SJ Markich, AR King, and SP Wilson, 2006. Non-effect of water hardness on the accumulation and toxicity of copper in a freshwater macrophyte (*Ceratophyllum demersum*): How useful are hardness-modified copper guidelines for protecting freshwater biota? *Chemosphere* 65, 10: 1791-800.

3.4 Review of water chemistry effects on acute zinc toxicity

For zinc, there are multiple studies that have assessed the effect of pH, hardness and/or DOC on acute toxicity to fish and invertebrates (summarised in Table 3.2). Not all studies have investigated each of the TMFs. Further, no information could be found regarding the effect of pH, hardness or DOC on acute toxicity to plants or algae, though information is available from chronic testing.

The effect of pH on zinc toxicity is complex–in fish toxicity has been reported to increase as pH increases, up to around pH 7.0, and then to decrease as pH increases further. This has been explained as an effect of H^+ competition for binding sites at low pH, then effects of speciation (reducing free zinc concentration) at higher pH.[39] In the crustacean *C. dubia*, zinc toxicity was lower at pH 6.0-6.5 than at 7.0-7.5, and most toxic at 8.0-8.5.[40] For the crustaceans *D. magna* and *D. pulex*, EC50 values did not change significantly with changes in pH.[41]

Hardness, or in some studies, the increased concentrations of calcium, decreased zinc toxicity substantially for fathead minnow, rainbow trout and crustacean (*Daphnia*) species. Positive relationships were also reported for four additional fish species and the snail *Physa heterostropha* in the US EPA's hardness correction for zinc.[42] The effect of hardness on toxicity has been reported to be stronger for zinc than for copper.[43] The importance of hardness is likely to be highest in low DOC waters (including laboratory waters), though as DOC increases (and free zinc concentrations decrease) the importance of hardness reduces.

Organic matter generally decreases zinc toxicity, though for some species (*P. promelas, C. dubia*) this may occur only at DOC concentrations around 10 mg/L or above.[44] The importance of DOC also depends somewhat on organism sensitivity. For sensitive species, low concentrations of DOC may bind sufficient zinc to cause an observable reduction in toxicity, whereas for insensitive species, a larger concentration of DOC is needed to reduce the available zinc to an extent that causes the same relative toxicity reduction. This effect may be more apparent for zinc than for copper, due to weaker binding affinity of zinc to DOC.

The effect of alkalinity on acute zinc toxicity has rarely been tested as a single varying factor–in most studies hardness and/or pH has also varied in the test waters.[45] This makes it difficult to separate out the effect of alkalinity; however, through meta-analysis Meyer et al. concluded that the acute toxicity of zinc to *D. magna* and rainbow trout were reduced as alkalinity increased.[39]

Again, through meta-analysis Meyer et al. concluded that the acute toxicity of zinc generally increased as temperature increased.[39] However, water temperature can itself exert thermal stress on organisms and it can be complex to distinguish toxicity modifying effects from the effect of multiple stressors.[46] Furthermore, it has been difficult to determine general relationships across species, possibly as organisms have individual ranges for thermal tolerance.

[39] Meyer et al., 2007.
[40] Hyne et al., 2005. Schubauer-Berigan et al., 1993.
[41] M Clifford and JC McGeer, 2009. Development of a biotic ligand model for the acute toxicity of zinc to *Daphnia pulex* in soft waters. *Aquatic Toxicology* 91, 1: 26-32; Meyer et al., 2007.
[42] US EPA, 1987. *Ambient water quality criteria for zinc - 1987*, United States Environmental Protection Agency, Criteria and Standards Division (Washington D.C.).
[43] Hyne et al., 2005.
[44] RB Bringolf et al., 2006. Influence of dissolved organic matter on acute toxicity of zinc to larval fathead minnows (*Pimephales promelas*). *Archives of Environmental Contamination and Toxicology* 51, 3: 438-44; Hyne et al., 2005.
[45] CCME, 2018. *Scientific criteria document for the development of the Canadian water quality guidelines for the protection of aquatic life: Zinc*, Canadian Council of Ministers for the Environment, National Guidelines and Standards Office, Water Policy and Coordination Directorate, Environment Canada (Winnipeg, MB, January 2018), https://ccme.ca/fr/res/2018-zinc-cwqg-scd-1580-en.pdf.
[46] Z Wang et al., 2019. Thermal extremes can intensify chemical toxicity to freshwater organisms and hence exacerbate their impact to the biological community. *Chemosphere* 224: 256-64; CCME, 2018.

Table 3.2: Effect of key TMFs on **acute zinc** toxicity across different species. Downwards arrow indicates toxicity decreases (↑LC50 increases) as TMF increases. Sideways arrow indicates toxicity does not change substantially with increases in TMF. There was no information available regarding the effect of TMFs on acute toxicity to plants or algae.

Species	Effect of:				
	pH	**Hardness**	**DOC**	**Alkalinity**	**Temperature**
Fish					
Fathead minnow (*P. promelas*) [47]	↑	↓	↓	↔	↔
Rainbow trout (*O. mykiss*) [48]	↑↓	↓	Not tested	↓	↔
Invertebrates					
Crustacean (*D. magna*) [49]	↔↓	↓	↓	↔	↑
Crustacean (*D. pulex*) [50]	↔	↓	↓	Not tested	Not tested
Crustacean (*C. dubia*) [51]	↑	↓	↔↓	Not tested	Not tested
Crustacean (*Paratya australiensis*) [52]	Not tested	Not tested	Not tested	Not tested	↑
Amphipod (*Hyalella azteca*) [53]	↔↑		Not tested	Not tested	Not tested
Clam (*Anodonta cygnea*) [54]	Unclear	↑	Not tested	Not tested	Not tested
Sludge worm (*Tubifex tubifex*) [55]	↓*	↓*	Not tested	Not tested	↑

Note: * Both pH and hardness increased in test waters, so influencing factor cannot be confirmed.

3.5 Summary

In acute exposures, DOC reduces the toxicity of both copper and zinc to fish and invertebrates, though there has been less testing with zinc. Hardness also reduces toxicity of both copper and zinc to fish, and also clearly reduces toxicity of zinc to invertebrates. The effect of hardness on copper toxicity to invertebrates is less clear. For copper, toxicity pH tends to be lower at higher pH, whereas for zinc, the reverse is true.

There are some differences between trophic levels, and/or species in the way TMFs affect toxicity of copper and zinc. These differences may be more significant for pH and hardness; however, there is insufficient information to assess the effect of TMFs on copper or zinc toxicity to plants and algae. Figure 3.1 provides a simplified view of the way water chemistry affects metal bioavailability.

[47] Meyer et al., 2007.
[48] Meyer et al., 2007; RW Bradley and JB Sprague, 1985. The influence of pH, water hardness, and alkalinity on the acute lethality of zinc to rainbow trout (*Salmo gairdneri*). *Canadian Journal of Fisheries and Aquatic Sciences* 42, 4: 731-36.
[49] Meyer et al., 2007; KAC De Schamphelaere, DG Heijerick, and CR Janssen, 2004. Comparison of the effect of different pH buffering techniques on the toxicity of copper and zinc to *Daphnia magna* and *Pseudokirchneriella subcapitata*. *Ecotoxicology* 13, 7: 697-705; DG Heijerick, KAC De Schamphelaere, and CR Janssen, 2002. Predicting acute zinc toxicity for *Daphnia magna* as a function of key water chemistry characteristics: Development and validation of a biotic ligand model. *Environmental Toxicology and Chemistry* 21, 6: 1309-15; GA Chapman, S Ota, and F Recht, 1980. *Effects of water hardness on the toxicity of metals to Daphnia magna (Status Report 1980)*, U.S. EPA (Corvallius, Oregon 97330.).
[50] Clifford and McGeer, 2009.
[51] Hyne et al., 2005. Schubauer-Berigan et al., 1993.
[52] Skidmore and Firth, 1983.
[53] Schubauer-Berigan et al., 1993.
[54] K Pynnonen, 1995. Effect of pH, hardness and maternal pre-exposure on the toxicity of Cd, Cu and Zn to the glochidial larvae of a freshwater clam *Anodonta cygnea*. *Water Res.* 29, 1: 247-54.
[55] Rathore and Khangarot, 2002.

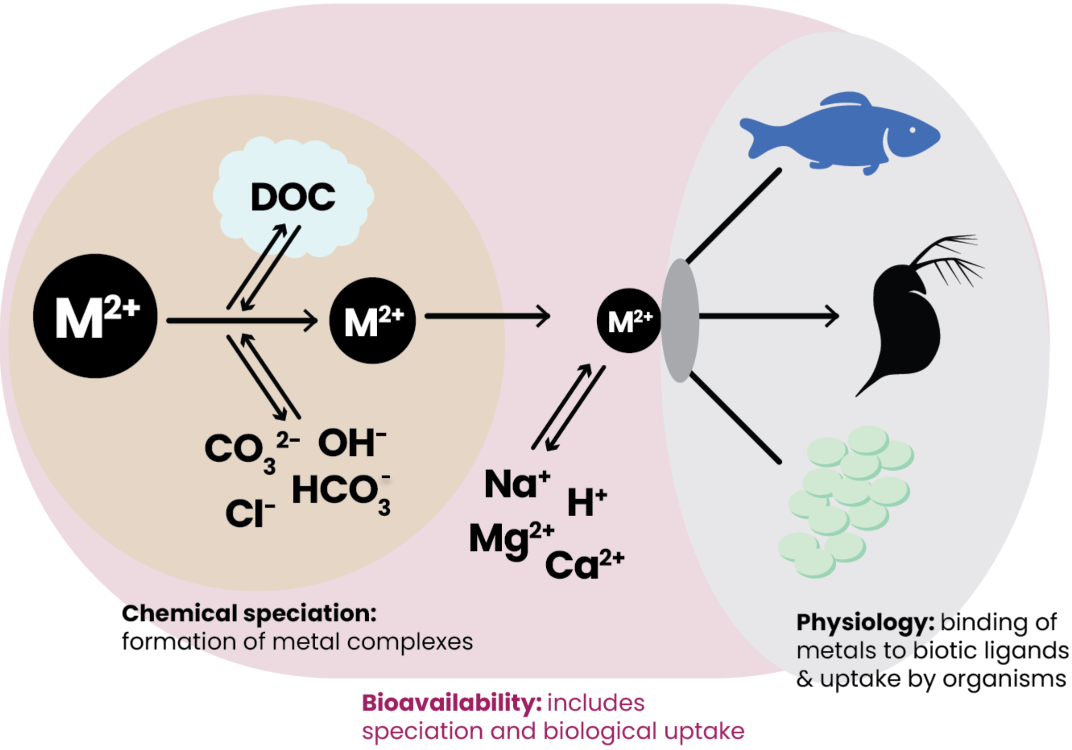

Figure 3.1: Simplified conceptual outline for metal bioavailability, incorporating both chemical speciation and physiology of exposed organisms. .M^{2+} represents metals. The reducing size of the circle from left to right indicates a decrease in concentration due to complexation with DOC and inorganic ions, and due to competition at the biotic ligand.

4 Toxicity testing for this project

4.1 Acute toxicity testing

Acute toxicity testing was undertaken with the native cladoceran ("water flea") *Daphnia thomsoni* in a 48-hour survival (immobilisation) test (see Appendix C for test method details). This species was also used in the chronic toxicity testing of zinc for a previous project for derivation of the chronic zinc guideline values and has been demonstrated to be sensitive to zinc.[56] Testing was undertaken in natural water samples collected from around Aotearoa, aiming to represent a variety of different conditions where the acute guideline values may be applied. The location of those samples was the same as used in the chronic toxicity testing, to enable a direct comparison between short-term and long-term toxicity.

4.2 Acute toxicity results

The chemistry of water samples collected (Table 4.1) varied considerably for DOC (<0.3-12 mg/L), but less so for hardness (2.7-74 mg $CaCO_3$/L) and four of the natural waters tested had similar pH (7.2-7.6). The similarity in pH may be an artefact of the water storage prior to test initiation, which was several months, due to a change from the initially proposed toxicity test species.[57] The dissolved zinc concentration ranged from 2.9 to 4.4 µg/L and copper from <0.5 to 1.3 µg/L. Those concentrations are well below expected acute toxicity values.

The Okutua Creek water had very low pH (around 5.0). Initial tests suggested that the *Daphnia* could survive in that water, however when the copper toxicity test was undertaken there was 0% survival in all controls and test concentrations after 48 hours, meaning no copper toxicity results could be obtained from that test. The pH of that water was increased with NaOH to pH 6 prior to retesting.

Table 4.1: Details of water chemistry for the five natural waters as tested.

Water sample	pH (as collected)	pH (zinc test)[b]	pH (copper test)[b]	Hardness (mg $CaCO_3$/L)	Ca (mg/L)	Mg (mg/L)	DOC (mg/L)[a]	Dissolved zinc (µg/L)[b]	Dissolved copper (µg/L)[b]
Waihou River	7.3	7.6	7.7	15.7	3.2	1.8	<0.3	3.3	0.8
Clutha River/Mata-Au	7.2	7.5	7.7	34	12	0.74	0.4	2.9	<0.5[c]
Hōteo River	7.5	7.8	7.7	58	14	5.7	3.7	4.4	1.1
Mahurangi River (Redwoods)	7.6	7.9	7.7	74	16	8.1	2.2	3.2	<0.5[c]
Okutua Creek	5.0	6.1	6.1	2.7	0.48	0.37	11.9	4.4	1.3

[a] Measured as dissolved non-purgeable organic carbon (DNPOC). [b] Test initiation and test termination mean measured pH/concentrations. [c] Less than detection limit.

The results from the toxicity testing (Table 4.2) indicated an ~8-fold range in the copper EC50 values and a ~2-fold range in the zinc EC50 values. The copper EC50 values were highest in the Hōteo and Mahurangi River waters which had higher hardness and DOC than the Waihou and Clutha River/Mata-Au waters (lowest DOC, low hardness). The copper EC50 was moderate in the water from Okutua Creek which had the highest DOC of the five sampled waters, but low hardness and pH. The zinc EC50 values were also higher in the Hōteo and Mahurangi River waters (higher hardness and moderate DOC), than in the Waihou and Clutha River/Mata-Au waters. However, the zinc EC50 was lowest in the Okutua Creek water with highest DOC and lowest pH. The latter results suggests that either DOC may not be a strong influence on zinc toxicity or that pH is a strong influence. These data were used in the model evaluation, as part of both cross-species validation and native-species validation (section 6).

[56] J Stauber et al., 2021. Application of bioavailability models to derive chronic guideline values for nickel in freshwaters of Australia and New Zealand. *Environmental Toxicology and Chemistry* 40, 1: 100-12.

[57] The tests were initially planned with larvae/glochidia from a native freshwater mussel (kakāhi, *Echyridella menziesii*) however there were insufficient brooding females available for collection at the time of the testing.

Table 4.2: Results from the acute toxicity testing [a]

Water sample	Copper		Zinc)	
	EC10 (µg/L)	EC50 (µg/L)	EC10 (µg/L)	EC50 (µg/L)
Waihou River	23 (n/c-30)[b]	41 (33-51)	204 (121-252)	404 (344-474)
Clutha River/Mata-Au	22 (n/c-26)	32 (26-39)	243 (124-311)	526 (432-641)
Hōteo River	180 (178-183) [c]	272 (261-284) [d]	374 (279-442)	751 (661-853)
Mahurangi River (Redwoods)	89 (65-150) [c]	211 (159-255) [d]	511 (459-551)	826 (781-873)
Okutua Creek	74 (n/c-93)	103 (78-135)	162 (78-208)	343 (282-416)

Notes: [a]EC50 (95% confidence interval) concentrations determined by non-linear regression (log-logistic) against measured metal concentrations unless noted. [b]Lower confidence interval cannot be calculated. [c] EC15 value as EC10 could not be calculated with the linear interpolation analysis method used for these tests. [d]EC50 concentrations determined by linear interpolation as there were insufficient treatments with partial mortality to enable a non-linear regression to be fitted.

4.3 Comparison of acute and chronic results

Chronic tests with zinc, using the same species and waters from the same locations, were previously undertaken for the development of the chronic zinc DGVs.[58] The toxicity data from that testing is compared in Table 4.3 and indicated ratios between acute and chronic zinc toxicity (i.e., ACR values) ranged from 4.8 to 51. Comparison of the "no effect" ratios for acute and chronic tests (i.e., acute EC10/chronic EC10 values) for zinc indicated that acute toxicity may be 2.3- to 26-fold higher than the chronic toxicity when measured without consideration of TMF levels (i.e., a 10-fold range). This suggests that acute zinc GVs may be in the range of 2- to 26-fold higher than the chronic zinc DGVs.

Table 4.3: Comparison of acute and chronic **zinc** toxicity testing with *D. thomsoni* "as measured" in five natural waters.

Water source	Acute EC50 † (µg/L)	Acute EC10 (µg/L)	Chronic EC50 ‡ (µg/L)	Chronic EC10 ‡	Ratio (ACR) acute EC50: chronic EC10	Ratio acute EC10 to chronic EC10
Waihou River	404	204	34	8	51	26
Clutha River/Mata-Au	526	243	65	55	9.6	4.4
Hōteo River	751	374	115	36	21	10
Mahurangi River (Redwoods)	826	511	188	46	18	11
Okutua Creek	343	162	91	72	4.8	2.3

Notes: † 48 hour survival test. ‡ 21 day reproduction test.

[58] JL Stauber et al., 2023. Applicability of chronic multiple linear regression models for predicting zinc toxicity in Australian and New Zealand freshwaters. *Environmental Toxicology and Chemistry* 42, 12: 2614-29.

5 Bioavailability models and evaluation process

5.1 Introduction

This section outlines the currently available models for copper and zinc acute toxicity, how metal bioavailability models are used in deriving water quality guideline values, and criteria for selecting the most appropriate models for this use. Unless specified, the models discussed are based on acute toxicity data and applicable to deriving acute guideline values. Models for chronic toxicity are not generally included, as the mechanisms of toxicity, and the effect of TMFs on toxicity, can vary between short-term and long-term exposures.

5.2 Existing bioavailability models for acute toxicity

There are numerous models available that relate acute toxicity for copper (Table 5.1) and zinc (Table 5.2) to TMFs (see Appendix B for more details for each model). Almost all these models are for fish (primarily rainbow trout and fathead minnow) and invertebrates (primarily cladocerans–water fleas). There is only one model available that is specific to plants and algae. Lack of models for plants and algae may be because much of the model development has been in the United States, and the US EPA do not include plants and algae when calculating their criteria.

Hardness-based algorithms, as first used by the US EPA, are based on a linear regression model of metal toxicity versus hardness. The US EPA algorithms were based on averaged slopes from data for fish and invertebrates: 8 species for copper (no. individual tests = 124) and for zinc (no. tests = 109).

The BLM was developed to account for other factors that are also important in metal toxicity, including those that affect metal speciation (such as pH and alkalinity) through the incorporation of a metal speciation model. There are multiple BLM models in use (Table 5.1), each of which may be based on different datasets and may have different model parameters. To date, BLMs for copper have been adopted for use within acute water quality criteria/guideline values in the US and Canada, replacing hardness algorithms. BLMs have also been used in developing bioavailability-based water quality guidelines in the EU, though these are based on chronic exposures, rather than acute. While some of the BLMs listed in Table 5.1 are used within regulatory systems, others have been developed for research purposes.

Table 5.1: Models currently used or with potential for use in deriving acute **copper** GVs.

Model type	Key References	Species/group coefficients derived from	TMFs included
Hardness	US EPA water quality criteria[59]	Pooled model based on *Daphnia magna, D. pulicaria, Oncorhynchus clarkii, O. mykiss, O. tshawytscha, Pimephales promelas, Poecilia reticulata, Lepomis macrochirus*	Hardness
Species-specific MLR	Welsh et al.[60] research paper	*P. promelas*	pH & DOC; pH & DOC & Ca
Species-specific MLR	Rogevich et al.[61] research paper	*Pomacea paludosa*	pH & DOC & organism age
Species-specific MLR	Brix et al.[62] alternative US criteria	Individual species models for *Ceriodaphnia dubia, D. magna, D. obtuse, D. pulex, O. mykiss, P. promelas*	Hardness, pH, DOC (not all significant for each species model)
Pooled MLR	Brix et al.[63] alternative US criteria	Pooled model, based on all above species	Hardness, pH, DOC
Fish BLM	Di Toro et al. original BLM[64]	*P. promelas* and *O. mykiss*	Temp., pH, DOC, humic acid, Ca, Mg, Na, K, Cl, SO4, alkalinity
Invertebrate BLM	De Schamphelaere et al. research papers[65]	*D. magna*	Temp., pH, DOC, humic acid, Ca, Mg, Na, K, Cl, SO4, alkalinity
Fish/ invertebrate BLM	US EPA water quality criteria[66]	As for Di Toro et al. (2001)	Temp., pH, DOC, humic acid, Ca, Mg, Na, K, Cl, SO4, alkalinity
Fish BLM	Crémazy et al. research paper[67]	*O. mykiss*	Temp., pH, DOC, humic acid, Ca, Mg, Na, K, Cl, SO4, alkalinity
Fish/ invertebrate BLM	Canadian Federal and British Columbia water quality guidelines[68]	Not specifically reported by BC or ECCC but model files state "derived from fathead minnow" and changed based on an "updated database".	Temp., pH, DOC, humic acid, Ca, Mg, Na, K, Cl, SO4, alkalinity
Plant BLM	Canadian Federal water quality guidelines[69]	Source not reported, but model files suggest adopted from BLM for barley & soils.	Temp., pH, DOC, humic acid, Ca, Mg, Na, K, Cl, SO4, alkalinity

[59] US EPA, 1985. *Ambient water quality criteria for copper - 1984*, United States Environmental Protection Agency, Criteria and Standards Division (Washington D.C.).
[60] Welsh et al., 1993; Welsh et al., 1996.
[61] Rogevich, Hoang, and Rand, 2008.
[62] KV Brix et al., 2017. Use of Multiple Linear Regression models for setting water quality criteria for copper: A complementary approach to the Biotic Ligand Model. *Environmental Science & Technology* 51, 9: 5182-92; KV Brix et al., 2021. Comparative performance of Multiple Linear Regression and Biotic Ligand Models for estimating the bioavailability of copper in freshwater. *Environmental Toxicology and Chemistry* 40, 6: 1649-61.
[63] Brix et al., 2017; Brix et al., 2021.
[64] DM Di Toro et al., 2001. Biotic ligand model of the acute toxicity of metals. 1. Technical Basis. *Environmental Toxicology and Chemistry* 20, 10: 2383-96.
[65] De Schamphelaere and Janssen, 2002; KAC De Schamphelaere, DG Heijerick, and CR Janssen, 2002. Refinement and field validation of a biotic ligand model predicting acute copper toxicity to *Daphnia magna*. *Comparative Biochemistry and Physiology C-Toxicology & Pharmacology* 133, 1-2: 243-58.
[66] US EPA, 2007.
[67] Crémazy et al., 2017.
[68] ECCC, 2021. *Canadian Environmental Protection Act, 1999. Federal Environmental Quality Guidelines. Copper*, Environment and Climate Change Canada (Ottawa: Government of Canada), https://www.canada.ca/content/dam/eccc/documents/pdf/pded/feqg-copper/Federal-Environmental-Quality-Guidelines-Copper.pdf; B.C. Ministry of Environment and Climate Change Strategy, 2019. *Copper Water Quality Guideline for the Protection of Freshwater Aquatic Life. Technical Report.*, British Columbia Ministry of Environment and Climate Change Strategy (British Columbia, Canada).
[69] ECCC, 2021; B.C. Ministry of Environment and Climate Change Strategy, 2019.

Table 5.2: Models currently used or with potential for use in deriving acute **zinc** GVs.

Model type	Key References	Species/group coefficients derived from	TMFs included
Hardness	US EPA aquatic criteria[70]	*D. magna, Physa heterostropha, O. mykiss, P. promelas, Salvelinus fontinalis, P. reticulata, Morone saxatilis, L. macrochirus*	Hardness
Species-specific MLR	Canadian water quality guidelines[71]	Species-specific models for *D. pulex, D. magna, Ceriodaphnia dubia, O. mykiss, Salmo trutta, P. promelas*	Hardness, DOC, pH (not all significant for each species model)
Pooled MLR	Canadian water quality guidelines[72]	Pooled *Daphnia*	Hardness, DOC (pH included but not significant)
Species-specific MLR	DeForest et al.[73] alternative to US criteria	Species-specific models for *D. pulex, D. magna, C. dubia, O. mykiss, S. trutta, P. promelas, Pomacea paludosa*	Hardness, pH, DOC
Pooled MLR	DeForest et al.[74]	Pooled fish & invertebrates as listed above	Hardness, pH, DOC
Fish BLM	Santore et al.[64]	*P. promelas, O. mykiss*	Temp., pH, DOC, humic acid, Ca, Mg, Na, K, Cl, SO4, alkalinity
Invertebrate BLM	Heijerick et al.[75]	*D. magna*	Temp., pH, DOC, humic acid, Ca, Mg, Na, K, Cl, SO4, alkalinity
Fish/ invertebrate BLM	HydroQual[76]	*D. magna, P. promelas, O. mykiss*	Temp., pH, DOC, humic acid, Ca, Mg, Na, K, Cl, SO4, alkalinity
Invertebrate BLM	Clifford & McGeer[77], soft waters	*D. pulex*	Temp., pH, DOC, humic acid, Ca, Mg, Na, K, Cl, SO4, alkalinity
Unified fish/ invertebrate BLM	DeForest et al.[78]	Unified/pooled model based on *D. magna, D. pulex, P. promelas, O. mykiss*	Temp., pH, DOC, humic acid, Ca, Mg, Na, K, Cl, SO4, alkalinity
Fish/ invertebrate BLM	Windward research model[79]	Not specified, model files state based on pooled data, presumably same as earlier HydroQual version	Temp., pH, DOC, humic acid, Ca, Mg, Na, K, Cl, SO4, alkalinity
Recalibrated fish/ invertebrate BLM	DeForest et al.[80]	6 fish & invertebrate species (as per MLRs above)	Temp., pH, DOC, humic acid, Ca, Mg, Na, K, Cl, SO4, alkalinity

[70] US EPA, 1996. *1995 Updates: Water quality criteria documents for the protection of aquatic life in ambient water*, United States Environmental Protection Agency, Office of Water (Washington D.C., September 1996), https://nepis.epa.gov/Exe/ZyPURL.cgi?Dockey=20002924.TXT.
[71] CCME, 2018.
[72] CCME, 2018.
[73] DK DeForest et al., 2023. Comparison of Multiple Linear Regression and Biotic Ligand Models for predicting acute and chronic zinc toxicity to freshwater organisms. *Environmental Toxicology and Chemistry* 42, 2: 393-413.
[74] DeForest et al., 2023.
[75] DG Heijerick et al., 2005. Development of a chronic zinc biotic ligand model for *Daphnia magna*. *Ecotoxicology and Environmental Safety* 62, 1: 1-10.
[76] HydroQual, 2007. *The Biotic Ligand Model Windows Interface: User's Guide and Reference Manual, Version 2.2.3*, HydroQual (Mahwah, NJ, USA).; RC Santore et al., 2002. Application of the biotic ligand model to predicting zinc toxicity to rainbow trout, fathead minnow, and *Daphnia magna*. *Comparative Biochemistry and Physiology C-Toxicology & Pharmacology* 133, 1-2: 271-85.
[77] Clifford and McGeer, 2009.
[78] DK DeForest and EJ Van Genderen, 2012. Application of U.S. EPA guidelines in a bioavailability-based assessment of ambient water quality criteria for zinc in freshwater. *Environmental Toxicology and Chemistry* 31, 6: 1264-72.
[79] Windward Environmental, 2019. *Biotic Ligand Model Windows® interface, research version 3.41.2.45: User's guide and reference manual* (Windward Environmental, May 2019).
[80] DeForest et al., 2023.

MLR models are related to single linear models, such as that used for hardness, but include multiple factors. For example, Welsh et al.[81] developed models to assess key modifying factors for acute copper toxicity as part of research studies on fathead minnow. These models were not intended for use in water quality guidelines. In more recent cases[82] MLRs were developed as a simplification of, or an alternative to BLMs for use in deriving water quality guideline values—based on the key TMFs but requiring fewer input data. Most of those models are based on hardness, pH and DOC, though some are based only on a subset of those three, either due to lack of data during model development, or non-significance of slope relationships for some species. Pooled MLRs use existing toxicity data for a number of fish and invertebrate species to derive the statistical relationships.

The models listed in Table 5.1 and Table 5.2 were included in either qualitative and/or quantitative assessments to select the most appropriate model for acute guideline value derivation in Aotearoa. It was not in the project scope to develop new bioavailability models.

5.3 Using bioavailability models in toxicity guidelines

The selected model or models will be applied both to the toxicity dataset used to derive the guideline values (i.e., to normalise the dataset to the same water chemistry), and to adjust the guideline values for site-specific water chemistry (see Figure 5.1).[83]

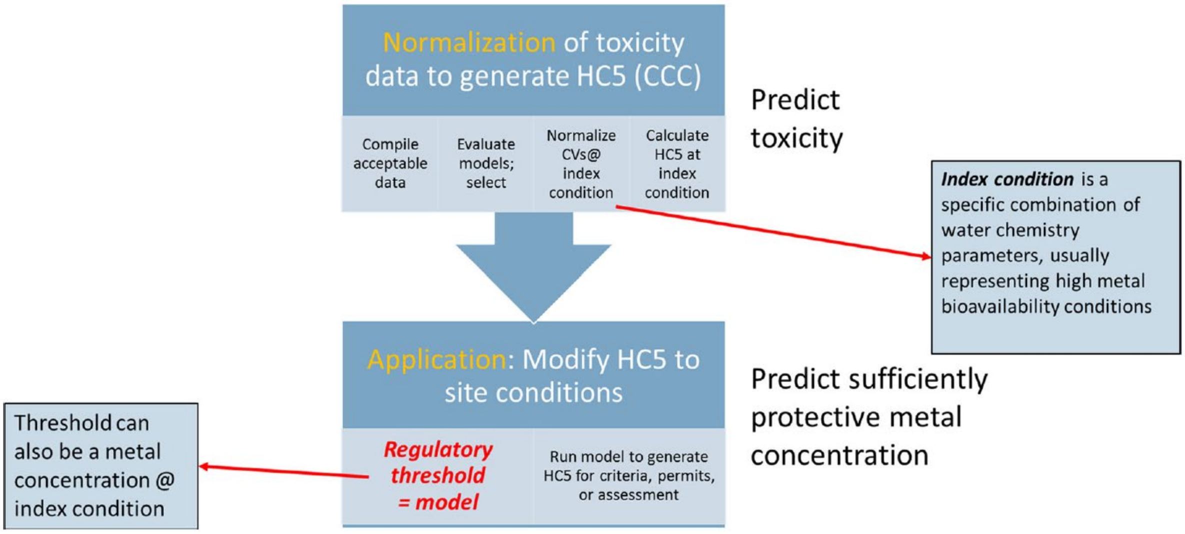

Figure 5.1: Flow chart for use of bioavailability models in deriving water quality guideline values.[84] CCC = criterion continuous concentration (term used by US EPA), this chart relates to chronic guideline values but is equally relevant for acute guideline values. HC5 = 5% hazardous concentration, equivalent to the 95% level of protection used in ANZG; CV = chronic value, although an acute value is used in this project (i.e., EC50 value).

In deriving water quality guidelines, a single bioavailability model can be applied to all species. The hardness-based algorithms widely used for deriving and adjusting acute copper and zinc guideline values are examples of this approach. The hardness equation was applied to all species (fish, invertebrates, plants and algae) to normalise all toxicity data to an equivalent hardness prior to calculating a guideline value. Similarly, the US EPA copper criteria use a BLM that is applied to all fish and invertebrate toxicity data used to calculate the guideline values.

[81] Welsh et al., 1996; Welsh et al., 1993.
[82] Brix et al., 2017; Brix et al., 2021; CCME, 2018.
[83] Although it would be possible to use different models for the two different steps, this would be somewhat unusual.
[84] E Van Genderen et al., 2020. Best practices for derivation and application of thresholds for metals using bioavailability-based approaches. *Environmental Toxicology and Chemistry* 39, 1: 118-30.

Alternatively, multiple models may be used–for example, different models for different trophic levels. In that approach, a model developed from one or more fish species could be applied to all vertebrate species (fish & amphibians) in the dataset, and a model developed from one or more invertebrate species could be applied to all invertebrates in the dataset.[85] These trophiclevel models have been preferred for Australian and New Zealand Guidelines[86] and have also been used in Europe.[87]

Single linear regressions, multiple linear regressions (MLR, considering more than one factor) and BLMs can be used in a trophic level approach. For example, to derive bioavailability-based nickel chronic guideline values, Stauber et al.[88] used four MLR models–separate ones for fish, invertebrates, plants and algae. Similarly, the copper BLM used in deriving chronic guideline values for Canada[89] uses one set of BLM parameters applied to all fish and invertebrates, and a second set of parameters applied to plants and algae.

"Hybrid normalisation" (as described by van Genderen et al.[90]) using a mixture of different models could also be used. For example, BLM for fish and invertebrate species and a simple regression model for plants and algae. This approach was used by EU in developing a risk assessment for zinc.[91] A hybrid option could also be to use the BLM where the required data exist for that test, and a hardness equation or MLR where there are insufficient data.

Application of different models to different groups can be useful if not all TMFs mediate toxicity to the same extent for all species. Differences could be expected to occur across different tropic levels/phyla due to differences in physiology. The review of effects of water chemistry on copper and zinc toxicity (see section 3.4) indicated that there can be differences between trophic levels, and/or species in the way the key TMFs affect toxicity. This is most apparent for the effect of hardness on copper toxicity: while hardness appears to affect copper toxicity to fish, it is unclear if hardness influences toxicity to all invertebrates. Therefore, the use of multiple models (either different types or the same type with different coefficients), specific to different species or trophic groups could be useful for deriving acute copper and zinc guideline values.

Despite these differences, it is also possible that a single model could explain differences in toxicity sufficiently well to use for GV derivation (e.g., within a factor of two). The ideal approach is to test the ability of different models to account for differences in species sensitivity due to water chemistry and apply the best model. This is the approach that has been taken for chronic nickel and zinc DGVs for Australia and New Zealand, and internationally for nickel.[92]

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[85] Note there may be exceptions to this: for example, a separate chronic zinc BLM has been developed for *C. dubia* as TMFs affect this species in a different way to *D. magna*.
[86] ANZG, 2024. *Toxicant default guideline values for aquatic ecosystem protection: Nickel in freshwater. Draft*, Australian and New Zealand Governments and Australian state and territory governments (Canberra, ACT, Australia, July 2024); ANZG, 2024. *Toxicant default guideline values for aquatic ecosystem protection: Zinc in freshwater. Draft*, Australian and New Zealand Governments and Australian state and territory governments (Canberra, ACT, Australia, May 2024).
[87] European Commission, 2018. *Technical guidance for deriving environmental quality standards. Guidance document No. 27. Updated Version 2018*, Common Implementation Strategy (CIS) for the Water Framework Directive, (European Commission).
[88] Stauber et al., 2021.
[89] ECCC, 2021.
[90] Van Genderen et al., 2020.
[91] The Netherlands, 2010. *European Union risk assessment report - zinc metal*, European Commission – Joint Research Centre, Institute for Health and Consumer Protection (Luxembourg).
[92] A Peters et al., 2021. Empirical bioavailability corrections for nickel in freshwaters for Australia and New Zealand water quality guideline development. *Environmental Toxicology and Chemistry* 40, 1: 113-26; ANZG, 2024; ANZG, 2024.; A Peters et al., 2023. Updating the chronic freshwater ecotoxicity database and biotic ligand model for nickel for regulatory applications in europe. *Environmental Toxicology and Chemistry* 42, 3: 566-80.

5.4 Model selection and evaluation methods

5.4.1 Guidance on model evaluation

Guidance on the selection of bioavailability models is provided for the Australian and New Zealand Guidelines [93], in European Commission [94] and OECD [95] guidance, and in scientific journals for international application. [96]

Best practice in model selection includes consideration of the following:

1. Ease of use: how user-friendly a model is, or how easily a user-friendly version can be developed with the time and resources available.
2. Level of input: the amount of data required to make the predictions.
3. Model representation: whether it covers the range of toxicity data (including species) and the range of water chemistry to which it would be applied (both toxicity data and local waters).
4. Model accuracy: the ability of the model to predict toxicity for different species (including species not used in model development) and different water chemistries.

In assessing model accuracy, OECD and Garman et al.[96] distinguish between autovalidation, independent validation and cross-species validation. Autovalidation measures the ability of a model to predict toxicity for the dataset that was used to parameterise or calibrate a model. In contrast, "independent validation" uses different toxicity datasets (not those used in model development) to test for accuracy of the model's predictions. Cross-species validation uses toxicity data for species that were not used to develop the model, and in that way determines whether models can be confidently applied to the range of species that would be included in a species sensitivity distribution.

In their guidance for metal GV derivation, [97] EU recommend assessing the ability of a model to extrapolate between species by testing with at least three additional taxonomic groups from different phyla. If extrapolation is not supported by the data, then a single, most conservative model (which could be a speciation model), should be used. [98]

Garman et al. [99] and Van Genderen et al. [100] also detailed quantitative measures that can be used to evaluate the accuracy of models for application to water quality guideline derivation. These were subsequently tested by Brix et al. [101] to compare copper BLM and MLR models and by Besser et al. [102] in assessing nickel and zinc BLMs. Both groups suggested modifications: for using the methods with a single toxicity dataset and for scoring slopes. This model evaluation uses a single toxicity dataset, and therefore the suggestions by both are relevant and considered here.

5.4.2 Key considerations for acute GVs in Aotearoa

The model evaluation needs to consider the use of the acute GVs within Aotearoa. That is, the models need to be suitable for enabling protection of our native freshwater species; they need to be applicable to the water chemistry of our rivers and streams; and they need to be practical for use within the resources available to users.

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[93] Warne et al., 2018.
[94] European Commission, 2018.
[95] OECD, 2017. *Guidance on the incorporation of bioavailability concepts for assessing the chemical ecological risk and/or environmental thresholds values of metals and inorganic metal compounds*, Organisation for Economic Co-operation and Development (19-Dec-2016, published April 2017).
[96] ER Garman et al., 2020. Validation of bioavailability-based toxicity models for metals. *Environmental Toxicology and Chemistry* 39, 1: 101-17; Van Genderen et al., 2020.
[97] European Commission, 2018.
[98] In the EU approach, the use of this single model is only accepted if this reduces the within-species variability in the reported toxicity data (NOECs/EC10s), demonstrating that the model can account for differences in test water chemistry. The EU also require that bioavailability models cover the range of water qualities to be encountered (first decision diamond).
[99] Garman et al., 2020.
[100] Van Genderen et al., 2020.
[101] Brix et al., 2021.
[102] JM Besser et al., 2021. Modeling the bioavailability of nickel and zinc to *Ceriodaphnia dubia* and *Neocloeon triangulifer* in toxicity tests with natural waters. *Environmental Toxicology and Chemistry* 40, 11: 3049-62.

All the available models have been developed overseas, based on species not native to Aotearoa. The evaluation therefore needs to include an assessment of how the models perform for native species, particularly any species that are sensitive to copper and zinc.

Rivers and streams in Aotearoa tend to be more dilute than world averages.[103] This means the calcium, magnesium (and therefore hardness), other ions, and the DOC are typically lower than Europe and United States, where most models have been developed and tested. Models need to be applicable to those waters.

The acute GVs could be used in the following applications:

1. Assessing potential effects of intermittent discharges (including stormwater)
2. Assessing potential effects within initial mixing zones of industrial and sewage discharges
3. Assessing potential effects of spills and accidental releases
4. Grading of waterways as part of an attribute table used in implementation of NPS-FM

In considering the uses of the acute GVs in Aotearoa, a simple tool would be ideal. For example, in the case of spills, users may be under time pressure to undertake a rapid assessment–an acute GV that can be calculated in a spreadsheet, with minimal additional data requirements would be easiest. In the case of stormwater discharges, where metal concentrations change rapidly over time (e.g., in relation to rainfall intensity and duration; first-flush after a dry period), there is high uncertainty in the concentrations. That uncertainty implies that striving for an overly precise model for GV derivation may be unnecessary. Instead, the GVs should be simple to use, to enable users to identify where potential issues can be expected and then managed.

5.4.3 Model evaluation

A suite of qualitative and quantitative measures was developed (Table 5.3) based on the guidance in the above documents, as well as those previously used for the nickel[104] and zinc[105] guideline value derivations.

The qualitative assessment screening was based on three factors as outlined below:

1. **Ease of use** of the model, or the ability to make an easy-to-use app within a reasonable timeframe.
2. **Data inputs** required to use each model, and whether those data are likely to be available in toxicity test data for deriving guideline values; and whether those variables are regularly monitored by regulators or could be obtained from existing data.
3. **Inclusion of key TMFs** identified by laboratory and mechanistic studies as most important. A model will be more accurate and rigorous if its structure and formulation are consistent with current understanding of metal bioavailability and uptake.

The quantitative assessment was based on five factors as outlined in Table 5.3. The scores from each of these measures were averaged to rank the models.

Scores 1 and 2 address model accuracy. Autovalidation and independent validation, although recommended by Garman et al.,[106] were not included in the assessment as this had already been undertaken for several of the models.[107] Further, there was insufficient information available for the copper BLMs (plant and fish/invertebrate) to assess what data had been used in model development, and

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[103] ME Close and RJ Davies-Colley, 1990. Baseflow water chemistry in New Zealand rivers 1. Characterization. Article, *New Zealand Journal of Marine and Freshwater Research* 24, 3: 319-41.
[104] Stauber et al., 2021.
[105] J Gadd, 2023. *Methodology for derivation of zinc freshwater guideline values*, National Institute for Water and Atmospheric Research (Auckland, NZ, September 2023).
[106] Garman et al., 2020.
[107] Brix et al., 2021; DeForest et al., 2023; GAV Price et al., 2023. Development and validation of multiple linear regression models for predicting chronic zinc toxicity to freshwater microalgae. *Environmental Toxicology and Chemistry* 42: 1-10.

therefore what data could be used for independent validation. Cross-validation (application to different species, Score 1) is the most important when using models in deriving water quality guideline values.

As all models listed in section 5.1 were developed overseas, and from species not native to Aotearoa, a specific score was added for validation of the models for species native to Aotearoa (Score 2). This evaluation was somewhat restricted by the lack of data for native species with differing TMFs, other than the data generated through this project (section 4). However, including this aspect in the evaluation provides further confidence in the use of bioavailability models in deriving guideline values for Aotearoa.

Scores 3, 4 and 5 relate to model representation, and whether the model covers the range of toxicity data (including species) and the water chemistry to which it would be applied. This includes assessing the applicable TMF range of the models compared to the range of waters in Aotearoa (Score 3), where the acute GVs may be used.

Table 5.3: Proposed scoring system for evaluating bioavailability model performance for acute guideline derivation.

Aspect	Details	Proposed metric(s)
Score 1: Model performance – cross-species validation	Dataset comprises additional species not used in model build, but that the model would be applied to. This approach was used in Peters et al. (2021) though not all metrics were calculated. This is termed read-across in the EU.	Average of 3 metrics: • Correlation coefficient • $RF_{x,2.0}$ (% data within factor of 2) • Score based on slope of model residuals vs: toxicity, hardness, pH, DOC, alkalinity[108]
Score 2: Model performance – native species validation	This is a subset of the cross-species validation but only for native species where suitable data exist.	As above but based on native species only.
Score 3: TMF range of model to NZ natural waters	TMF range of the model compared to the range in NZ waters, based on a database collated for Australian & New Zealand guidelines.	Percentage of NZ waters where all TMF values are within the range of the model being used. Calculated from number of samples where hardness, pH and DOC were inside model boundary range, as a proportion of total samples with data.
Score 4: TMF range of model compared to toxicity dataset	Range of pH/DOC/hardness (toxicity modifying factors, TMFs) of the model compared to toxicity dataset it will be applied to when deriving guideline values.	Percentage of toxicity data points where TMF values are within the range of the model being used, calculated as: For each toxicity data point, a grade of 0 is assigned if any TMF value is outside model boundary range; grade 1 if all are within. Overall score is the proportion of data with grade 1.
Score 5: Taxonomic coverage	How well does the model(s) represent the taxonomy of the toxicity dataset it is being applied to when deriving guideline values.	Each species to be used in the SSD assigned a grade based on taxonomy relative to the species used to develop the model as follows: 0 (outside kingdom), 1 (kingdom), 2, (phylum), 3 (class), 4 (order), 5 (family), 6 (genus), 7 (species). Average taxa grade for the dataset divided by 7 to get a ratio (from 0 to 1).

[108] Following formula from Besser et al., 2021.

5.5 Results of qualitative assessment

5.5.1 Inclusion of key TMFs

Multiple factors have been reported to be important in modifying **copper** toxicity – with pH, hardness, DOC; and possibly temperature and alkalinity indicated as factors that can modify speciation and therefore bioavailability (refer to section 3.3). While there are some differences between studies and species in the findings regarding the importance of each factor, it is generally accepted (in most recent publications) that pH, hardness and DOC are key factors for predictions relevant to freshwater environments.

Acute copper BLM models include pH, hardness (as calcium and magnesium ions) and DOC, along with other anions and cations as normally used in chemical speciation modelling.

These three key factors have also been the basis of most MLR models and are all present in the pooled copper model developed by Brix et al.[109] as an alternative to the BLM. However, not all of these three factors are included in the species-specific models. The *D. pulex* and *O. mykiss* models are based on hardness and DOC only – although pH was included in model development, it was not a statistically significant factor (Table 5.1). The *P. promelas* model by Welsh et al. was initially based only on pH and DOC, though this was improved later to include calcium concentration.

For **zinc**, many studies indicate that hardness is not the only factor that influences acute zinc toxicity, though for some species (e.g., rainbow trout) and in some waters, it may be the most important. However, it is generally accepted that pH and DOC are also important factors for inclusion in bioavailability models, while the importance of alkalinity is less clear.

The BLMs for zinc include temperature (used only within the inorganic speciation models in the BLM), pH, DOC, major cations (including hardness) and alkalinity, though the effect of alkalinity on free zinc concentration and on toxicity is minor compared to pH, DOC and hardness (e.g., a factor of 1.4 across an alkalinity range of 5 to 160 mg $CaCO_3$/L with the Windward model). The MLRs for zinc typically include pH, hardness and DOC, but none include alkalinity.

5.5.2 Data inputs

The **hardness algorithms** require only measurement of hardness and therefore are the simplest option available.[110] Most of the toxicity data for copper and zinc report hardness (or the water type, from which hardness can be estimated). Users of metal guideline values in Aotearoa are familiar with measuring hardness for use with existing chronic guideline values, so application for acute guideline values would be straightforward.

Existing **MLR models** for copper and zinc are predominantly based on pH, hardness and DOC, though there are some that require calcium. Most of the studies in the toxicity dataset report these variables, or they can be estimated (with some caveats, see section 7.6). Draft chronic copper and zinc guideline values include pH, hardness and DOC as TMFs, and therefore inclusion of these three TMFs for calculating site-specific acute guideline values may not require additional resources if being used alongside chronic guideline values.

The full **BLM models** have a long list of water chemistry inputs, including individual cations and alkalinity. Few of the papers describing toxicity data also report all of these variables. However, although the BLM models include many TMFs for input, not all substantially affect the predicted toxicity (or criteria). These can therefore be estimated for use in the BLM, for example, based on the known composition of specific media (such as US EPA low hardness waters) or based on typical ion ratios in natural waters. Furthermore, there are simplified versions of BLMs, that require only temperature, pH, DOC and hardness, making them similar to MLR models in terms of user inputs.

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[109] Brix et al., 2017; Brix et al., 2021.

[110] A regression based on DOC or pH only would be similarly simple; however, there are no existing regressions based on these single factors.

5.5.3 Ease of use

The **hardness algorithms** currently used in the US zinc acute criteria, and previously used for copper, are simple to apply, either with a calculator, within Excel or within any other data analysis package. Any other model based on a single TMF could similarly be straightforward to implement.

Whether **MLR models** are easy to apply or not depends on whether there is a single (pooled) model or multiple models, applied to different trophic levels. If a pooled model is used and applied to all species in the SSD, then adjustments of the guideline values can be made simply within Excel or within any other data analysis package. However, if (like the nickel and zinc chronic guideline values) different MLR models are applied to different trophic levels, then the SSD needs to be re-modelled for each water chemistry. This then requires either lookup tables for use, or for a simple tool to be developed (though that is outside the scope of this project).

The **BLM models** currently require specific software to be downloaded and installed. Furthermore, the full BLM is not user-friendly in terms of the required water quality data or in the way that data are entered. However, there are simplified versions of BLMs (such as bio-met[111]) that run in a spreadsheet and are more amenable to copy and pasting in data. If BLM model(s) are selected as the most appropriate for Aotearoa acute guideline values, then similar options could be created (though that is outside the scope of this project). A simple tool for the BLM could be equally as user-friendly as a simple tool developed for multiple MLR models.

5.5.4 Summary of qualitative assessment

The outcome of the qualitative assessment is summarised in Table 5.4. The hardness algorithm is the simplest option; however, it does not include all key TMFs for either copper or zinc. The available pooled MLR models for copper and zinc do include the three key TMFs of pH, hardness and DOC; and are simple to use (with a calculator or within a spreadsheet). This would be the preferred option for acute GVs, if the accuracy of the models is acceptable.

There is little difference in between trophic-level MLR or BLM approaches with respect to the three aspects considered. Existing models of both types include the key TMFs (for both copper and zinc) of pH, hardness and DOC, have similar input requirements (if using a simplified BLM) and can be either complex or simplified in terms of their use. If a BLM model (or models), or trophic-level MLRs are selected, a simplified tool would likely be required to be developed to assist users.

Table 5.4: Qualitative assessment of broad model options. Recommended option highlighted in green.

Model type	Inclusion of key TMFs	Input requirements	Ease of use
Hardness/single TMF model	No, multiple TMFs shown to be important for both copper and zinc	Minimal	Easy
Pooled MLR	Yes	pH, hardness, DOC	Easy
Trophic level MLRs	Yes, specific to trophic-level	pH, hardness, DOC	Complex
BLM (including simplified versions)	Yes	pH, hardness, DOC, temperature	Complex, but simplified versions can be created

[111] https://bio-met.net/

5.6 Models selected for further evaluation

Based on the qualitative assessment, **a pooled MLR is the preferred option for both copper and zinc**. However, since BLM models are regarded as the state-of-the-art for assessing copper and zinc bioavailability, the use of a pooled MLR should be carefully compared and evaluated against them. Furthermore, trophic-level MLRs can be considered as an intermediate option, providing for trophic-level differences in the way TMFs affect toxicity, but requiring fewer data inputs than a full BLM.

As outlined in section 5.2, pooled MLR models are available for both copper and zinc. These are based solely on toxicity data for fish and invertebrates, as there is limited acute toxicity data available for algae or plants. Additionally, algae and plants are not included when deriving US EPA guideline values, and the pooled MLRs has been developed for the US. These models may or may not be suitable for application to plants and algae.

There are several BLM models available for both copper and zinc, from the first widely available versions developed and subsequently used by the US EPA[112] to recent updates that have been calibrated with additional data or for additional species.[113] The most recent models were selected for further assessment.

A suite of trophic-level MLR models was selected, based on the approach of using a fish MLR model applied to vertebrates, an invertebrate model applied to invertebrates and a plant or algal model applied to plants and algae. For copper, species-specific models had been developed as a part of a study into alternatives to the BLM. This included a model based on *P. promelas* (fathead minnows), the key fish species used in developing the copper BLM, and a model based on the water flea *D. magna*. However, there were no models available for plants or algae. Instead, the plant BLM used within the Canadian acute copper guideline values was assessed as a possible option (Appendix E), although this option could be problematic when using the derived guideline values.

The Canadian water quality guideline values for zinc use an MLR based on two cladoceran species (*D. magna* and *D. pulex*) for adjusting their short-term/acute GVs. Although pH was included in the development of that model, it was not a statistically significant factor and is not included in the MLR equation. Although they also developed models for three different fish species, there was no data available with varying DOC and so this was not included in the models, and the predictive power of the models was low (adjusted R^2 values all <0.5) and therefore not suitable for use. DeForest et al. developed MLR models for rainbow trout based on data that included DOC, though these still had relatively low predictive power (adjusted R^2 0.5). As with copper, there are no existing models for predicting acute toxicity to plants or algae. Chronic models were evaluated for their applicability to the acute data (Appendix E) leading to the selection of an *R. subcapitata* model for use with algae and plants (Table 5.5).

The US EPA hardness regressions are also included alongside the pooled MLRs, trophic MLRs and BLMs to determine if these newer models offer improved performance over the traditional method. In the next section, the performance of these models (Table 5.5) is assessed using the quantitative assessment outlined in section 5.4.3.

[112] Santore et al., 2002; US EPA, 2007.
[113] B.C. Ministry of Environment and Climate Change Strategy, 2019; DeForest et al., 2023.

Table 5.5: Models included for further evaluation for normalising acute copper toxicity data for fish and invertebrates. Additional information on each model including the applicable TMF ranges and taxonomic groups included in their development is available in the excel files associated with this project.

Model		TMFs included	Application to:
Copper			
Pooled hardness regression [114]		Hardness	All species
Pooled fish & invertebrate acute MLR [115]		pH, hardness, DOC	All species
Trophic-level MLRs comprising:	*P. promelas* MLR [115] *D. magna* MLR [115] Plant BLM [116]	pH, hardness, DOC pH, hardness, DOC pH, DOC, cations/anions	Vertebrates Invertebrates Plants & algae
Fish/invertebrate BLM [116]		pH, DOC, cations/anions	All species
Zinc			
Pooled hardness regression [117]		Hardness	All species
Pooled fish & invertebrate acute MLR		pH, hardness, DOC	All species
Trophic-level MLRs comprising:	*O. mykiss* MLR [118] *D. magna & D. pulex* MLR [119] *R. subcapitata* MLR [118]	pH, hardness Hardness, DOC pH, DOC	Vertebrates Invertebrates Plants & algae
Fish/invertebrate BLM [118]		pH, DOC, cations/anions	All species

[114] Copper US EPA, 1985.
[115] Brix et al., 2017; Brix et al., 2021.
[116] ECCC, 2021; B.C. Ministry of Environment and Climate Change Strategy, 2019.
[117] Copper US EPA, 1985.; zinc: US EPA, 1987.
[118] DeForest et al., 2023.
[119] CCME, 2018.

6 Results of quantitative model evaluation

6.1 Introduction

Only some of the models selected for potential use had previously been assessed for their cross-species performance. That is, there had been no evaluation of their ability to predict toxicity for species not included in their development. This ability is crucial when using a model to derive metal guidelines, as the model is applied to a broad range of species.

Additionally, the models must be applicable to species native to Aotearoa, applicable to the toxicity dataset being used to derive the GVs, and to the waters where the GVs would be used in water management.

This section outlines the results of that model testing, to compare the pooled fish/invertebrate MLR models to other (potentially more accurate) bioavailability models. The existing hardness models for copper and zinc were also included in this quantitative analysis to highlight the improvements achieved using models that reflect more up-to-date understanding of metal toxicity. The model testing used the quantitative methods outlined in section 5.4.3. The following sections provide a detailed account of the scores calculated based on each factor, the overall model performance scores, and then the recommended models for deriving acute GVs for copper and zinc.

6.2 Score 1: Cross-species validation

6.2.1 Data used

To ensure that model performance statistics would be comparable across models,[120] only species that were not used in developing *any* of the models were used for the cross-species validation. Toxicity data were collated for such species (see Table 6.1) where tests were undertaken at a range for the important toxicity modifying factors (e.g., pH, calcium, magnesium, DOC, alkalinity). There were no applicable validation data for plants or algae for copper (see section 6.2), so no models were included for that trophic group in the trophic-level MLR suite.

Data were only included for tests where the pH, calcium, magnesium and DOC had been varied and measured in the test waters.[121] Not all studies reported all cations and anions required for testing the BLMs, but these could largely be obtained from existing compilations of toxicity data, previously used with BLMs.[122] For species not included in those compilations (e.g., native species), cations and anions were estimated based on the ion ratios from other reported data for the same location. Alkalinity was frequently unreported. If bicarbonate was reported, alkalinity was calculated from this.[123] In most cases, alkalinity was estimated by entering the pH and hardness into the simplified chemistry input of the BLM then switching to full chemistry to obtain the alkalinity estimated using the BLM protocols.[124]

[120] For example, p-values decrease as n increases.
[121] In some cases, these data were not reported within the same paper as the toxicity data but were obtained from additional papers or reported or directly from the authors.
[122] Copper Brix et al., 2021; ECCC, 2021.; zinc: DeForest et al., 2023.
[123] Alkalinity (as $CaCO_3$) = 1.22 × HCO_3
[124] See Windward Environmental, 2019. for a description of the algorithms used in calculating alkalinity.

Table 6.1: List of species used for evaluating copper and zinc bioavailability models for fish and invertebrates. More information for each species including the detailed water chemistry test conditions is available in the excel files associated with this project. * Indicates species native to Aotearoa.

Taxonomic group	Species for copper validation	Species for zinc validation
Fish	*Acipenser transmontanus* *Cottus bairdii* *Lepomis macrochirus* *Mogurnda mogurnda* *Perca flavescens* *Salvelinus confluentus*	*Oncorhynchus clarkii* ssp. *Lewisi*
Invertebrate	*Acroperus harpae* *Daphnia thomsoni** *Hyalella azteca* *Hyridella depressa* *Lampsilis siliquoidea* *Lymnaea stagnalis* *Villosa iris* *Paracalliope fluviatilis** *Paratya australiensis* *Potamopyrgus antipodarum**	*Daphnia thomsoni** *Gyraulus* sp. *Neocloeon triangulifer* *Rhithrogena* sp. *Paracalliope fluviatilis** *Potamopyrgus antipodarum**
Plants & algae	No data available	*Chlorella* sp. *Raphidocelis subcapitata*

6.2.2 Results and scores

For copper, the pooled fish/invertebrate MLR and the fish/invertebrate BLM showed similar performance (Figure 6.1), based on the correlation between predicted and observed EC50 values (R^2 = 0.66 for the MLR and 0.64 for the BLM, Table 6.2), the proportion of predictions within a factor of two of observed (0.75 and 0.74 respectively; Figure 6.2) and for scores based on residuals (see Table 6.2). These two models predicted toxicity marginally better than the trophic level models (R^2 = 0.6, $RF_{x,2.0}$ 0.71). The hardness regression had the lowest correlation coefficient (R^2 = 0.30) and $RF_{x,2.0}$ (0.46), and had the lowest residual metrics due to significant slopes for residuals versus observed EC50 and DOC. The relatively poor predictions for the hardness model are observable by the number of data to the right of the black line Figure 6.2.

With all models, there were some species with EC50 values that were over-predicted or under-predicted by more than a factor of two (i.e., points below and above the dotted line in Figure 6.1, bars to right of black line in Figure 6.2). In particular, none of the models predicted the toxicity of the fish species *Acipenser transmontanus* very well, with most predictions outside of a factor of two (blue dots outside dashed lines on Figure 6.1). There were also some tests with *D. thomsoni* that were not well predicted with any model.

Overall, the cross-validation score for copper was highest for the pooled fish/invertebrate MLR, at 0.78, compared to 0.76 for the BLM.

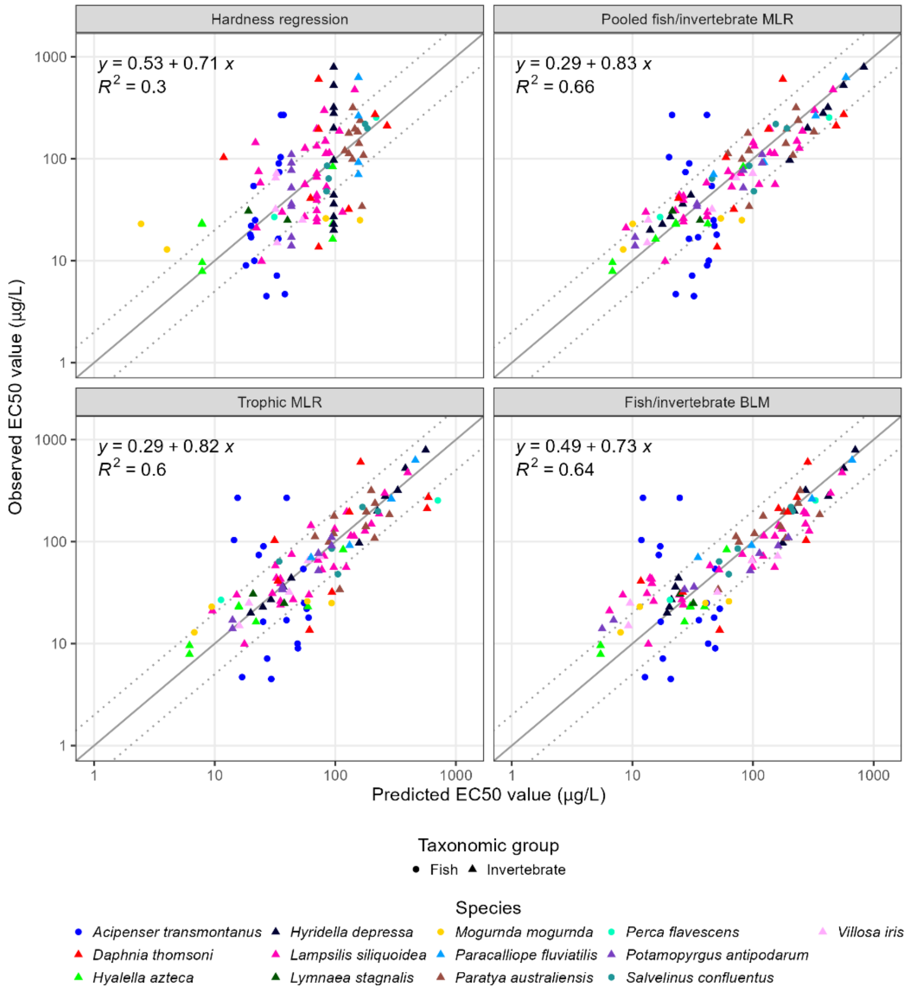

Figure 6.1: Observed EC50 values for **acute copper** toxicity to species not used in model development, compared to EC50 values predicted with four different models. Solid line is line of 1:1 agreement between observed and predicted EC50 values. Dotted lines indicate a factor of ±2 difference. Slightly more values are within a factor of two when used the pooled acute MLR model.

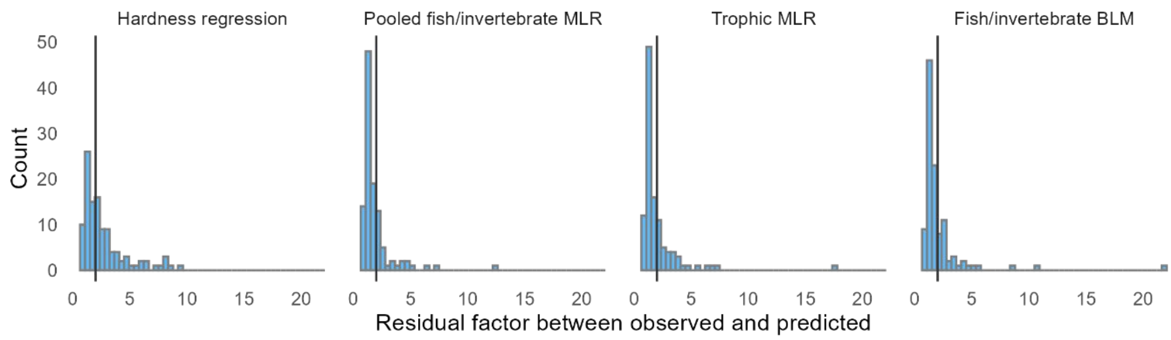

Figure 6.2: Residual factors (observed/predicted) for **acute copper** toxicity to species not used in model development, compared to EC50 values predicted with four different models. Solid black line is factor of two difference.

Table 6.2: Cross-species model performance metrics for **copper** and **zinc**. Each metric ranges from 0 (low/poor performance) to 1 (high, good performance). Cross validation score is calculated from the mean of the R^2, $RF_{x,2.0}$ and the mean of the five residual scores. Score in bold indicates best score for that metal.

Model	R^2	$RF_{x,2.0}$ †	Residual scores ‡					Cross-validation score (score 1)
			Log (Obs. EC50)	pH	Log (hard-ness)	Log (DOC)	Log (Alkalinity)	
Copper								
Hardness	0.30	0.46	0.42	1.00	0.76	0.60	0.89	0.50
Fish/ invertebrate MLR	0.66	0.75	0.78	1.00	0.92	0.88	1.00	**0.78**
Trophic MLR	0.60	0.71	0.70	1.00	0.85	0.99	0.97	0.74
Fish/ invertebrate BLM	0.64	0.74	0.87	0.95	1.00	0.75	0.96	0.76
Zinc								
Hardness	0.59	0.76	0.65	0.62	0.66	0.81	0.55	0.67
Fish/ invertebrate MLR	0.73	0.81	0.71	0.76	0.80	0.97	0.69	**0.78**
Trophic MLR	0.65	0.66	0.95	0.97	0.99	0.67	0.93	0.74
Fish/ invertebrate BLM	0.61	0.61	0.68	0.78	0.77	0.92	0.77	0.67

Notes: † Predictions within a factor of two of observed. ‡ Residual score for each variable calculated as 2/(1+10^ABS(slope × (1-p-value)))[125] See plots in Appendix F for relationships between residuals and each of these variables.

Compared to copper, there were fewer species and fewer data available for assessing model performance for zinc. Despite that, observed EC50 values ranged over two orders of magnitude (from 27 to 3300 µg/L) and there was a broad range in the pH (6.1-8.5), DOC (0.15-40 mg/L) and hardness (2.7-410 mg $CaCO_3$/L) concentrations of the validation data.

The pooled fish/invertebrate MLRs showed the best correlation (Figure 6.3) between predicted and observed EC50 values for the cross-species validation (R^2 = 0.73) and the most values within a factor of two (81%). The model did not accurately predict toxicity to *Chlorella* sp. but surprisingly for a fish/invertebrate model did predict toxicity for the other algal species, *R. subcapitata*. This model had the highest overall cross-validation score (0.78).

The suite of trophic-level MLRs had the next highest overall score (0.74), with an R^2 value of 0.65, meaning these models could explain 65% of the variance in the toxicity. Surprisingly the BLM had a lower overall score (0.67), perhaps due to poor predictions of the algal toxicity. Predictions for the mollusc *P. antipodarum* were very good – almost lying on the 1:1 line (yellow triangles in Figure 6.3). However, compared to the hardness and pooled MLR models, there were more predictions that were above a factor of two different (data to the right of the black line in Figure 6.4).

The hardness regression had the lowest R^2 value, however (unlike for copper) it did predict 76% of data within a factor of two. This was more than the trophic-level models or the fish/invertebrate BLM. However, residual scores for this model were lower, indicating where the model could not account for the effects of pH, DOC or alkalinity on toxicity.

The scores for each model from this cross-validation are combined with the other factors to calculate model performance scores in section 6.6.

[125] Besser et al., 2021..

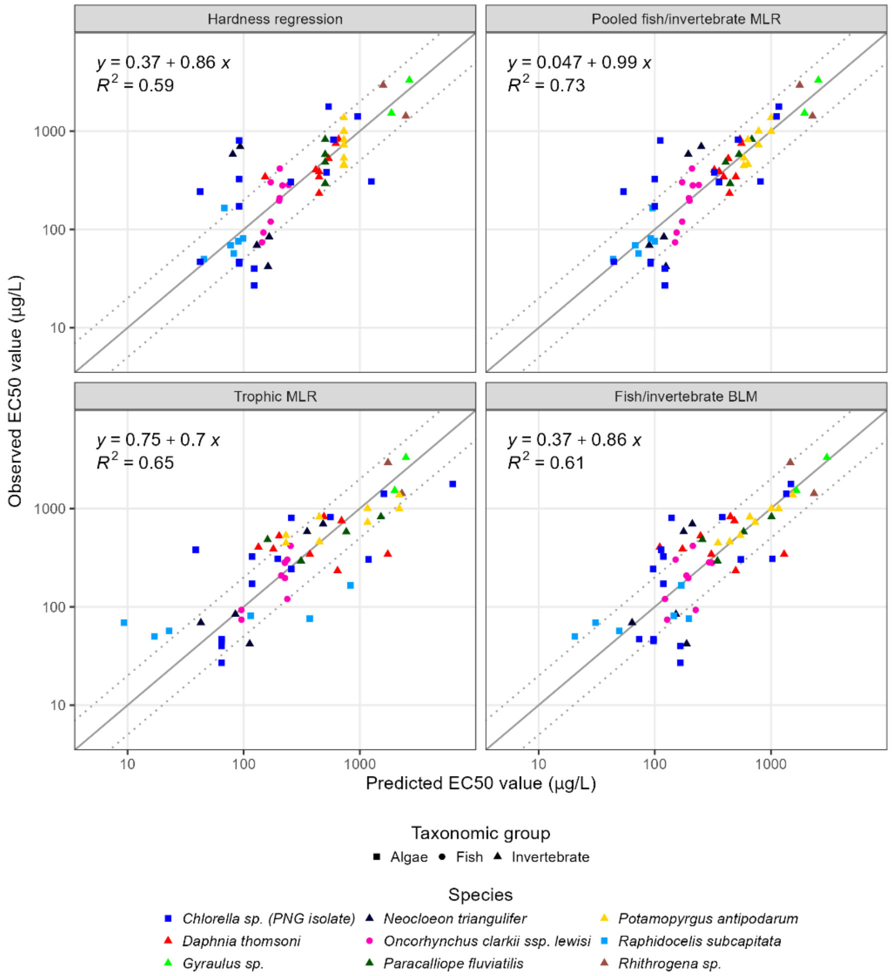

Figure 6.3: Observed EC50 values for **acute zinc** toxicity to species not used in model development, compared to EC50 values predicted with four different models. Solid line is line of perfect agreement between observed and predicted EC50 values. Dotted lines indicate a factor of ±2 difference. Slightly more values are within a factor of two when used the pooled acute MLR model.

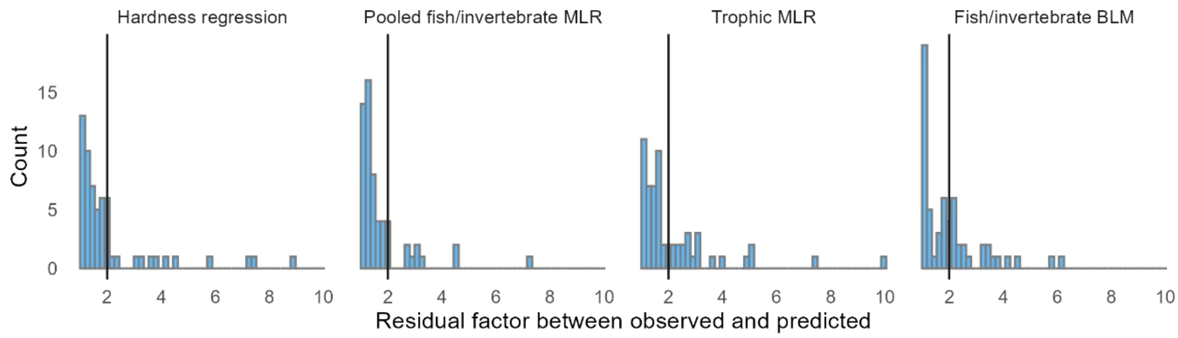

Figure 6.4: Residual factors (observed/predicted) for **acute zinc** toxicity to species not used in model development, compared to EC50 values predicted with four different models. Solid black line is factor of two difference.

6.3 Score 2: Native species validation

6.3.1 Data used

The bioavailability models were separately tested with data for native species, primarily from the testing undertaken for this project, and with additional support data where available from previous toxicity testing undertaken in Aotearoa (Table 6.3). As there were relatively few species for this testing, the validation dataset was also supplemented with species native to Australia but related to those native to Aotearoa. These Australian species included the freshwater shrimp, *Paratya australiensis*, within the same genus as the Aotearoa endemic shrimp *Paratya curvirostris*; and the freshwater mussel, *Hyridella depressa*, within the same family as the Aotearoa endemic mussels in the *Echyridella* genus (e.g., *E. menziesii*).

Table 6.3: List of Aotearoa native and Australian species used for evaluating bioavailability models for **copper** and **zinc** for fish and invertebrates. More information for each species including the detailed water chemistry test conditions is available in the excel files associated with this project.

Species	Taxonomic group	Indigenous status	Duration and effect	EC50 values	TMF variations for:
Copper					
Galaxias maculatus	Fish	Aotearoa & Australia	96-h mortality	59-85	pH, hardness, DOC
Ceriodaphnia dubia*	Crustacea	Aotearoa & Australia	48-h mortality	70-681	pH, hardness, DOC
Daphnia thomsoni	Crustacea	Aotearoa	48-h mortality	14-603	pH, hardness, DOC
Paracalliope fluviatilis	Crustacea	Aotearoa	96-h mortality	70-629	DOC
Paratya australiensis	Crustacea	Australia, related species *Paratya curvirostris*	96-h mortality	34-317	DOC and alkalinity
Potamopyrgus antipodarum	Mollusc	Aotearoa	96-h mortality and morbidity	14-110	DOC
Hyridella depressa	Mollusc	Australia, related species *Echyridella*	48-h duration of valve opening	20-792	DOC
Zinc					
Galaxias maculatus	Fish	Aotearoa & Australia	96-h mortality	59-85	pH, hardness, DOC
Ceriodaphnia dubia*	Crustacea	Aotearoa & Australia	48-h mortality	70-681	pH, hardness, DOC
Daphnia thomsoni	Crustacea	Aotearoa	48-h mortality	14-603	pH, hardness, DOC
Paracalliope fluviatilis	Crustacea	Aotearoa	96-h mortality	70-629	DOC
Potamopyrgus antipodarum	Mollusc	Aotearoa	96-h mortality and morbidity	14-110	DOC

Notes: * *C. dubia* are found in many locations globally. Data were only included for specimens collected in Australian waters, which may be a different subspecies.

Ideally pH, DOC, calcium, magnesium and other cations and anions would be measured in all test waters with the native species. However, requiring this would have resulted in minimal data for the validation. Therefore, compared to the cross-species validation step described above, added leniency was accepted for native species. As long as pH and either hardness or DOC were measured in the test waters,[126] and the test water was described, values were estimated from other sources of data for that water. *Galaxias maculatus* was the only native fish species with toxicity data and DOC was estimated from other reports

[126] In some cases, these data were not reported within the same paper as the toxicity data but were obtained from additional papers or reported or directly from the authors.

using the same water. This increases uncertainty, which was considered when evaluating the model results for this species.There was a total of eight species included in the validation for copper and seven species for zinc.

6.3.2 Results and scores

With this evaluation of model performance for native species, the pooled fish/invertebrate MLR, trophic level MLRs and the fish/invertebrate BLM performed similarly for copper, whereas predictions with the hardness regression were poor (Figure 6.5). The R^2 values were similar for the MLR (0.87) and BLM (0.87), and slightly lower for the trophic level MLRs (0.8). Similarly, these models predicted at least 74% of data within a factor of two, whereas with the hardness model, only 48% were within a factor of two (Table 6.4). The pooled fish/invertebrate MLR model had the highest overall score, based on the R^2 value, species within a factor of two, and residual metrics.

Predictions were generally poor for the Australian collected *C. dubia* species, which is very sensitive to copper. Predictions for the native species *D. thomsoni* were better with the pooled MLR model than with the invertebrate MLR developed from *D. magna* toxicity data (Figure 6.5). Although there was some uncertainty in the *G. maculatus* DOC, these values are unlikely to have significantly influenced the model performance metrics as these two values were close to the 1:1 line for all but the BLM, and were within a factor of two for all models.

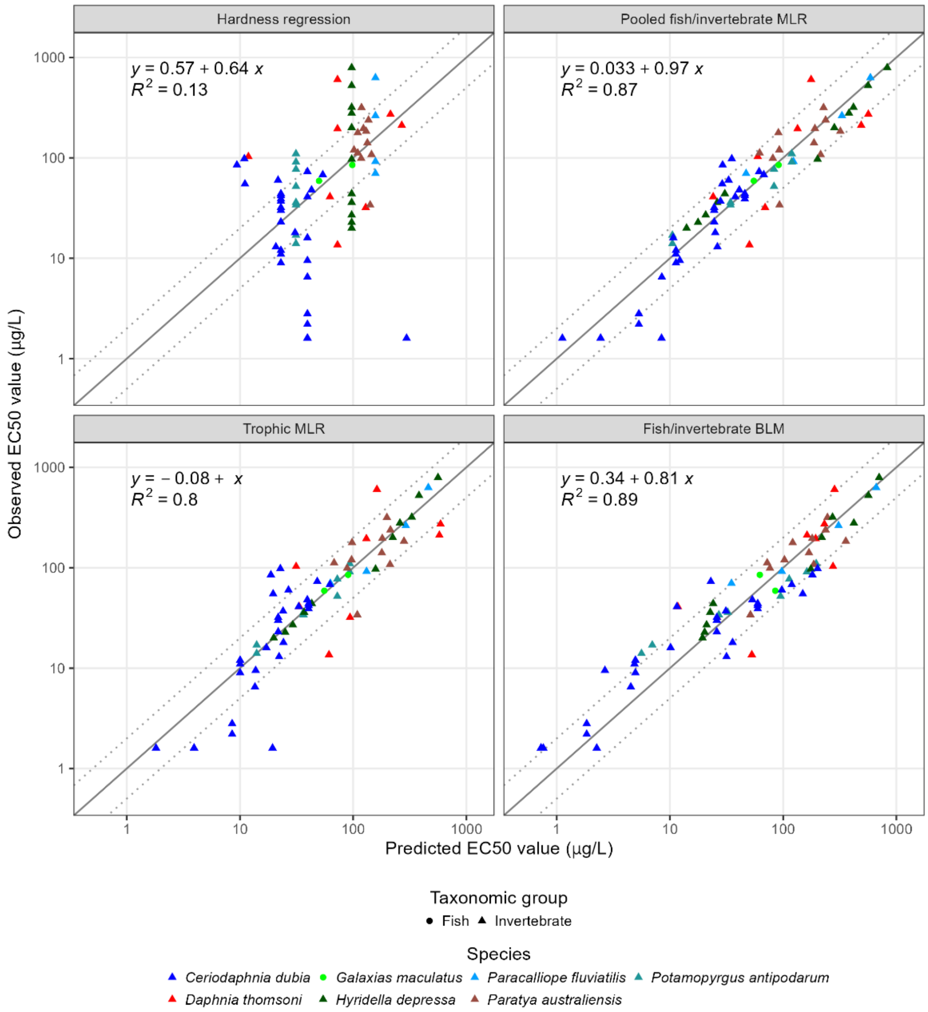

Figure 6.5: Observed EC50 values for acute **copper** toxicity to **native species**, compared to EC50 values predicted with four different models. Solid line is line of perfect agreement between observed and predicted EC50 values. Dotted lines indicate a factor of ±2 difference. Slightly more values are within a factor of two when used the pooled MLR model.

Table 6.4: Native-species model performance metrics for **copper** and **zinc**. Each metric ranges from 0 (low/poor performance) to 1 (high, good performance). Native validation score is calculated from the mean of the R^2, $RF_{x,2.0}$ and the mean of the five residual scores. Score in bold indicates best score for that metal.

Model	R^2	$RF_{x,2.0}$ †	Residual scores ‡					Native validation score (score 2)
			Log (Obs. EC50)	pH	Log (hardness)	Log (DOC)	Log (Alkalinity)	
Copper								
Hardness	0.13	0.48	0.27	0.82	0.11	0.34	0.35	0.33
Fish/ invertebrate MLR	0.87	0.84	0.89	0.98	0.59	0.98	0.82	**0.86**
Trophic MLR	0.80	0.77	0.74	0.95	0.41	0.79	0.63	0.76
Fish/ invertebrate BLM	0.89	0.74	0.89	0.95	0.75	0.83	0.70	0.83
Zinc								
Hardness	0.52	0.70	0.89	0.57	0.79	0.92	0.54	0.67
Fish/ invertebrate MLR	0.71	0.85	0.78	0.76	0.78	0.96	0.69	**0.79**
Trophic MLR	0.48	0.46	0.99	0.97	0.95	0.51	0.79	0.60
Fish/ invertebrate BLM	0.59	0.64	0.77	0.99	0.96	0.97	0.93	0.71

Notes: † Predictions within a factor of two of observed. ‡ Residual score for each variable calculated as 2/(1+10^ABS(slope × (1-p-value)))[127] See plots in Appendix F for relationships between residuals and each of these variables.

For zinc, the pooled fish/invertebrate MLR had the highest overall score (Table 6.4), based on the highest R^2 value (0.71) and the most values predicted within a factor of two of observed ($RF_{x,2.0}$ 0.85). The trophic level MLRs performed poorly (R^2 0.48, 46% within a factor of two), and worse than the hardness model for this dataset (Figure 6.6.). Surprisingly, predictions for the native species *D. thomsoni* were better with the pooled fish and invertebrate MLR model than with the invertebrate MLR based on *D. magna* and *D. pulex* (Figure 6.6). This may be due to the absence of all three TMFs in the invertebrate (hardness and DOC only) MLR. Similarly, the fish MLR is also based on only two TMFs (hardness and pH only) which may explain the overall poor performance with this set of models.

The overall native validation score for the fish/invertebrate BLM was the second highest, based on high residual scores. This, along with R^2 and $RF_{x,2.0}$ values suggests that although there may be some uncertainty in the predictions with the BLM, there was minimal bias.

[127] Besser et al., 2021..

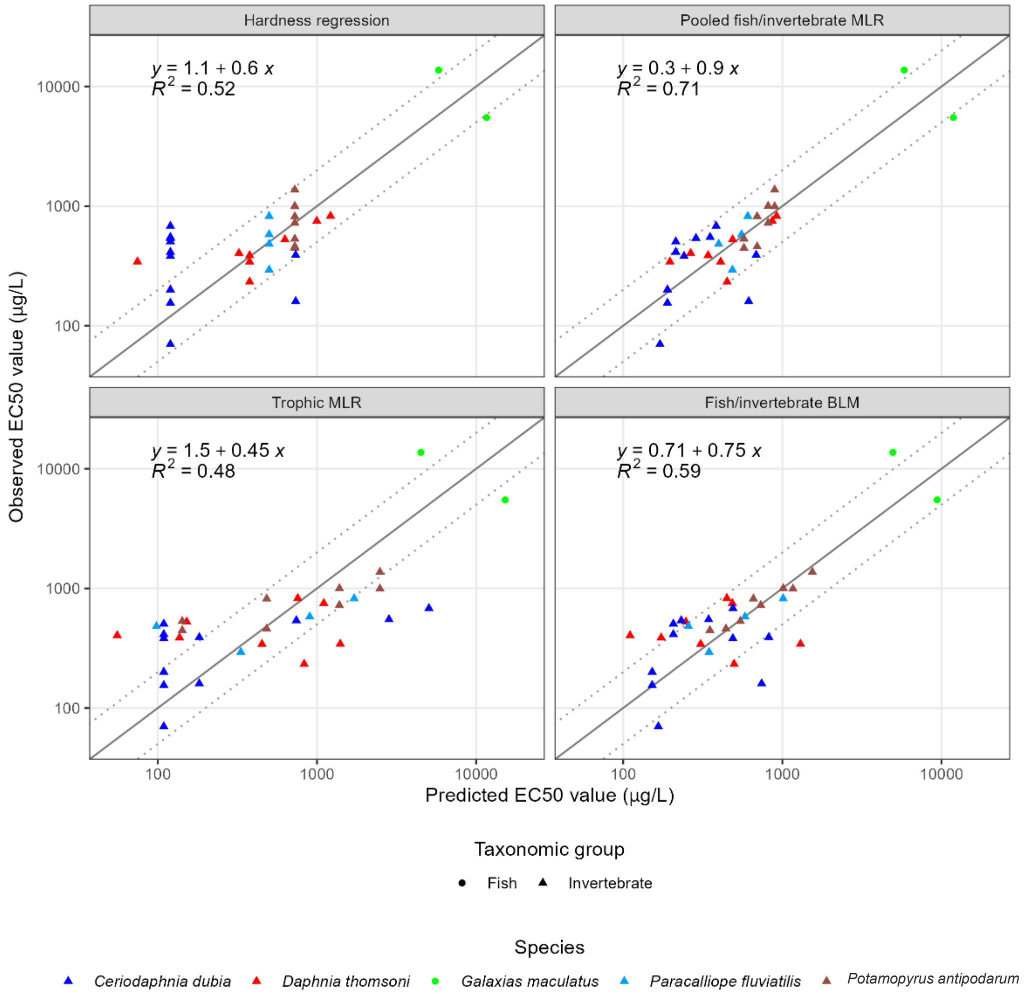

Figure 6.6: Observed EC50 values for acute **zinc** toxicity to **native species**, compared to EC50 values predicted with four different models. Solid line is line of perfect agreement between observed and predicted EC50 values. Dotted lines indicate a factor of ±2 difference. Slightly more values are within a factor of two when used the pooled MLR model.

6.4 Scores 3 and 4: TMF (water chemistry) coverage

Each of the models have an application range for the toxicity modifying factors (TMFs, Table 6.5, Table 6.6). These application ranges are based on the data used to develop the model.[128] The trophic MLRs had the narrowest application range for all TMFs, and this did not span the full breadth of pH or DOC in the copper or zinc toxicity datasets (Figure 6.7). The pooled MLR and BLM models had a broader range that spanned most, but not all, of each of the toxicity datasets. The copper hardness regression did not cover values of low hardness (<13 mg/L) and also excluded some toxicity data at high hardness (>400 mg/L). The regression for hardness does not have an applicable range for pH and DOC. For the scoring, it was assumed that there was a wide range that encompassed all data.

[128] For some chronic BLM models there have been additional studies to assess and extend the range of the model T Van Regenmortel et al., 2017. Analyzing the capacity of the *Daphnia magna* and *Pseudokirchneriella subcapitata* bioavailability models to predict chronic zinc toxicity at high pH and low calcium concentrations and formulation of a generalized bioavailability model for *D. magna*. *Environmental Toxicology and Chemistry* 36, 10: 2781-98..

Table 6.5: TMF range of **copper** models, toxicity data and waters in Aotearoa.

	pH range (unitless)	Hardness range (mg/L as $CaCO_3$)	DOC range (mg/L)
Hardness	N/A	13-400	N/A
Pooled MLR	5.0-9.0	3-898	0.1-33
Trophic MLRs Fish	5.9-9	10-440	0.3-33
Invertebrates	5.5-8.6	5-591	0.1-18
Plant/algae BLM*	4.5-8.0	25-525	0.2-33
Fish/ invertebrate BLM	5.5-8.8	8-525	0.2-33
Toxicity dataset (all acceptable data)†	5.0-9.0	2.7-898	0.1-38
NZ waters [129]	4.2-9.7	1-739	0.2-58

Note: * Barley BLM † When deriving GVs the data would be constrained to the applicable range for the selected model.

Table 6.6: TMF range of **zinc** models, toxicity data and waters in Aotearoa.

	pH range (unitless)	Hardness range (mg/L as $CaCO_3$)	DOC range (mg/L)
Hardness	N/A	5-360	N/A
Pooled MLR	5.4-8.5	14-826	0.1-22
Trophic MLRs Fish	5.7-8.3	20-398	0.3-10
Invertebrates	N/A	14-251	0.3-17
Plant/algae MLR*	5.6-8.5	7-529	0.3-22
Fish/ invertebrate BLM	5.4-8.5	14-826	0.1-22
Toxicity dataset (all acceptable data)†	4.0-9.1	2.7-412	0.1-40
NZ waters	4.2-9.7	1-739	0.2-58

Note: * *R subcapitata* model. † When deriving GVs the data would be constrained to the applicable range for the selected model.

[129] TMF database collated for use with implementing Australian and New Zealand guideline values. JB Gadd et al., 2024. *Implementation of bioavailability-based metal guideline values for Australia and New Zealand. Part 1: Report on water chemistry data collation. Report prepared for Metals Environmental Research Associations.*

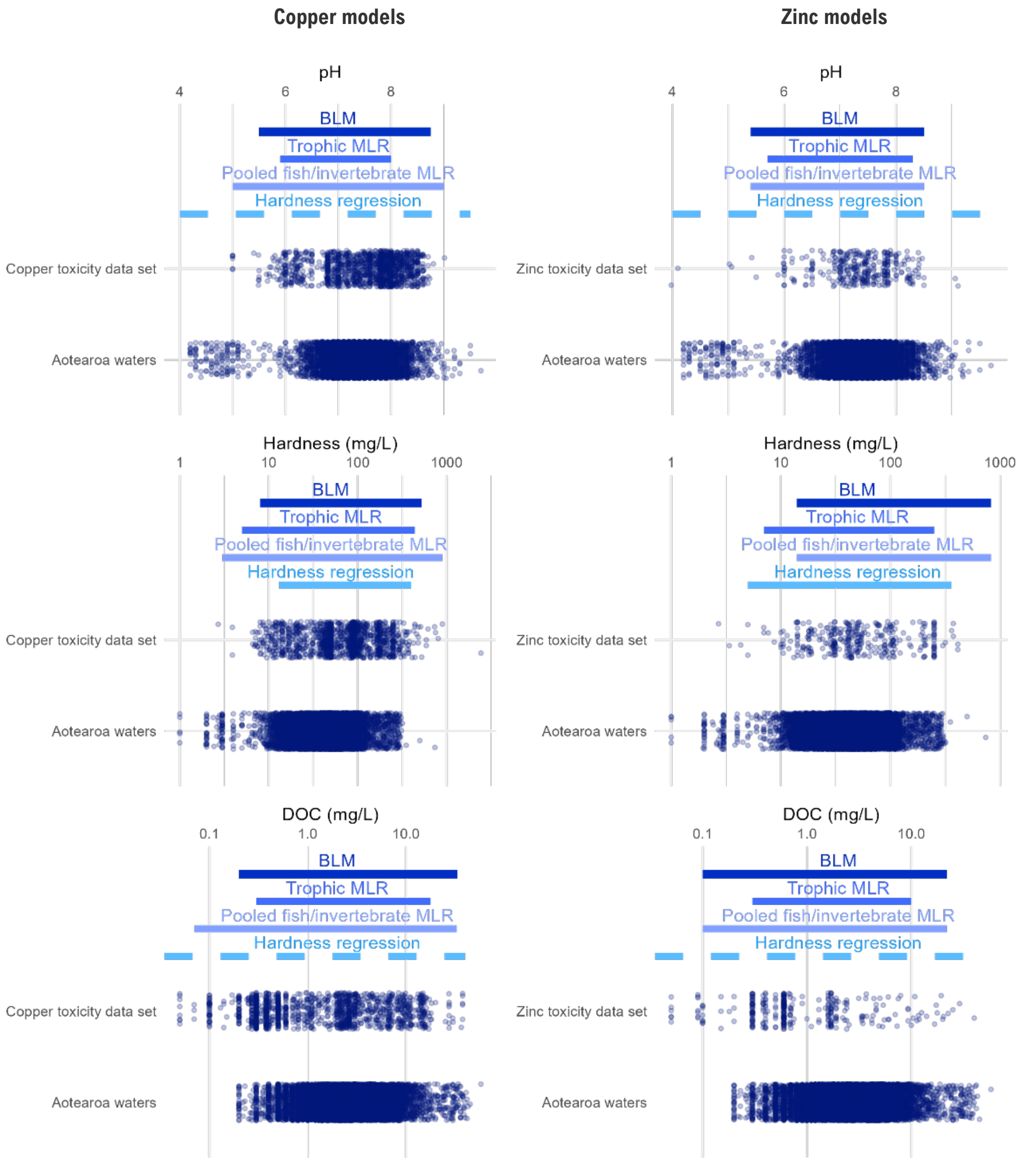

Figure 6.7: Applicable TMF range of **copper** and **zinc** model options compared to the relevant toxicity dataset and to the range found in natural waters of Aotearoa. Model range indicated by bar width. Hardness regression shown as dashed line for pH and DOC as no applicable range is stated by US EPA. Points in toxicity data and Aotearoa waters indicate individual data.

There was minimal difference between models based on a comparison to the Aotearoa waters dataset (Table 6.7). This is because of the distribution of that dataset, which is dominated by values around neutral pH, hardness 10-100 mg $CaCO_3$/L and DOC 0.5 to 10 mg/L (demonstrated by dark blue area in Figure 6.7 where multiple points overall).

The scores for the hardness regression are highest of all models as this scoring assumed that the regression is valid across all pH and DOC concentrations (as no other guidance is provided for that regression). This likely means the score for the hardness regression is less comparable to the other models. Overall, the TMF scores showed minimal differences between models except for the trophic-level MLRs. These had lower scores for the toxicity dataset. Those models are based on either one or two species, and typically a smaller number of data points and a narrow TMF range in the data, when compared to pooled models. Pooled models use multiple species and therefore generally include a greater number of data points which often means a wider TMF range.

Table 6.7: Scores based on TMF range of **copper** and **zinc** models compared to the toxicity datasets and waters in Aotearoa. The score represents the proportion of toxicity data or Aotearoa waters within the range of

the models and can be converted to a percentage (e.g., 92% of the toxicity dataset is within the range of the hardness regression)

	Copper		Zinc	
	Model TMF range compared to toxicity dataset (Score 3)	Model TMF range compared to Aotearoa waters (Score 4)	Model TMF range compared to toxicity dataset (Score 3)	Model TMF range compared to Aotearoa waters (Score 4)
Hardness regression	0.92	0.99	0.97	1.00
Pooled fish/invertebrate MLR	0.98	0.98	0.85	0.93
Trophic MLRs	0.89	0.90	0.34	0.81
Fish/ invertebrate BLM	0.91	0.98	0.85	0.93

6.5 Score 5: Taxonomic coverage of models

All models are based on toxicity data for species that are also to be included in the guideline value derivation; except the copper plant BLM. That model is based on terrestrial plants but could be used within a trophic-level bioavailability adjustment, as there were no copper MLR models for plants or algae.

There is some uncertainty regarding the models used to develop the copper BLM. The documentation of the model indicates that it was based on the US EPA model, which was based on two fish species, however the updates may have included new species.[130] This means the taxonomic score calculated for the copper BLM may be an underestimate.

The model development datasets are less diverse than the toxicity datasets (and than the freshwater ecosystems to which GVs are applied). Although the toxicity datasets for both copper and zinc include many molluscs, a few insects and a few other invertebrates, the model development datasets are dominated by fish and crustaceans. The zinc pooled MLR and the BLM did include one mollusc in the model development. The cross-validation dataset also included at least one mollusc for both copper and zinc, and the zinc dataset included two insects (both mayflies). The coverage of the toxicity datasets in relation to freshwater ecosystems in Aotearoa is discussed in section 9.3

The trophic-level MLRs had the greatest diversity in terms of a greater number of trophic levels, with at least one fish, one crustacean and one plant or algae represented. However, there were few species used in the construction of each of the trophic-level MLRs, and therefore a low number of species overall (three for copper and four for zinc). There were more species included in the development of the hardness equations, the pooled MLRs and the zinc BLM. This resulted in higher scores for those models (Table 6.8).

[130] US EPA, 2007.

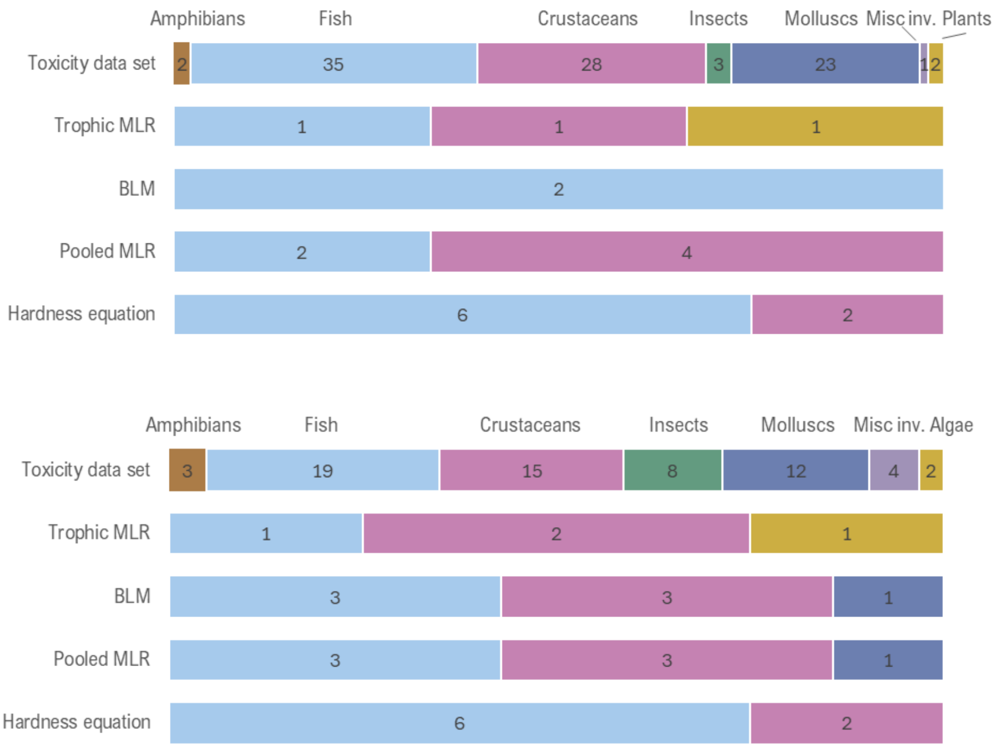

Figure 6.8: Taxonomic groups included in the **copper** (top) and **zinc** (bottom) toxicity datasets compared to the taxonomic groups of species used to develop bioavailability models. Numbers on bars represent the number of species, width of bar represents proportion of total species for that group.

Table 6.8: Taxonomic scores (score 5) for **copper** and **zinc** models.

	Copper	Zinc
Hardness	0.45	0.47
Pooled fish/invertebrate MLR	0.44	0.47
Trophic-level MLRs	0.41	0.39
Fish/ invertebrate BLM	0.30*	0.47

Note: * This may be an under-estimate as there is uncertainty regarding the species used to develop the copper BLM.

6.6 Overall performance of bioavailability models for copper and zinc

The individual scores for each of the aspects evaluated in the preceding sections were averaged (with equal weighting) to calculate overall model performance scores (MPS). The higher the MPS, the better the model performance, with a maximum of 1.0.

For **copper**, the pooled fish/invertebrate MLR model had the highest score (0.81), followed by the BLM (0.77); both of which were higher than the trophic MLRs (0.68) and the hardness regression (0.65).

For **zinc**, although the hardness regression and the pooled fish/invertebrate MLR model had equally high scores (0.76), this is primarily due to the high scores for the TMF range for the hardness regression. As that regression is based only on a single TMF (hardness), there was no boundary for pH or DOC, unlike the other three models, which are based on multiple factors. This is a limitation of the scoring system when comparing scores across models with different TMFs. The cross-species and native-species validation scores for the hardness regression were much lower than for the pooled fish/invertebrate MLR, and the plots of predicted versus observed toxicity showed a poor relationship for the hardness regression (sections 6.2.2 and 6.3.2). When this is considered, the pooled MLR is clearly better than the hardness regression for zinc.

Although using trophic-level MLRs can have some advantages, with different models applied to different groups of taxa, the evaluation suggests models currently available for that approach are not yet adequate. The TMF range for these models is significantly narrower than the pooled models (hardness regression, pooled MLR or BLM), which means that GVs based on that option would have a more limited range of applicability, a limitation for implementation across Aotearoa.

Based on the model evaluation, the pooled fish/invertebrate MLR models for copper and zinc are the preferred option for use in deriving acute GVs for Aotearoa.

Table 6.9: Overall model performance scores for **copper** and **zinc**. Scores for individual components all vary from 0 to 1, with higher scores indicating better performance. All scores are equally weighted to calculate the overall model performance score. Value in bold has highest value for that metal.

	Hardness regression	Pooled fish/ invertebrate MLR	Trophic-level MLRs	BLM
Copper				
Score 1: Cross-species validation (13 species, incl. fish, invertebrates; no plants or algae)	0.50	**0.78**	0.74	0.76
Score 2: Native-species validation (7 species, fish & invertebrates)	0.33	**0.86**	0.76	0.83
Score 3: TMF range of model compared to toxicity dataset	0.92	**0.98**	0.89	0.91
Score 4: TMF range of model compared to NZ natural waters	**0.99**	0.98	0.90	0.98
Score 5: Taxonomic coverage of models	**0.45**	0.44	0.41	0.30
Model performance score	0.64	**0.81**	0.74	0.77
Zinc				
Score 1: Cross-species validation (9 species, incl. fish, invertebrates and algae)	0.67	**0.78**	0.74	0.67
Score 2: Native-species validation (5 species, fish & invertebrates)	0.67	**0.79**	0.60	0.71
Score 3: TMF coverage compared to toxicity dataset	**0.97**	0.85	0.34	0.85
Score 4: TMF range of model compared to NZ natural waters	**1.00**	0.93	0.81	0.93
Score 5: Taxonomic coverage of models	**0.47**	**0.47**	0.39	**0.47**
Model performance score	**0.76**	**0.76**	0.57	0.73

7 Toxicity data collation and screening

7.1 Introduction

This section outlines the toxicity data collated for the acute GV derivation, and the steps that have been taken to screen that data for suitability for use.

7.2 Statistical estimates

Batley et al.[131] recommend use of negligible and low effect concentration (e.g., EC10) for deriving acute water quality guideline values, to develop protective GVs. However, there were comparatively few EC10 values reported in the literature for short-term tests. For example, for zinc there were about 100 records with LC10/EC10 values where zinc was measured in solution. These represented only 16 species: (5 fish, 9 invertebrates and 2 algae). There were around 90 values for copper, covering 20 species (9 fish, 10 invertebrates and 1 plant).

Instead LC50, EC50 or IC50 values were collated. These are also the statistics used internationally for deriving acute or short-term GVs, though the treatment of the data differs between jurisdictions. In the US EPA, an assessment factor (AF) of 2 is applied to the final acute value (FAV) calculated from the EC50 toxicity dataset to generate their acute GVs.[132] In the EU, the guidance requires an AF to be applied to the 5th percentile concentration from an SSD based on EC50 values as that 5th percentile represents a 50% or greater effect for 5% of the species. The default AF for the EU is 10, unless other lines of evidence (such as acute EC50:EC10 ratios) suggest a higher or lower value is appropriate.[133] In Canada, no AF is applied for short-term GVs, though their guidance notes that the "short-term benchmark" concentrations (as they are called) are **not** protective levels. These GVs are designed to estimate severe effects and provide guidance on the impacts of transient situations, such as spill events and infrequent releases of contaminants.

For the deriving acute (short-term) GVs for copper and zinc for Aotearoa, **conversion of the EC50 data to EC10 data** was recommended, as advised by Batley et al. This step is undertaken prior to modelling in the SSD to avoid issues with application of AFs when multiple levels of species protection are calculated.[134]

7.3 Data sources

Copper and zinc acute toxicity data that have been assessed for quality were collated from the following sources.

Copper:

- Copper Water Quality Guideline for the Protection of Freshwater Aquatic Life prepared by British Columbia's Ministry of Environment and Climate Change Strategy,[135] which includes 730 toxicity data points published up to around 2014.
- Papers by Brix et al. (2017, 2021)[136] that collated copper toxicity data from the US EPA and up to 2018.
- US EPA Aquatic Life Ambient Freshwater Quality Criteria for Copper[137] which includes acute toxicity data published up to around 2000.

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[131] GE Batley et al., 2018. *Technical rationale for changes to the method for deriving Australian and New Zealand water quality guideline values for toxicants*, CSIRO Land and Water Report Prepared for the Council of Australian Government's Standing Council on Environment and Water (SCEW) (Sydney, Australia).
[132] US EPA, 2007. *Water quality standards handbook: Second edition*, United States Environmental Protection Agency, Office of Water (Washington D.C.), (https://www.epa.gov/wqs-tech/water-quality-standards-handbook). .
[133] European Commission, 2018.
[134] DR Fox and GE Batley, 2022. Assessment factors in species sensitivity distributions for the derivation of guideline values for aquatic contaminants. *Environmental Chemistry* 19, 4: 201-09.
[135] B.C. Ministry of Environment and Climate Change Strategy, 2019.
[136] Brix et al., 2017; Brix et al., 2021.
[137] US EPA, 2007.

- Australasian Ecotoxicology Database.[138]

Zinc:

- Scientific criteria document for the development of the Canadian water quality guidelines for the protection of aquatic life—zinc,[139] which included the derivation of a short-term benchmark concentration and provides 727 acceptable datapoints.
- Papers by van Genderen et al. (2020) and DeForest et al. (2023)[140] that include collations of zinc toxicity data including from short-term toxicity tests.
- A database of toxicity data maintained by the International Zinc Association (IZA).
- Australasian Ecotoxicology Database.

The EU risk assessment reports[141] were also reviewed but these data were almost entirely for test periods longer than would be considered acute or short-term, and no additional data were obtained from these.

In addition, data from published studies in Aotearoa were reviewed and included. Researchers known to be working on metal toxicity in Aotearoa and Australia were asked for any updated material.

Despite a reasonably large database for both copper and zinc, there were few toxicity data for plant/algae species, particularly if restricted to studies where pH, hardness and/or DOC were reported. Algal toxicity tests with an exposure duration greater than 24 hours (such as the typically used 48 or 72 hour tests) are considered chronic studies.[142] Toxicity over shorter time periods is rarely assessed for algae. However, measurements of cell yield (or algal growth) are made during the 48- & 72-hour tests, as required to measure growth rates over time. These interim algal data, as measured at 24 hours of exposure, were requested and received from researchers working with algal toxicity in Aotearoa and Australia.[143]

US EPA ECOTOX database was searched because the other existing compilations (derived from US EPA and Canadian guideline documents) generally excluded species that are found outside of North America. A search for data from 1980 onwards, restricted to measured data only, and for acute studies, yielded nearly 3000 toxicity data points for copper for 184 species and over 1100 data points for zinc for 101 species. Note that many of these species would already be included in the quality assured databases listed in the bullets above.

With a greater number of species, there can be greater confidence in the fit of models to the species sensitivity distribution, and a narrower confidence interval around the GVs (i.e., increased certainty). However, due to the large amount of data, not all the ECOTOX data would be able to be quality checked. This means there is increased potential for data that are not suitable or that contain errors to be included in the derivation, decreasing the certainty. A decision was made to restrict the data to only the already collated and reviewed data, supplemented with native species data (green and yellow circles in Figure 7.1). The alternative, of including all available data without quality assessment (including orange circle in Figure 7.1) was not recommended by peer reviewers.

However, a few additional studies were added to the database as they were encountered during the project, where water chemistry (e.g., pH, DOC or hardness) was varied between toxicity tests and all TMFs were reported.[144]

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[138] SI Markich et al., 2002. A compilation of data on the toxicity of chemicals to species in Australasia. Part 3: Metals. *Australasian Journal of Ecotoxicology* 8, 1: 1-72; K Langdon, M Warne, and R Sunderam, 2009. A compilation of data on the toxicity of chemicals to species in Australasia. Part 4: Metals (2000-2009). *Australasian Journal of Ecotoxicology* 15, 2-3: 51-186.
[139] CCME, 2018.
[140] Van Genderen et al., 2020; DeForest et al., 2023.
[141] The Netherlands, 2010; PA Van Sprang et al., 2009. Environmental risk assessment of zinc in European freshwaters: A critical appraisal. *Science of the Total Environment* 407, 20: 5373-91.
[142] Warne et al., 2018.
[143] Personal communication, G. Price, Australian Antarctic Division; K. Thompson, NIWA.
[144] Copper: P Welsh et al., 1998. Data report: Acute copper toxicity to salmonids in surface waters in the vicinity of the Iron Moutain Mine, California. Volume I: Study objectives, methods summary, water chemistry characterization and toxicity test results. *Report Prepared by Hagler Baily Services, Inc.for: Breidenbach, Buckley, Huchting, Halm & Hamblet, California Office of Attorney General:* NA, NA: Breidenbach, Buckley, Huchting, Halm & Hamblet, California Office of Attorney

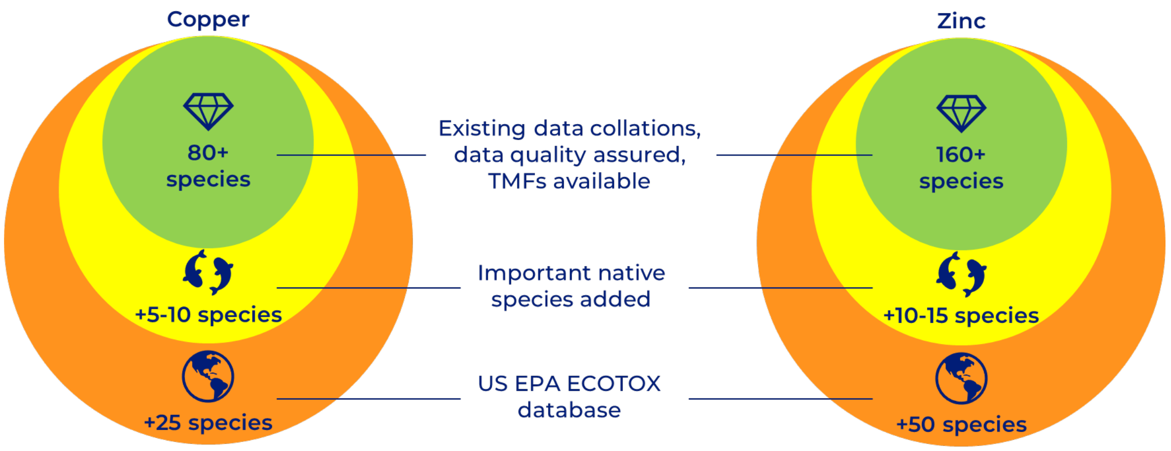

Figure 7.1: Indication of number of species with acute **copper** and **zinc** toxicity data based on different data sources.

7.4 Exposure durations and endpoints

Acute toxicity is defined as that occurring over a short period relative to an organism's life span. Warne et al.[145] recommend durations for different types of organisms and effects–with durations up to 21 days considered acute for adult fish (see Appendix A). Generally, a period of 96 hours or 48 hours is the standard for acute toxicity test procedures,[146] though this depends on the species and not all species have standardised tests with defined exposure periods. For many species there were toxicity data reported for different exposure durations, e.g., 24, 48 and 96 hours. These were standardised within a species, and where possible, across species to ensure that the data included for the derivation represent a similar exposure duration (Table 7.1).

Only data for effects (or endpoints in ecotoxicology lexicon) that are considered ecologically relevant[147] were included to derive the acute GVs. These include tests of survival/mortality, development (e.g., of a sensitive life stage) and population growth (generally for algae).[148] While reproduction tests can also be used, these are more regularly associated with chronic toxicity testing. Non-traditional endpoints such as photosynthesis inhibition, or fluorescence (for algae) were not included.

General; Rogevich, Hoang, and Rand, 2008; N Wang et al., 2007. Acute toxicity of copper, ammonia, and chlorine to glochidia and juveniles of freshwater mussels (Unionidae). *Environmental Toxicology and Chemistry* 26, 10: 2036-47; PL Gillis et al., 2008. Sensitivity of the glochidia (larvae) of freshwater mussels to copper: assessing the effect of water hardness and dissolved organic carbon on the sensitivity of endangered species. *Aquat Toxicol* 88, 2: 137-45; KJM Kramer et al., 2004. Copper toxicity in relation to surface water-dissolved organic matter: Biological effects to *Daphnia magna*. *Environmental Toxicology and Chemistry* 23, 12: 2971-80.; Zinc: CA Mebane, FS Dillon, and DP Hennessy, 2012. Acute toxicity of cadmium, lead, zinc, and their mixtures to stream-resident fish and invertebrates. *Environmental Toxicology and Chemistry* 31, 6: 1334-48; DW Vardy et al., 2014. Acute toxicity of copper, lead, cadmium, and zinc to early life stages of white sturgeon (*Acipenser transmontanus*) in laboratory and Columbia River water. Article, *Environmental Science and Pollution Research* 21, 13: 8176-87.

[145] Warne et al., 2018.

[146] E.g., *Standard guide for conducting acute toxicity tests on test materials with fishes, macroinvertebrates, and amphibians,* ASTM E729-96(2014), (Philadelphia, PA: ASTM, 2014).

[147] Warne et al., 2018.

[148] There were a handful of tests that measured fish growth and plant growth.

Table 7.1: Standard exposure durations used for the acute guideline value derivation.

Species type	Exposure duration (hours)	Comments
Fish and amphibia	96	Standard period used by US EPA for acute criteria
Invertebrates except as detailed below	48	If not available 24 hour or 96 hour data used (in that order of preference)
Glochidia (larval mussels)	24	48 hour period was used in the chronic derivation (6-hour would also be an option but for many species the data were reported as > values)
Hyalella azteca	96	Most reported tests were based on a 96 hour duration, so that duration was adopted
Hydra (e.g., *Hydra vulgaris*)	96	Most reported tests were based on a 96 hour duration, so that duration was adopted. Note that *H. viridissima* is a tropical species and a 96 hour period represents a chronic test duration, so 96 hour data for this species was not included in the derivation.
***Lampsilis siliquoida* (juvenile stage)**	96	Most reported tests were based on a 96 hour duration, so that duration was adopted
***Villosa iris* (rainbow mussel)**	96	More data available with varying DOC if using 96 hour duration
***Paratya australiensis* (Australian shrimp)**	96	More data available with varying DOC if using 96 hour duration

7.5 Metal concentrations and censored values

Many papers report metals in terms of the total concentrations in the test waters. In some guideline derivations these are first converted to the dissolved form for use. For example, US EPA recommends multiplying the total concentration by 0.96 to estimate the dissolved concentration. That system appears to also have been adopted by British Columbia in their copper short-term guideline and by CCME for zinc. However, recently conversions have been shown to be of limited reliability and recommendations are to use the measured concentrations with no conversion.[149]

Much of the data collated for these acute guideline values were from existing compilations, and in a few cases, it was not clear whether the dissolved concentrations were measured or had been estimated from the reported total. Where it was clear that data had been converted to dissolved, the reported total value has been used instead. However, there may be a few cases where converted data has been included in this derivation.

Data where copper or zinc were measured in the test solutions are preferred for the derivation. However, there are some native species data where metals were not measured. To ensure inclusion of those data, and increased relevance of the GVs for Aotearoa, such data were accepted (assuming other quality criteria were met) if the metal concentrations were verified in some way (e.g., analysis of stock solutions) AND the results demonstrated a verifiable (raw data tabulated or plotted) concentration-response relationship.

[149] Van Genderen et al., 2020.

EC50 values are sometimes reported as greater than (>) or less than (<) values (censored values). These can be used in deriving ANZG guidelines subject to professional judgement, using the reported number (e.g., 120 µg/L would be used for data reported as <120 µg/L).[150] There were few data reported as < values, and those could be excluded as there were sufficient other data for the same species. There were numerous data reported as > values. In most cases there were additional data for that species, or the species was not present in Aotearoa and of little relevance. However, there were only > value data for several native species (e.g., koura/freshwater crayfish, *Paranephrops planifrons*, LC50 values >447 µg/l for copper and >430 µg/L for zinc). Due to the high uncertainty in these values, they were excluded for the acute GV derivation but are used in the evaluation of the acute GVs (section 9).

7.6 TMF data requirements

Not all the tests in the collated toxicity database reported pH, hardness or DOC; the minimum variables that would be required to use bioavailability models. If BLMs are used for the bioavailability model, further variables are required such as alkalinity and major cations. Note that in many cases although the TMFs were not reported in the toxicity paper, information on the test waters was obtained by others using that data (e.g., US EPA, CCME). This may have been acquired either from the authors through direct communication, from other toxicity papers using the same source waters (such as laboratory waters used in the Laboratory of Environmental Toxicology and Aquatic Ecology, Ghent University), or from other information on the water sources (such as from regular monitoring of Lake Superior). Where those data have been obtained and approved in other jurisdictions, they were generally adopted for these guideline values.

The following rules (explained further below) were applied to screen data for suitability in using bioavailability models and deriving GVs:

- Require temperature to be reported
- Require pH to be reported, unless water is a standard synthetic media (with pH defined)
- Require hardness (or calcium and magnesium) to be reported, unless standard synthetic media (with hardness defined), or, if a native species, can be estimated from other information
- Require DOC to be reported unless it can be estimated.

Where temperature was not reported those data were excluded. This is regardless of whether temperature is included in the bioavailability model or not, as temperature is considered a basic reporting requirement (at least, of the room or the exposure chamber).

In a very few cases, pH was not reported. The following steps were taken to fill in missing data:

- Where data were available from a secondary paper by the same laboratory, and the test water was the same (e.g., dechlorinated tap water) the measurements from the secondary paper for the primary paper were adopted.
- If the water was described as a standard water (e.g., EPA soft reconstituted, ASTM-hard reconstituted) the pH can be assumed, based on the requirements of those documents. Although those typically specify pH within a range (e.g., pH 7.2-7.6 for EPA soft reconstituted water), the breadth of that range is expected to be no wider than that observed during toxicity tests.
- In all other cases, these data cannot be used as pH may vary substantially between different tap waters/natural waters and as required for tolerance of different aquatic organisms.

[150] Warne et al., 2018., page 8.

- An exception to this was made for native species toxicity data, where the test water was described, and the quality of that water is known from alternative data sources (such as river water quality reports).

In some cases, hardness was not reported. The following steps were taken to fill in missing data:

- If calcium and magnesium concentrations were reported, then hardness was calculated as 2.497×Ca+4.118×Mg (as mg $CaCO_3$/L).
- If the water was described as a "standard water" (e.g., EPA soft reconstituted, ASTM hard reconstituted) the hardness was assumed, based on the requirements of those documents.
- In all other cases, these data cannot be used as hardness may vary substantially between different tap/natural waters.
- An exception to this was made for native species toxicity data, where the test water was described, and the quality of that water is known from alternative data sources (such as river water quality reports).

In many cases DOC was not reported. The following steps have been taken to fill in missing data:

- Where data were available from a secondary paper by the same laboratory, and the test water was the same (e.g., dechlorinated tap water) measurements from the secondary paper were adopted for the primary paper.
- If the test water was listed as synthetic water, or reconstituted water and had been prepared from deionised or distilled water, a low DOC value of 0.3 mg/L was used. This value is lower than the value of 0.5 mg/L used for the chronic zinc guideline derivation,[151] and was selected based on the information provided in many studies that do report the DOC in deionised waters. This value is also consistent with that used in recent copper guideline value derivations in Canada.[152]
- If the water was from a groundwater or other natural water, and there is no reliable analytical reference data for that water (e.g., from the same laboratory around the same time) the DOC was not estimated and the toxicity data were not used. This is because the DOC in natural waters can fluctuate significantly, especially seasonally. Changes of 2-fold or more in the natural waters can be expected and these could result in significant differences between the normalised metal concentrations.

7.7 Data quality assessment and ranking

Data from studies that had not been quality assessed by other jurisdictions were quality assessed following the scheme used for the Australian and New Zealand guidelines.[153] Key factors included:

- There must be acceptable (typically >90%) survival in controls.
- There must be <10-fold range between sequential test concentrations and at least three test concentrations as well as the control.
- Tests with high metal concentrations in controls or in culture waters were excluded.

In addition to ensuring all data were of acceptable quality, the data were ranked based on the certainty of the TMF data. This was an important step as those TMF data influence the normalisation of the EC50 values and therefore the data used in the GV derivation. Data were ranked as follows:

Primary data (1°):	Copper/zinc was measured in the toxicity test solutions; pH was measured and reported and the range in pH was less than or equal to 1.0 pH units; hardness was measured and reported; DOC was measured and reported or was provided from other studies in the same waters.

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[151] ANZG, 2024.
[152] ECCC, 2021; B.C. Ministry of Environment and Climate Change Strategy, 2019.
[153] Warne et al., 2018; DA Hobbs, MSJ Warne, and SJ Markich, 2005. Evaluation of criteria used to assess the quality of aquatic toxicity data. *Integrated Environmental Assessment and Management* 1, 3: 174-80.

Secondary data (2°): Copper/zinc was measured in the toxicity test solutions or in the stock solutions; pH, hardness or DOC were estimated; but at least two of the three TMFs were measured.

Tertiary data (3°): Copper/zinc was not measured in the toxicity test solutions but was measured in the stock solutions (only nominal data available); pH, hardness and/or DOC were estimated; at least one of the three key TMFs must be measured.

For each species, the best data available were used as follows:

1. If primary data are available for a species, use those and no other data for that species.
2. If no primary data are available for a species, use secondary data for that species.
3. For a native NZ species, if there are no primary or secondary data available, use tertiary data.
4. For other species, if there are no primary or secondary data available, exclude that species from the derivation.

This approach aimed to increase the number of species used in the derivation but weighted the dataset towards high quality data where those exist. The criteria are intentionally less stringent for species native to Aotearoa to increase the relevance of the guideline values to local ecosystems.

Figure 7.2 provides an overview of the decision tree related to reported metal concentrations (as detailed within previous section) and TMFs (as detailed within this section).

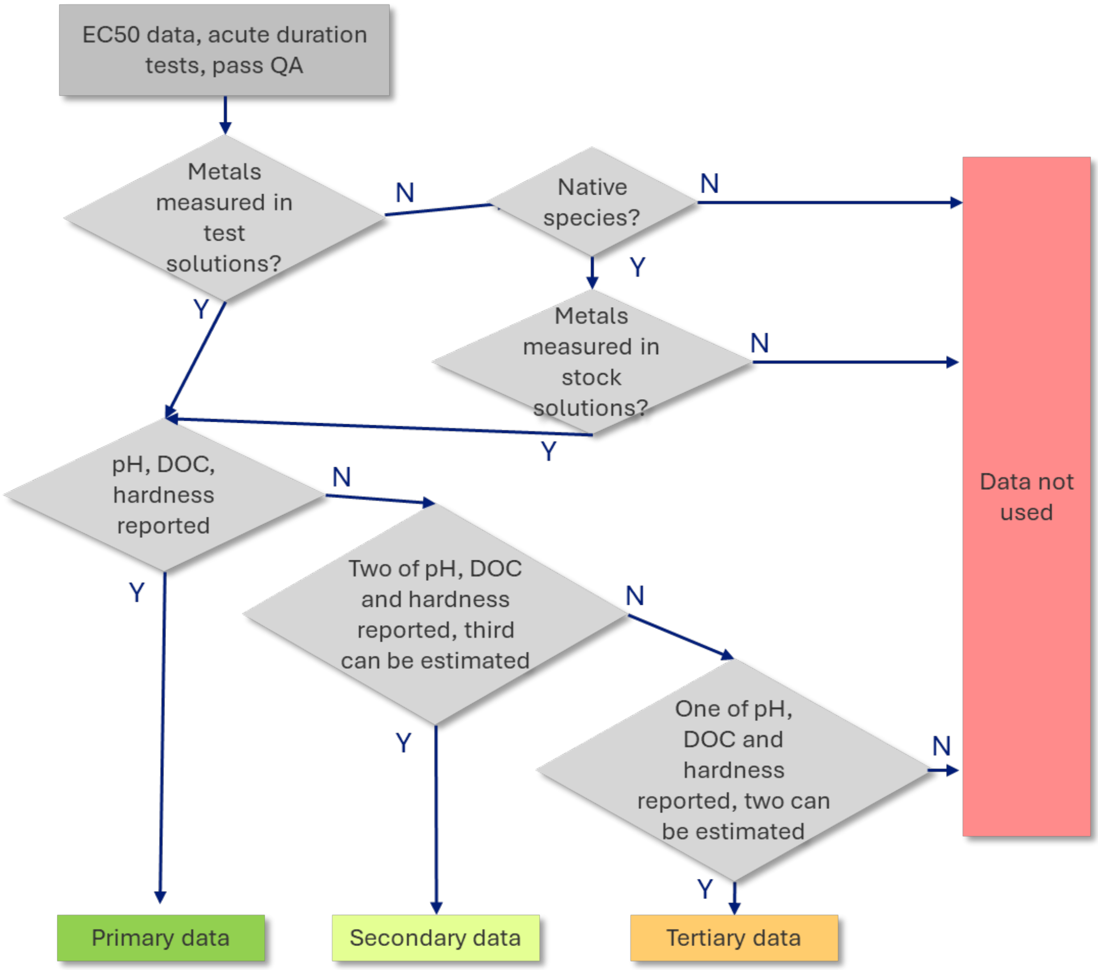

Figure 7.2: Decision tree related to ranking of data based on reporting of metal concentrations and TMFs.

7.8 Native species

There were 15 different native species with acute copper or zinc toxicity data potentially suitable for GV derivation (Table 7.2). Two values were unusable as the DOC either could not be estimated[154] or was affected by contamination.[155] Most were given a rank of 3 as metal concentrations were not measured in the test solutions (nominal data only), and DOC was not measured. In many cases DOC could be estimated based on the water type used in the test, and our knowledge of the quality of that water. Inclusion of these species, based on nominal concentrations and estimates of DOC does add some additional uncertainty to the derived acute GVs, however, the data also makes the GVs more locally relevant to Aotearoa. The effect of including and excluding rank 3 data was assessed in the sensitivity analysis near the end of this report (section 9.4).

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[154] *Galaxias maculatus* Skidmore and Firth, 1983.

[155] *Echyridella menziesii* SJ Clearwater, KJ Thompson, and CW Hickey, 2014. Acute toxicity of copper, zinc, and ammonia to larvae (*Glochidia*) of a native freshwater mussel *Echyridella menziesii* in New Zealand. *Archives of Environmental Contamination and Toxicology* 66, 2: 213-26.

Table 7.2: List of native species with toxicity data, including values that cannot be used in acute guideline derivation. Data ordered approximately from most sensitive to least sensitive. Note this list includes data that may be excluded from the derivation if TMFs are outside the range of the selected bioavailability model.

Species name	Common name	Test details	Copper (µg/L)	Zinc (µg/L)	Rank	Comments
Echyridella menziesii	Kākahi	48-h juvenile survival 24-h glochidia survival	12.5 2.9-4.2	No data 202-557	1° Unusable	All reported Test water DOC contaminated
Ceriodaphnia dubia	Crustacean	48-h mortality	21-24	No data	3°	Nominal, DOC estimated, pH & hardness reported
Daphnia thomsoni	Crustacean	48-h mortality	32-272 14-603	343-826 275-387	1° 2°	All reported Hardness estimated
Paracalliope fluviatilis	Amphipod	96-h mortality	61-629	280-823	3°	Nominal, DOC nominal, pH & hardness reported
Potamopyrgus antipodarum	Mud snail	96-h mortality & morbidity	17-110	446-1372	3°	Nominal only, pH measured, DOC nominal, hardness estimated
***Deleatidium* spp.**	Mayfly	48 & 96-h mortality	86.3	570->25000	3°	> value, nominal, DOC estimated
Retropinna retropinna	Smelt	96-h mortality	No data	1450	3°	Nominal only, DOC estimated
Gobiomorphus cotidianus	Bully	96-h mortality		2270	3°	Nominal only, DOC estimated
Anguilla australis	Shortfin eel	96-h mortality	No data	8920	3°	Nominal only, DOC estimated
Galaxias maculatus	Inanga	48 & 96-h mortality		5500-13700	2-3°	Measured or nominal, DOC estimated for 2 data points
Anguilla dieffenbachii	Longfin eel	96-h mortality		11130	3°	Nominal only, DOC estimated
Paranephrops planifrons	Koura	96-h mortality	>447	>450	1°	Measured data but > values
Olinga feredayi	Caddisfly	48-h mortality	No data	>10,000	3°	> value, nominal, DOC estimated
Pycnocentria evecta	Caddisfly	48-h mortality	No data	>10,000	3°	> value, nominal, DOC estimated
Paratya curvirostris	Shrimp	96-h mortality	No data	14000	3°	Nominal only, DOC estimated

7.9 Summary of available data

Table 7.3 summarises the data available for deriving acute guidelines for copper and zinc. Note that these are preliminary estimates only. Some data may be from tests where TMFs are outside the range of the bioavailability model that is selected (e.g., tests at a pH lower than the model suitability).

The total number of species easily meets both EU[156] and Australian and New Zealand guideline[157] requirements or recommendations (minimum of 10 species and 5 species respectively) for both copper and zinc. There is also a variety of taxonomic groups represented, which would likely meet the criteria of the EU and US guidance. However, there are very few data for algae and plants – only two different plant species for copper and two green microalgal species for zinc.

Furthermore, there are few data available for species native to Aotearoa–seven species for copper and up to twelve for zinc. There are additional data for species native to Australia, some of which may be closely related (e.g., *Paratya australiensis*), and for species that are found in Aotearoa but not native (e.g., introduced and acclimated trout and water flea species)

Table 7.3: Summary of available data for the acute guideline value derivation. Note this summary includes data that may be excluded from the derivation if TMFs are outside the range of the selected bioavailability model.

	Copper	Zinc
Number of EC50 data points	1314	336
Number of different species	95	90
Species native to Aotearoa	7	12
Number of taxonomic groups represented	7: amphibian, fish, crustaceans, insects, molluscs, annelids, macrophytes	10: amphibians, fish, crustaceans, insects, molluscs, cnidaria, ostracod, rotifer, annelids, green algae
Range in EC50 values	0.5-81,000 µg/L	21-100,000 µg/L

[156] European Commission, 2018. *Technical guidance for deriving environmental quality standards. Guidance document no. 27 (2000/60/EC)*, European Commission (Brussels, Belgium).
[157] Warne et al., 2018.

8 Guideline derivation

8.1 Overall process

Deriving the acute GVs involves several steps (Figure 8.1). These include selecting appropriate data, using the pooled fish/invertebrate MLR models to normalise all toxicity data to a standard ("index condition") water chemistry, applying a conversion factor (CF) to the normalised EC50 values to generate EC10 values, selecting single values for each species, fitting a statistical model to the species sensitivity distribution and calculating guideline values based on that model. Finally the acute GVs should be defined in a manner that enables calculation of acute GVs adjusted to different sets of water chemistry.

The collation and quality checking of toxicity data was described in section 7. Each of the remaining steps are described in the sections that follow.

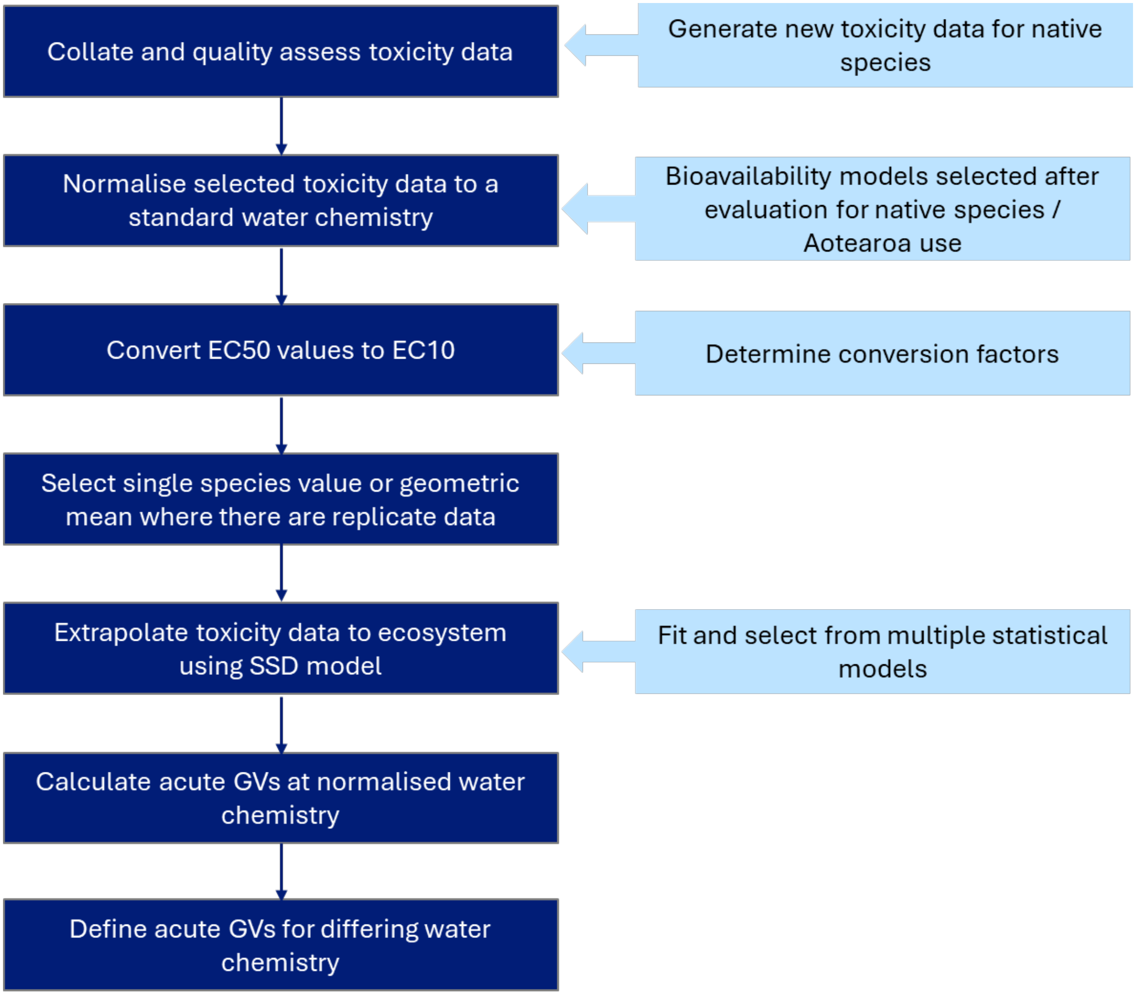


Figure 8.1: Outline of the steps for deriving bioavailability-based metal guideline values (dark blue boxes) indicating inputs and decision processes also described in this section (light blue boxes).

8.2 Normalisation of EC50 values

The EC50 values were generated in toxicity tests that had a range of different water chemistry (pH, hardness, DOC) conditions. The values therefore need to be normalised, using the selected bioavailability models, to a single set of chemistry conditions. 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.

For this step, all acceptable EC50 values were normalised to a set of water chemistry, representing high metal bioavailability conditions: pH 7.5, hardness 30 mg/L $CaCO_3$ and DOC 0.5 mg/L. These values are consistent with those used for chronic zinc DGVs derived under the ANZG framework and have been termed the "index condition".[158] This set of water chemistry is used in evaluating the GVs (including comparing to chronic DGVs) but may not be the most appropriate set of chemistry for *applying* the GVs. Application of the GVs is discussed in section 10.

The normalisation for water chemistry reduced the intra-species variation in EC50 values for most species (Figure 8.2), which is a key component in assessing the suitability of a model.[159] Exceptions were *Mogurnda mogurnda*, a tropical Australian fish, the macrophyte species *C. demersum* and salmonid *O. tshawytscha*. For these species variability increased 100-, 10- and 2-fold respectively. Excluding these anomalies, the normalisation for water chemistry greatly reduced the within-species variation for both copper and zinc, indicating the suitability of using the bioavailability models.

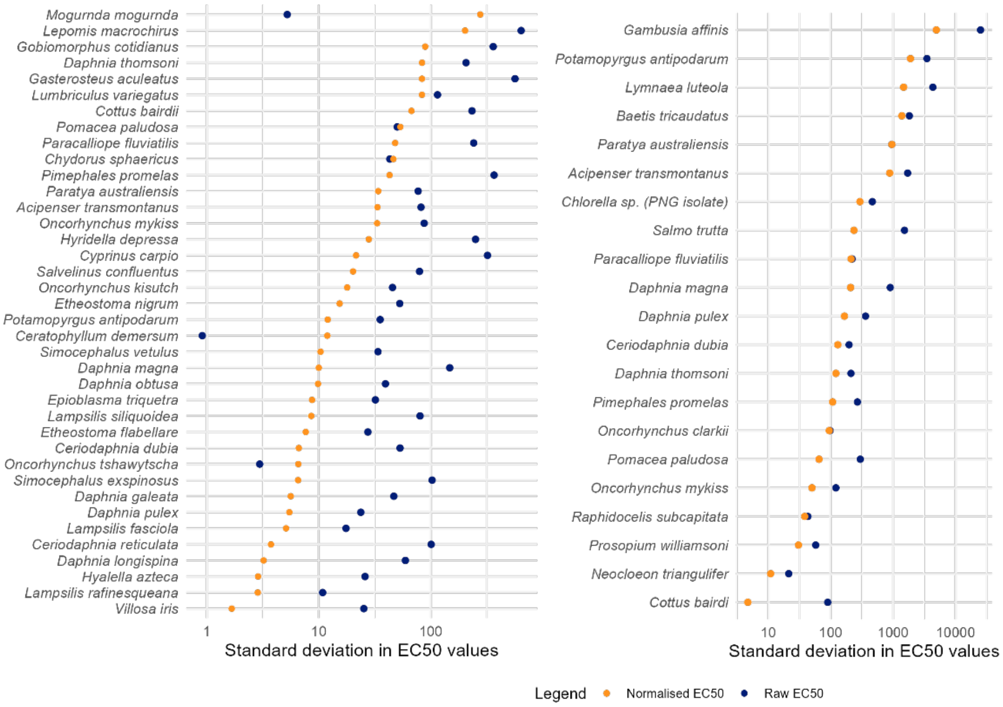


Figure 8.2: Intra-specific variation (standard deviation of EC50 values) in **copper** and **zinc** before (blue) and after bioavailability normalisation (orange). Only species with two or more data points are shown. For most species the variation reduced after normalisation, indicating the suitability of using a model to adjust for bioavailability. Three species showed higher variation between copper EC50 values after normalisation.

8.3 Conversion to EC10 values

The toxicity data collated for the derivation were EC50 values, which has implications on the meaning of a GV derived from these values, as discussed in section 7.2. When metal concentrations in the environment are below GVs derived from EC50 values, effects (such as lethal effects) may still occur on 50% of the individuals. That is, it is not a "protective" GV. Batley et al. recommend a conversion factor (CF) of 5 to convert from EC50 to EC10 values.[160] That value was based on data evaluated for the ANZECC 2000 guidelines and may not be appropriate.

Instead, data were obtained where both EC50 and EC10 values have been reported in acute tests, including results from the *D. thomsoni* tests in natural waters. The EC50:EC10 ratio was calculated as the CF.

[158] Stauber et al., 2021; ANZG, 2024. Recent work to assist in the implementation of those metal GVs has demonstrated that this water chemistry combination is within the range of natural waters in Aotearoa.
[159] European Commission, 2018.
[160] Batley et al., 2018.

The data were restricted to tests where pH, DOC and hardness were reported. Tests in very low bioavailability waters were excluded as these tests could have different slopes in a concentration-response curve and therefore different ratios. That is, tests with DOC >5 mg/L and hardness >150 mg $CaCO_3$ /L were excluded, as were tests in pH <6 or pH >8.5. The complete datasets used are provided in excel files and a summary of the data is shown in Table 8.1.

Table 8.1: Derived acute conversion factor (CF = EC50:EC10 ratios) calculated from reported EC50 and EC10 values for copper and zinc. Values in bold used in converting normalised EC50 values to EC10 values for acute GV derivation.

Species group	Copper conversion factor (CF)			Zinc conversion factor (CF)		
	Geometric mean	Minimum	Maximum	Geometric mean	Minimum	Maximum
Fish	**1.82**	1.2	8.6	**2.03**	1.2	3.9
Invertebrates	**1.61**	1.1	3.1	**1.94**	1.1	4.0
Plants/algae	**1.75**	1.7	1.9	**2.45**	1.3	8.1

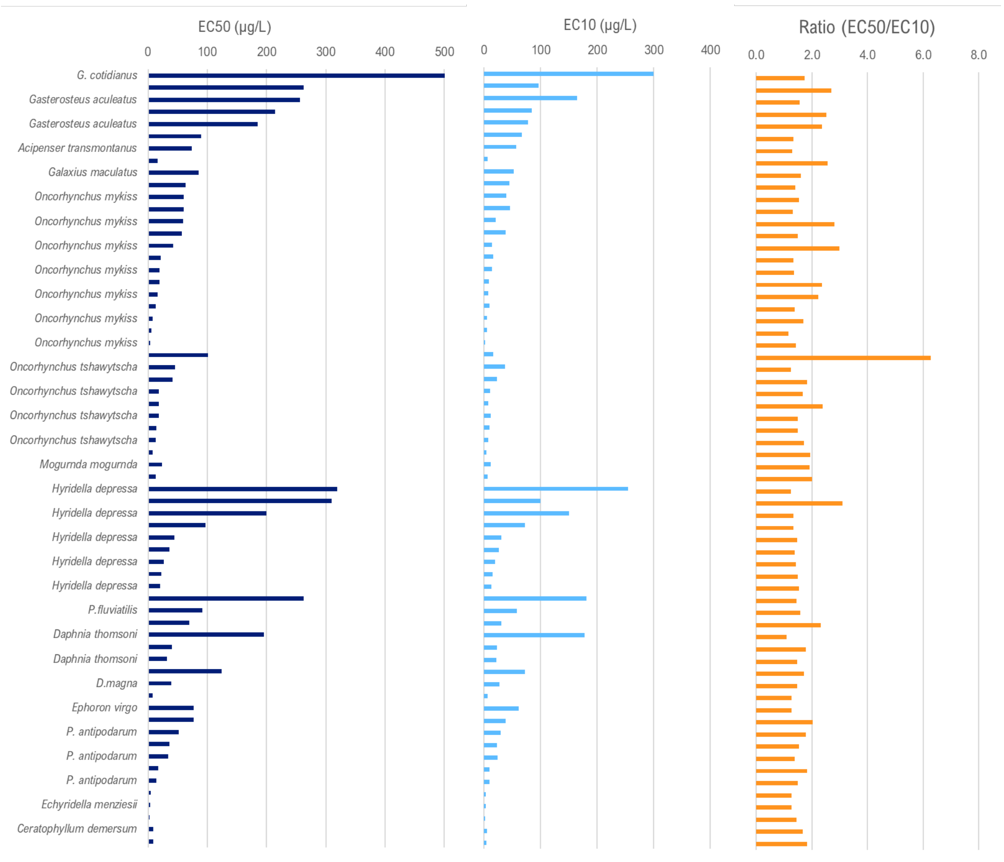


Figure 8.3: Comparison of as measured **copper** EC10 and EC50 values, and CF ratios across all species. Multiple bars shown for some species as there were multiple data (for example, at different pH or from different studies/authors). Values shown are not normalised for bioavailability.

These CFs (Table 8.1) were used to convert the EC50 values to EC10 values for use in the SSD. A comparison of the reported EC10 values and the converted EC10 values (using the CFs) indicated that almost all EC10 values were predicted within a factor of two (Figure 8.3). For zinc, slightly more of the EC10 values were underpredicted than over-predicted, adding some additional conservatism to the EC10 values.[161]

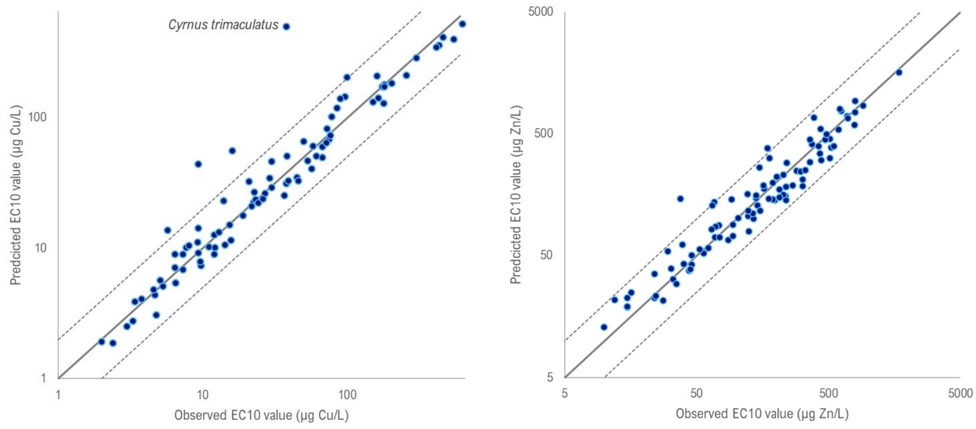


Figure 8.4: Comparison of converted EC10 values (using the CF), and the reported EC10 values for **copper** (left) and **zinc** (right). Solid line is line of 1:1 agreement between reported and converted EC10 values. Dashed lines indicate a factor of ±2 difference. Almost all predicted values are within a factor of two, or are higher than the observed EC10 value. Reported copper EC10 value for *Cyrnus trimaculatus* (labelled) had high uncertainty, with a confidence interval of 6-225 µg/L. Values shown are not normalised for bioavailability.

8.4 Single species values

The converted EC10 values at the index condition were then summarised to single species values for use in the SSD, based on the process outlined in Warne et al. (2018). First geometric means were calculated based on grouping by species, effect and life-stage, and then the lowest of these values was selected for use in the SSD.[162]

The toxicity data (one value per species, at the index condition) used to calculate the guideline values for dissolved copper and zinc in freshwater are provided in Appendix G.

There were 90 different species for copper from 7 different taxonomic groups (amphibians, fish, crustacea, insects, molluscs, annelids and macrophytes (Figure 8.5). The toxicity values in the SSD for copper ranged over four orders of magnitude, from 0.9 µg/L for the crustacean *Scapholeberis mucronata* (from 48 hour immobilisation tests) to 12,000 µg/L for the golden shiner fish *Notemigonus crysoleucas* (from 96 hour lethal tests). The lowest EC10 values were typically for species in the groups crustaceans and molluscs (Figure 8.5).

[161] This evaluation can be considered autovalidation as no additional data were used for the comparison (all values were used to calculate the geometric mean in Table 8.1).This figure (along with Figure 8.3) indicates the consistency in the ratios between species.
[162] Exposure duration was standardised during the data collation step (see Section 5.4).

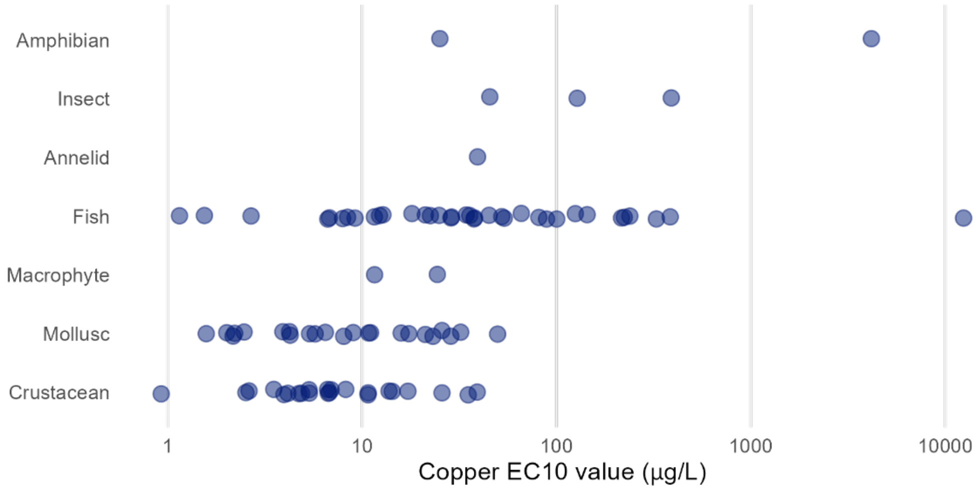


Figure 8.5: Comparison between taxonomic groups of normalised converted acute **copper** EC10 values.

There were 69 species for zinc, from 8 different taxonomic groups (amphibians, fish, crustaceans, insects, molluscs, annelids, rotifers and green algae). There was no one taxonomic group that had clearly lower EC10 values (Figure 8.6), with EC10 values <100 µg/L in all but amphibians. The toxicity values in the SSD for zinc ranged over three orders of magnitude up to a maximum value of 23,800 µg/L for the mayfly—*Cinygmula* sp., from a 96 hour lethal test. The lowest value was 16 µg/L for another mayfly *Neocloeon triangulifer*. Mayflies are known to be highly sensitive to metals, based on field studies, when using smaller specimens in toxicity tests and when including feeding in the toxicity test method.[163] The next lowest value was 26 µg/L for an alga.

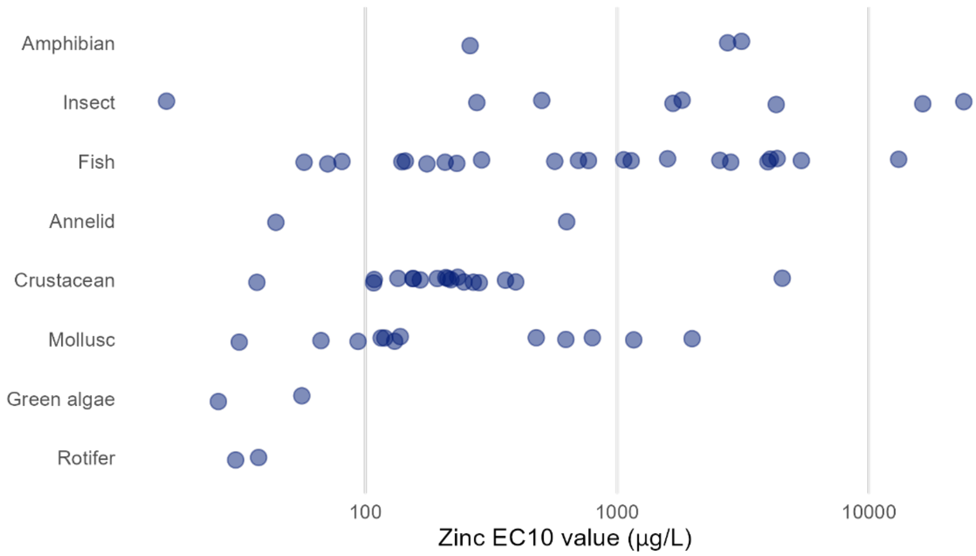


Figure 8.6: Comparison between taxonomic groups of normalised converted acute **zinc** EC10 values.

[163] See CW Hickey and LA Golding, 2002. Response of macroinvertebrates to copper and zinc in a stream mesocosm. *Environmental Toxicology and Chemistry* 21, 9: 1854-63. CA Mebane, TS Schmidt, and LS Balistrierix, 2017. Larval aquatic insect responses to cadmium and zinc in experimental streams. *Environmental Toxicology and Chemistry* 36, 3: 749-62. P Cadmus et al., 2020. Size-dependent sensitivity of aquatic insects to metals. *Environmental Science & Technology* 54, 2: 955-64. DJ Soucek et al., 2020. Acute and chronic toxicity of nickel and zinc to a laboratory cultured mayfly (*Neocloeon triangulifer*) in aqueous but fed exposures. *Environmental Toxicology and Chemistry* 39, 6: 1196-206.

8.5 Species sensitivity distributions

Multiple models were fitted to the species sensitivity data using the ssdtools package in R.[164] The models recommended for ANZG guideline value derivation are the log-logistic, log-normal, log-gumbel, Weibull, Gamma and log-normal/log-normal.[165] The Burr type III was previously recommended by ANZG and so was also included here. The ssdtools package provides goodness-of-fit statistics (Table 8.2) to evaluate and select the best fitting model. The Anderson-Darling, Kolmogorov–Smirnov and Cramér–von Mises statistics each evaluate whether the sample dataset is from the specified distribution. Each statistic differs in its calculation and so use of multiple statistics can be helpful in evaluating model fits. Where a p-value for these statistics is less than <0.01, the data are unlikely to come from the specified distribution.

Table 8.2: Goodness-of-fit statistics (p-value) for **copper** and **zinc** species-sensitivity-distributions. P-values <0.05 indicate the data are highly unlikely to come from the selected distribution. AICc (Akaike's information criterion corrected for sample size) is lowest for the log-gumbel model for both copper and zinc indicating it is the best fitting model. BurrIII model is not included in the ANZG set of distributions, so AICc, detail and weight are not calculated for this model. All models excluding BurrIII are weighted according to the weight factor to calculate the model averaged guideline value.

Distribution	Anderson-Darling statistic	Kolmogorov-Smirnov statistic	Cramer-von Mises statistic	AICc	Delta	Weight
Copper						
Log-logistic	0.50 (0.74)	0.05 (0.98)	0.05 (0.90)	858	8.0	0.017
Log-normal	1.0 (0.35)	0.09 (0.42)	0.16 (0.39)	865	14.5	0.001
Log-gumbel	0.22 (0.98)	0.06 (0.93)	0.04 (0.96)	851	0	0.959
Gamma	14 (<0.01)	0.32 (<0.01)	2.76 (<0.01)	974	123	0
Weibull	5.4 (<0.01)	0.17 (<0.01)	0.87 (<0.01)	914	63	0
Log-normal/log-normal	0.21 (0.99)	0.05 (0.96)	0.03 (0.97)	858	7.5	0.023
Burr III	0.18 (0.99)	0.053 (0.95)	0.03 (0.98)	N/C*	N/C	N/C
Zinc						
Log-logistic	0.8 (0.48)	0.11 (0.35)	0.12 (0.49)	1093	5.5	0.035
Log-normal	0.81 (0.47)	0.13 (0.17)	0.15 (0.38)	1090	2.8	0.14
Log-gumbel	0.34 (0.91)	0.07 (0.91)	0.05 (0.89)	1088	0	0.56
Gamma	3.75 (0.01)	0.21 (<0.01)	0.73 (0.01)	1120	32	0
Weibull	2.04 (0.09)	0.16 (0.05)	0.35 (0.1)	1107	20	0
Log-normal/log-normal	0.2 (0.99)	0.06 (0.97)	0.03 (0.99)	1089	1.5	0.26
Burr III	0.34 (0.91)	0.07 (0.84)	0.05 (0.88)	N/C	N/C	N/C

Note: * AICc, delta and weighting not calculated for Burr III model as this is not included in the list of distributions recommended for ANZG guideline values.

[164] ssdtools: Species Sensitivity Distributions. R package version 1.0.6.9011.

[165] DR Fox, R Fisher, and JL Thorley, 2024. *Final report of the joint investigation into SSD modelling and ssdtools implementation for the derivation of toxicant guidelines values in Australia and New Zealand.* , Environmetrics Australia, Beaumaris, Vic and the Australian Institute of Marine Science, Perth, WA. This marks a departure from the previous recommendation of the Burr type III model (Warne et al. 2018) and is based on updates to the model fitting method and frequent instability of the Burr model, where the model did not converge.

The log-gumbel and log-normal/log-normal models fitted well for copper (Figure 8.7). The log-normal model, as used in Europe, did not fit well to the copper dataset, based on goodness-of-fit statistics (low p-value indicating higher likelihood that the data do not come from a log-normal distribution).

For zinc, the log-gumbel, log-normal/log-normal models and log-normal models fitted reasonably well (Figure 8.8). There was some difference in the fit around the tail of the distribution – which is the area of importance for calculating guideline values (based on low % species affected). There was also variation at the top end of the SSD, with the log-gumbel model showing a poorer fit (red line below the black data points).

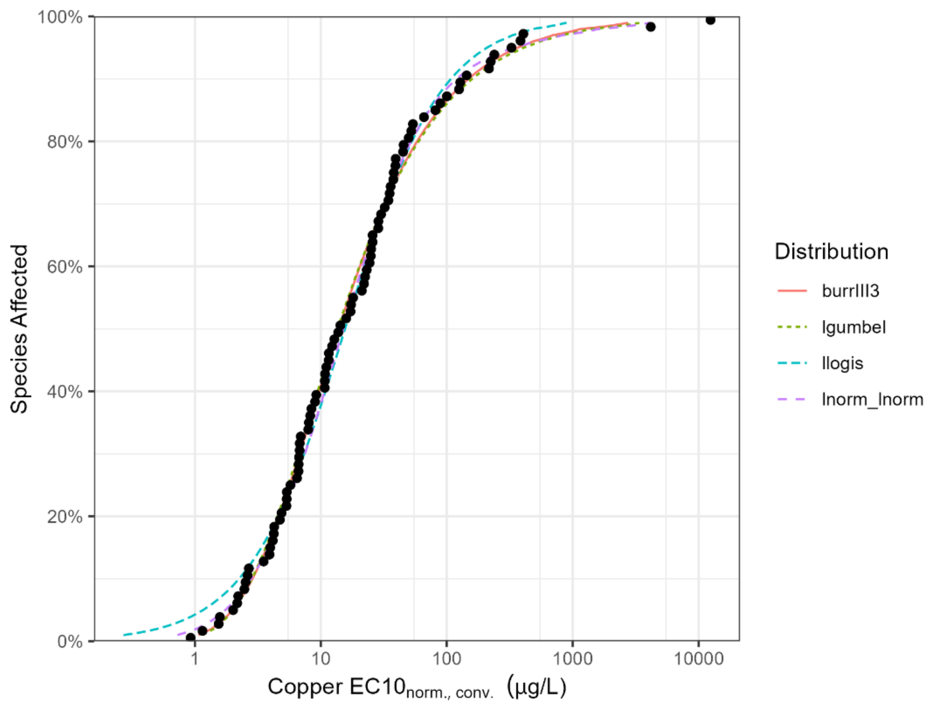


Figure 8.7: **Copper** species sensitivity distribution based on normalised and converted EC10 values (µg/L). Models fitted using the ssdtools package in R.[166] The log-gumbel, burrIII and log-normal/log-normal (abbreviated to lnorm_lnorm in legend) models have the best fit, based on both a visual assessment and the goodness-of-fit statistics (Table 8.2). Only models with reasonable fit are shown on plot.

[166] ssdtools: Species Sensitivity Distributions. R package version 1.0.6.9011.

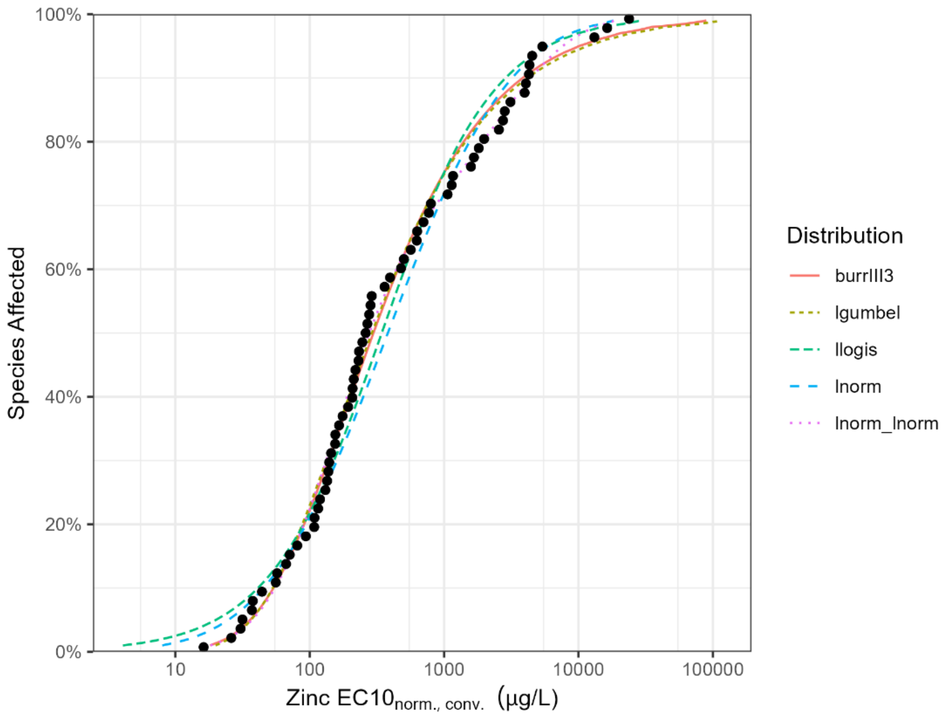


Figure 8.8: **Zinc** species sensitivity distribution based normalised and converted EC10 values. Models fitted using the ssdtools package in R[166]. The burrIII, log-gumbel and log-normal/log-normal (abbreviated to lnorm_lnorm in legend) models had the best fit, based on both a visual assessment and the goodness-of-fit statistics (Table 8.2). Only models with reasonable fit are shown on plot.

8.6 Calculation of guideline values

Guideline values were calculated from the models fitted to the normalised species-sensitivity-distributions using the ssdtools package. The GVs were calculated from the best-fitting model and using a model-averaging method, calculated from the four fitted distributions with weighting based on the goodness-of-fit statistics.[167]

The index condition GVs for copper (Table 8.3) are very similar with either the best-fitting log-gumbel model or the model averaging approach. The 95% and 90% level of protection GVs are identical when rounded to 2 significant figures. The acute GVs for copper are around 3-4-fold higher than the draft chronic DGVs for copper for the same water chemistry.

The index condition GVs for zinc (Table 8.3) show a slight variation between the model options. The 95% level of protection GVs for the model averaging approach are slightly lower (35 µg/L) than with the best-fitting log-gumbel model (37 µg/L) or the Burr type III model (36 µg/L). The zinc acute GVs based on the whole dataset are around 9-fold higher than the draft chronic DGVs at the same water chemistry.

[167] These GVs are estimated from a weighted average of the GVs calculated from each model fit, with the overall confidence interval calculated by bootstrapping. The method for calculation is described in more detail in C Schwarz and A Tillmanns, 2019. *Improving statistical methods for modeling species sensitivity distributions* (BC, Canada). and DR Fox et al., 2021. Recent Developments in Species Sensitivity Distribution Modeling. *Environmental Toxicology and Chemistry* 40, 2: 293-308..

Table 8.3: **Copper** and **zinc** acute GVs (and confidence intervals) at the index condition of pH 7.5, hardness 30 mg $CaCO_3$/L and DOC 0.5 mg/L. Model averaging method recommended and shaded in green. Chronic DGVs for copper and zinc at the index condition are also shown for comparison.

	Level of protection			
	99%	95%	90%	80%
Copper (acute GV): model averaging	1.1 (0.6-1.7)	2.0 (1.4-2.8)	2.8 (2.1-3.9)	4.5 (3.5-6.1)
Copper (acute GV): best model (log-gumbel)	1.2 (0.8-1.7)	2.0 (1.5-2.8)	2.8 (2.2-3.9)	4.5 (3.5-6.0)
Copper (acute GV): Burr type III	1.1 (0.6-1.6)	2.0 (1.5-2.8)	2.9 (2.2-3.9)	4.6 (3.6-6.3)
Chronic copper DGV[168]	0.20	0.47	0.73	1.3
Zinc (acute GV): model averaging	16 (4-32)	35 (17-56)	52 (33-79)	89 (64-133)
Zinc (acute GV): best model (log-gumbel)	20 (13-32)	37 (26-55)	53 (39-77)	88 (65-127)
Zinc (acute GV): Burr type III	18 (11-26)	36 (29-49)	54 (44-70)	91 (75-116)
Chronic zinc DGV[169]	1.5	4.1	6.8	12

[168] ANZG, 2023. *Toxicant default guideline values for aquatic ecosystem protection: Dissolved copper in freshwater. Draft for public comment*, Australian and New Zealand Guidelines for Fresh and Marine Water Quality. CC BY 4.0. Australian and New Zealand Governments and Australian state and territory governments (Canberra, ACT, Australia, July 2023).
[169] ANZG, 2024.

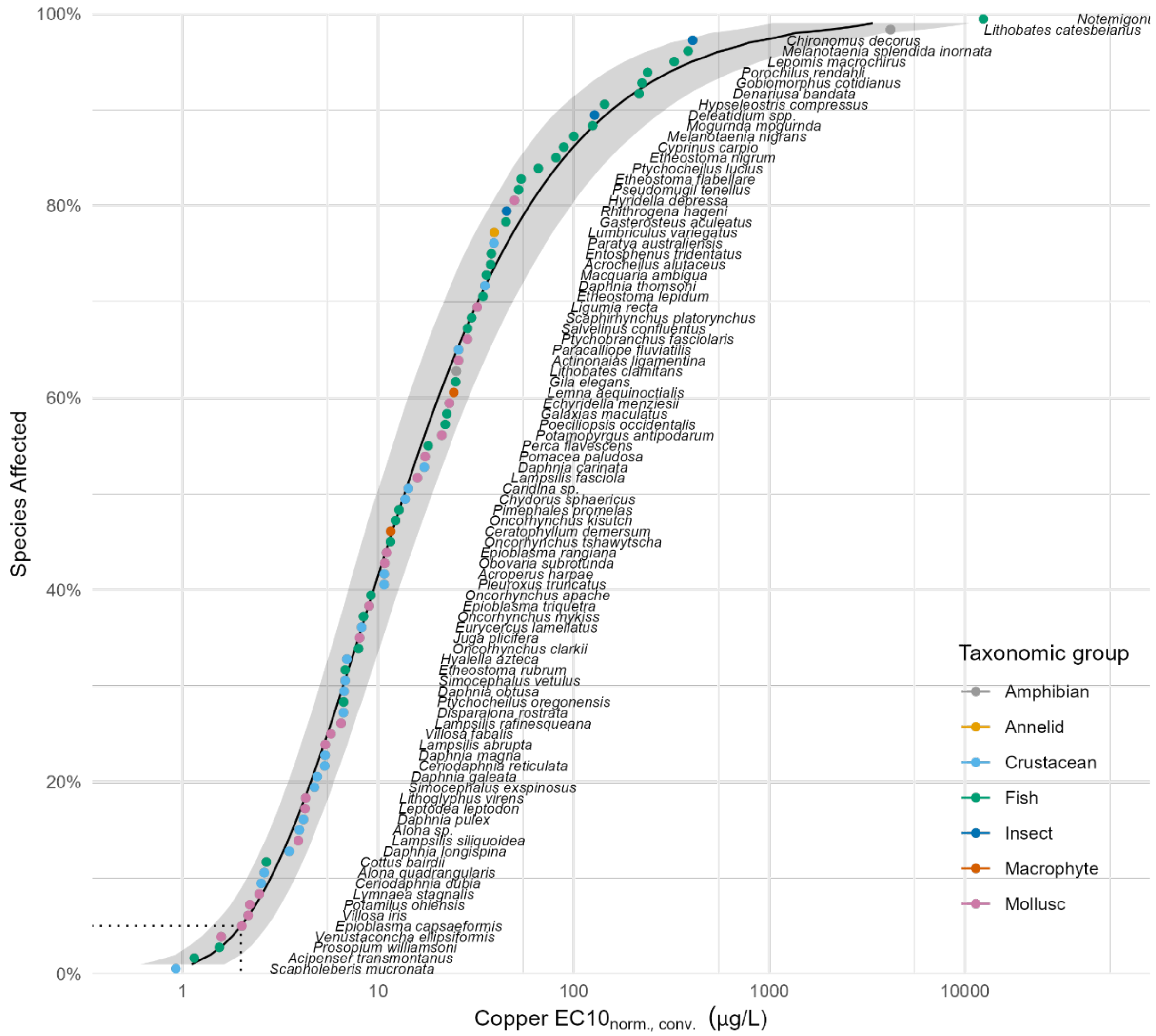


Figure 8.9: **Copper** species sensitivity distribution based on normalised and converted EC10 values. Toxicity data normalised to index condition (pH 7.5, hardness 30 mg/L and DOC 0.5 mg/L). Colour of points indicates taxonomic grouping of that species. Black line indicates model average fitted line, shaded area indicates the 95% confidence interval, dotted line indicates the model-averaged concentration for 95% species protection (5% species affected).

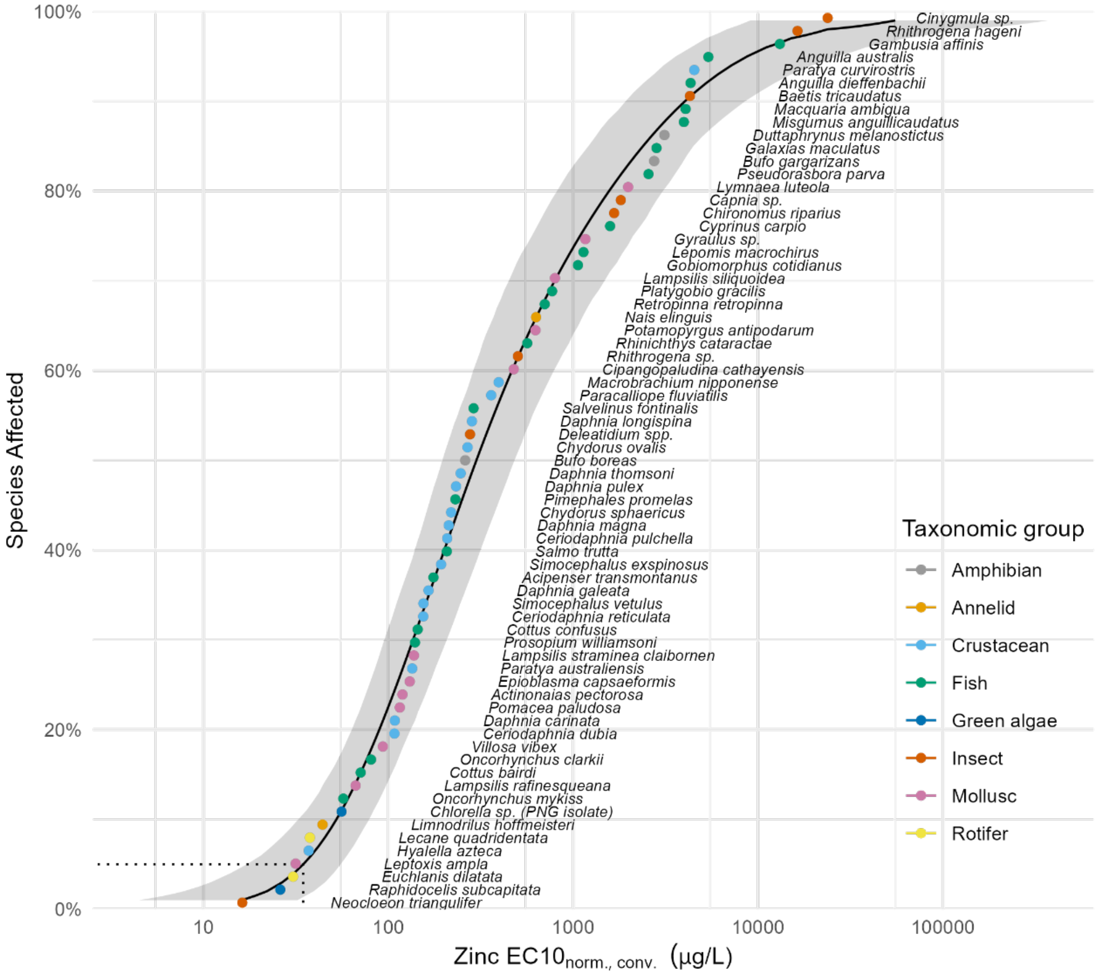


Figure 8.10: **Zinc** species sensitivity distribution based on normalised and converted EC10 values. Toxicity data normalised to index condition (pH 7.5, hardness 30 mg/L and DOC 0.5 mg/L). Colour of points indicates taxonomic grouping of that species. Black line indicates model average fitted line, shaded area indicates the 95% confidence interval, dotted line indicates the model-averaged concentration for 95% species protection (5% species affected).

8.7 Definition of guideline values

The derived acute GVs vary with water chemistry and therefore cannot be expressed as a single numeric value like traditional GVs. As a single MLR equation was used in deriving the copper and zinc acute GVs, these GVs can be defined as equations, which are used to calculate adjusted acute GVs for waters with different water chemistry. Those equations are related to the MLR equations used to normalise the toxicity values but include a y-intercept value that is calculated from the GVs at the index condition.[170] Equations are provided below for copper (Equation 8.1 to Equation 8.4) and zinc (Equation 8.5 to Equation 8.8).

$$Copper\ acute\ GV_{99} = \exp(-7.2 + 0.78\,pH + 0.58 \times \log(hardness) + 0.70 \times \log(DOC)) \quad \text{Equation 8.1}$$

$$Copper\ acute\ GV_{95} = \exp(-6.6 + 0.78\,pH + 0.58 \times \log(hardness) + 0.70 \times \log(DOC)) \quad \text{Equation 8.2}$$

$$Copper\ acute\ GV_{90} = \exp(-6.3 + 0.78\,pH + 0.58 \times \log(hardness) + 0.70 \times \log(DOC)) \quad \text{Equation 8.3}$$

$$Copper\ acute\ GV_{80} = \exp(-5.8 + 0.78\,pH + 0.58 \times \log(hardness) + 0.70 \times \log(DOC)) \quad \text{Equation 8.4}$$

$$Zinc\ acute\ GV_{99} = \exp(1.75 - 0.12 \times pH + 0.6 \times \log(hardness) + 0.13 \times \log(DOC)) \quad \text{Equation 8.5}$$

$$Zinc\ acute\ GV_{95} = \exp(2.5 - 0.12 \times pH + 0.6 \times \log(hardness) + 0.13 \times \log(DOC)) \quad \text{Equation 8.6}$$

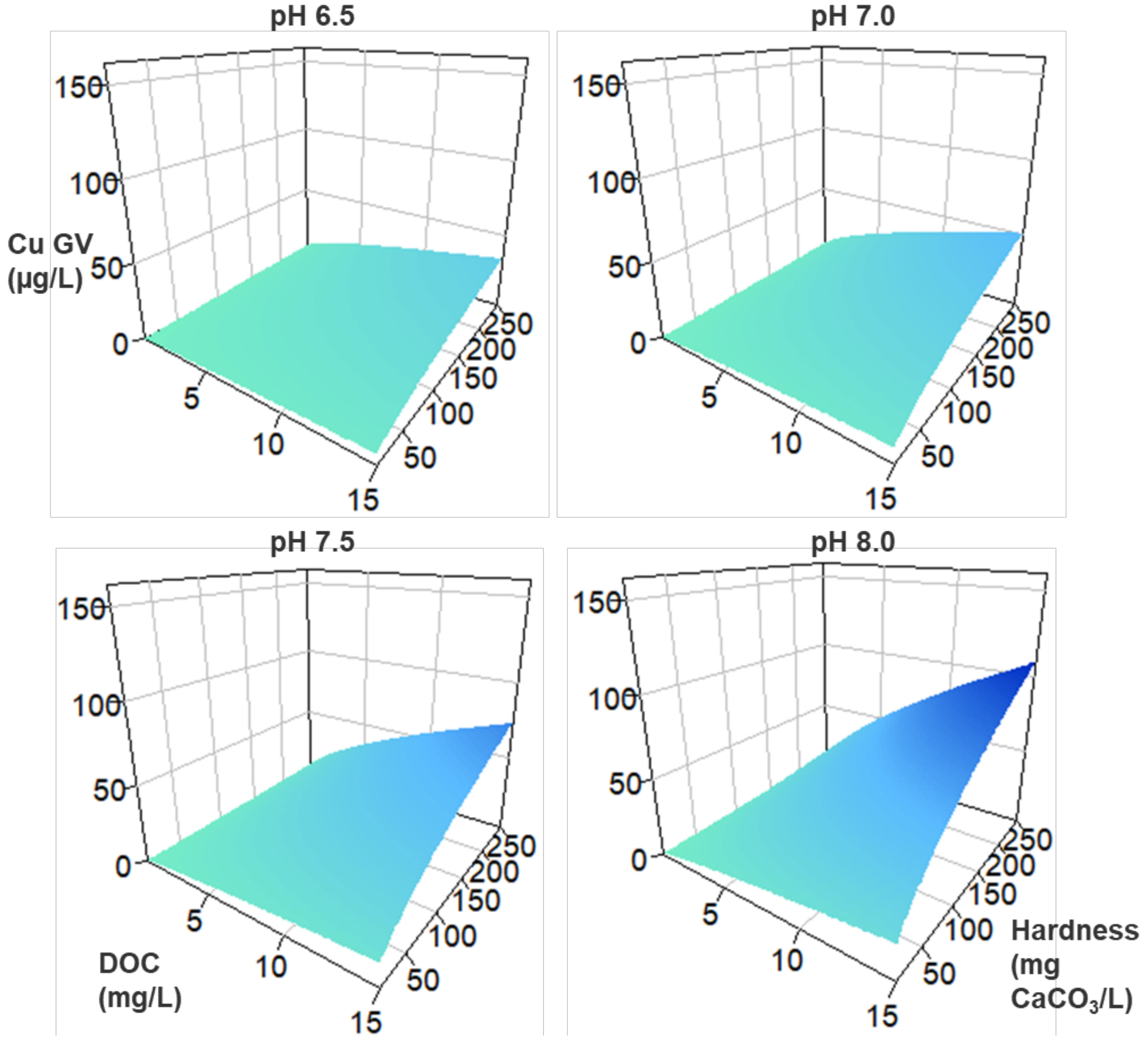
$$Zinc\ acute\ GV_{90} = \exp(2.9 - 0.12 \times pH + 0.6 \times \log(hardness) + 0.13 \times \log(DOC)) \quad \text{Equation 8.7}$$

$$Zinc\ acute\ GV_{80} = \exp(3.4 - 0.12 \times pH + 0.6 \times \log(hardness) + 0.13 \times \log(DOC)) \quad \text{Equation 8.8}$$

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

[170] CCME, 2018.

The effect of pH, DOC and hardness on the copper and zinc acute GVs for 95% species protection is shown



in

Figure 8.11 and

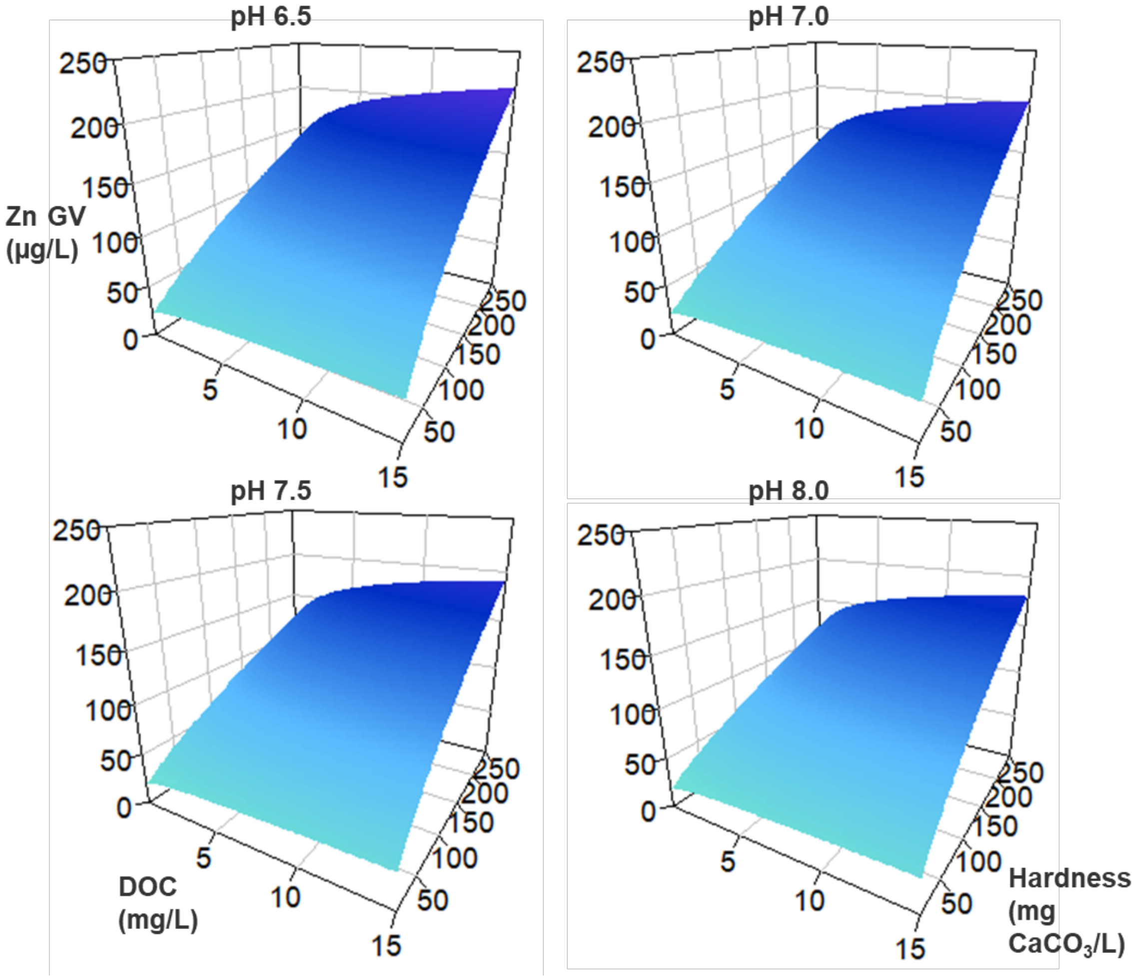


Figure 8.12. The copper acute GVs increase with increasing pH, hardness and DOC; though the effect of the latter two factors is minor at low pH. The zinc acute GVs decrease as pH increases, though the effect of both pH and DOC are smaller than the effect of hardness, based on the range of data shown.

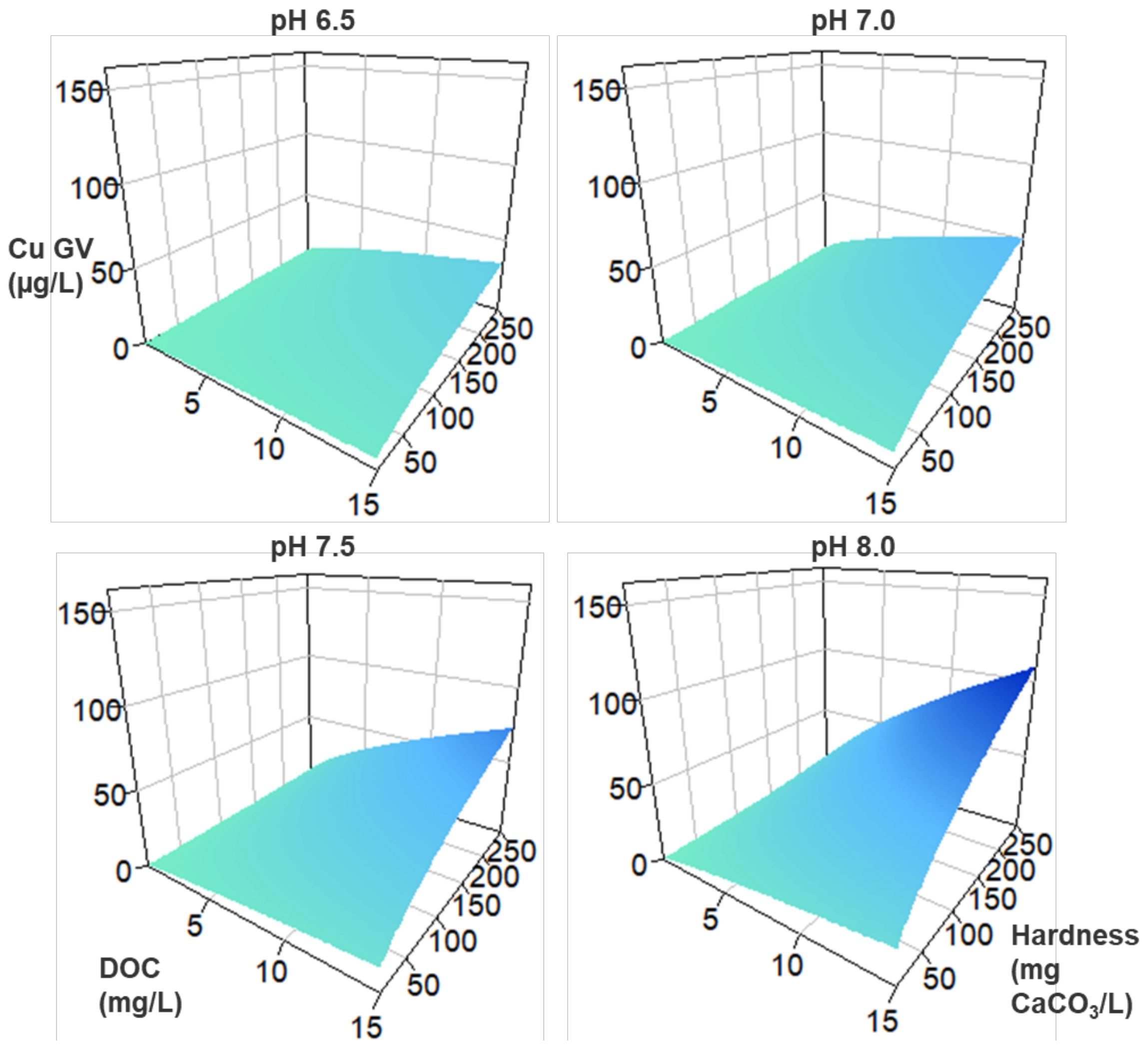


Figure 8.11: **Copper** acute GVs (for 95% species protection) at different pH values and as a function of hardness and DOC.

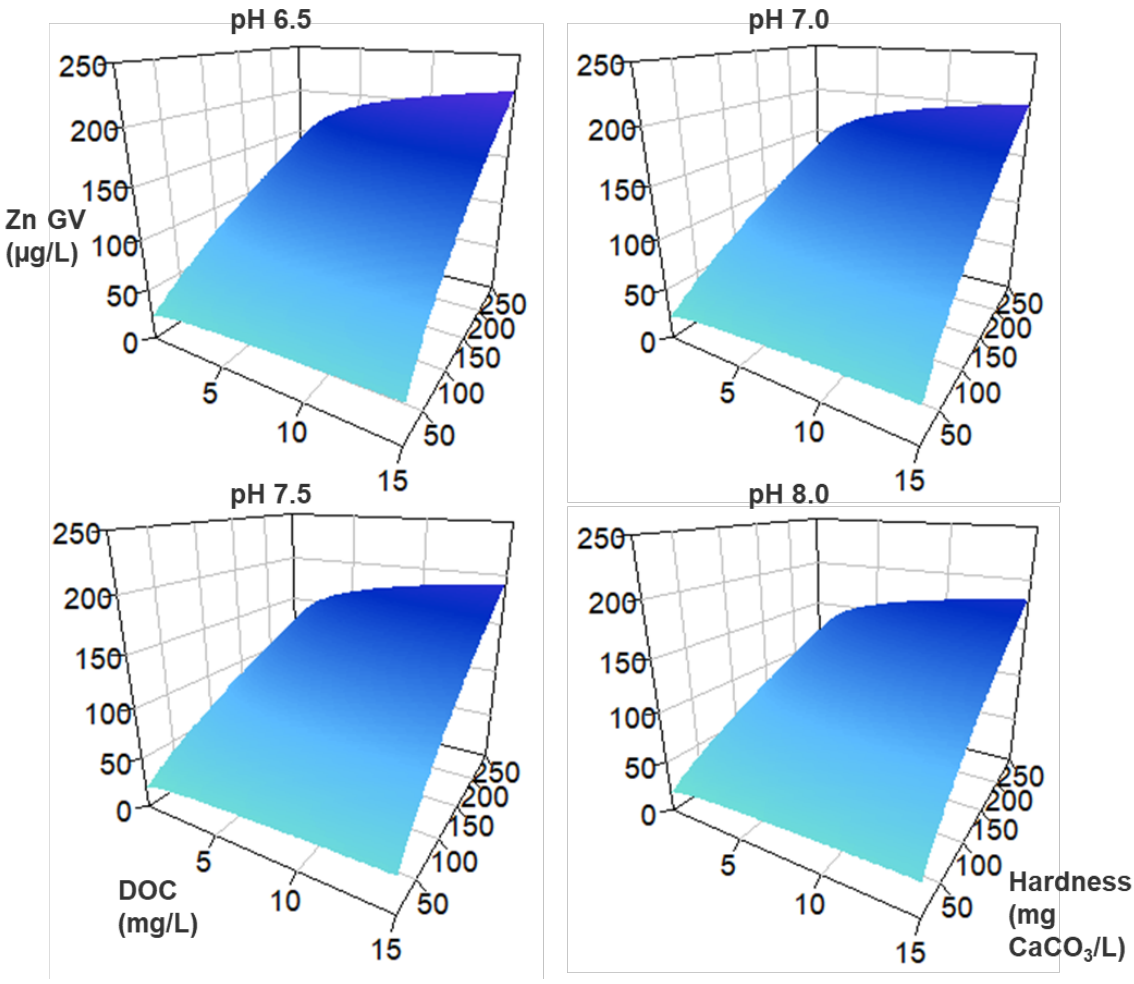


Figure 8.12: **Zinc** acute GVs (for 95% species protection) at different pH values and as a function of hardness and DOC.

9 Evaluation of the acute GVs

9.1 Introduction

In this section, the acute GVs are evaluated in terms of:

- the quality of the data included in the derivation,
- the diversity and inclusion of taxonomic groups,
- inclusion of native species,
- the water chemistry covered in the acute GV derivation compared with natural waters of Aotearoa, and
- measured copper and zinc concentrations in Aotearoa.

In addition, as there are many aspects to acute GV derivation where professional judgement is required, this section reports a sensitivity analysis. This aims to understand the effect of the various decisions on the derived acute GVs and provide confidence in the recommended values. Acute GVs presented in this section are based on normalisation to the index condition.

9.2 Quality of data included

Nearly 75% of the data used for the derivation of copper were primary-ranked data (Figure 9.1), whereas only 32% of data used for zinc were primary-ranked. This may reflect the extra effort invested internationally in developing toxicity data for copper BLMs. Few tertiary-ranked values were used in the derivation – and only from native species.

Approximately 91% of the data used in the copper acute GV reported the DOC concentration in the test solutions, whereas this figure was 65% for zinc (Table 9.1).

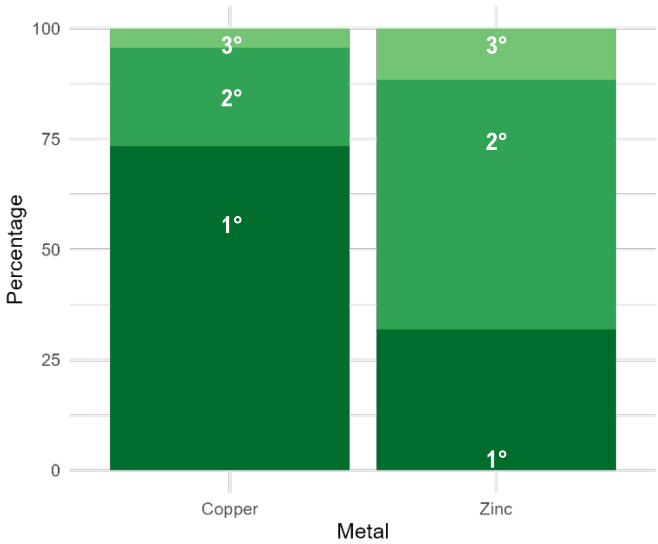


Figure 9.1: Quality of data used for deriving **copper** (left) and **zinc** (right) acute GVs.

Table 9.1: Reported and estimated water chemistry in the toxicity dataset used for the **copper** and **zinc** acute GV derivations .

	Copper	Zinc
pH reported	1294 (99.7%)	269 (100%)
pH estimated	3 (0.3%)	0
Hardness reported	932 (72%)	269 (100%)
Hardness estimated	365 (28%)	0
DOC reported	1209 (93%)	176 (65%)
DOC estimated	88 (7%)	93 (35%)

9.3 Diversity and inclusion of taxonomic groups

The data used to derive the acute GVs represented multiple taxonomic groups (Table 9.2, Figure 9.2), more than the four required by ANZG.[171] The copper dataset included species from seven taxonomic groups (as defined in Warne et al.) and the zinc dataset included species from eight. The datasets for copper and zinc were both dominated by fish, crustaceans and molluscs. No algae were included in the copper derivation and no plants were included in the zinc derivation due to lack of acceptable data.

Table 9.2: Number of species within each of the taxonomic groups included in deriving **copper** and **zinc** acute GVs. Taxonomic groups are as defined by Warne et al. and represent either phyla or subphyla.

Taxonomic group	Copper	Zinc
Amphibians	2	3
Fish	36	22
Molluscs	28	12
Crustaceans	23	18
Insects	3	8
Annelids	1	2
Rotifers	0	2
Macrophytes	2	0
Green algae	0	2

The lack of inclusion of macrophytes and algae is a limitation for application of these acute GVs for risk assessment to aquatic primary producers. This contrasts with the chronic DGVs for copper which include toxicity data for three plants and six microalgae. Similar to these acute GVs, the chronic DGVs for zinc do not include toxicity data for any plants, but do include data for three algal species. To some extent, there are methodological challenges in measuring suitably sensitive survival and growth endpoints for short-duration exposures to macrophytes and algae with most studies reported undertaking tests which are of sufficient duration to obtain measurable growth effects (i.e., chronic exposure periods). One algal study with a standard unicellular algal test species (*Raphidocelis subcapitata*) measured effects of five metals and three organic chemicals after 4-hours exposure measuring ATP and 'recovery' (i.e., growth in standard media for 96 hours after toxicant exposure) endpoints.[172] The results showed the acute recovery exposure for copper was 2.9x less sensitive and the zinc 167x less sensitive that the standard chronic exposure. The

[171] Warne et al., 2018.
[172] CW Hickey, C Blaise, and G Costan, 1991. Microtesting appraisal of ATP and cell recovery toxicity end points after acute exposure of *Selenastrum capricornutum* to selected chemicals. *Environmental Toxicology and Water Quality* 6, 4: 383-403.

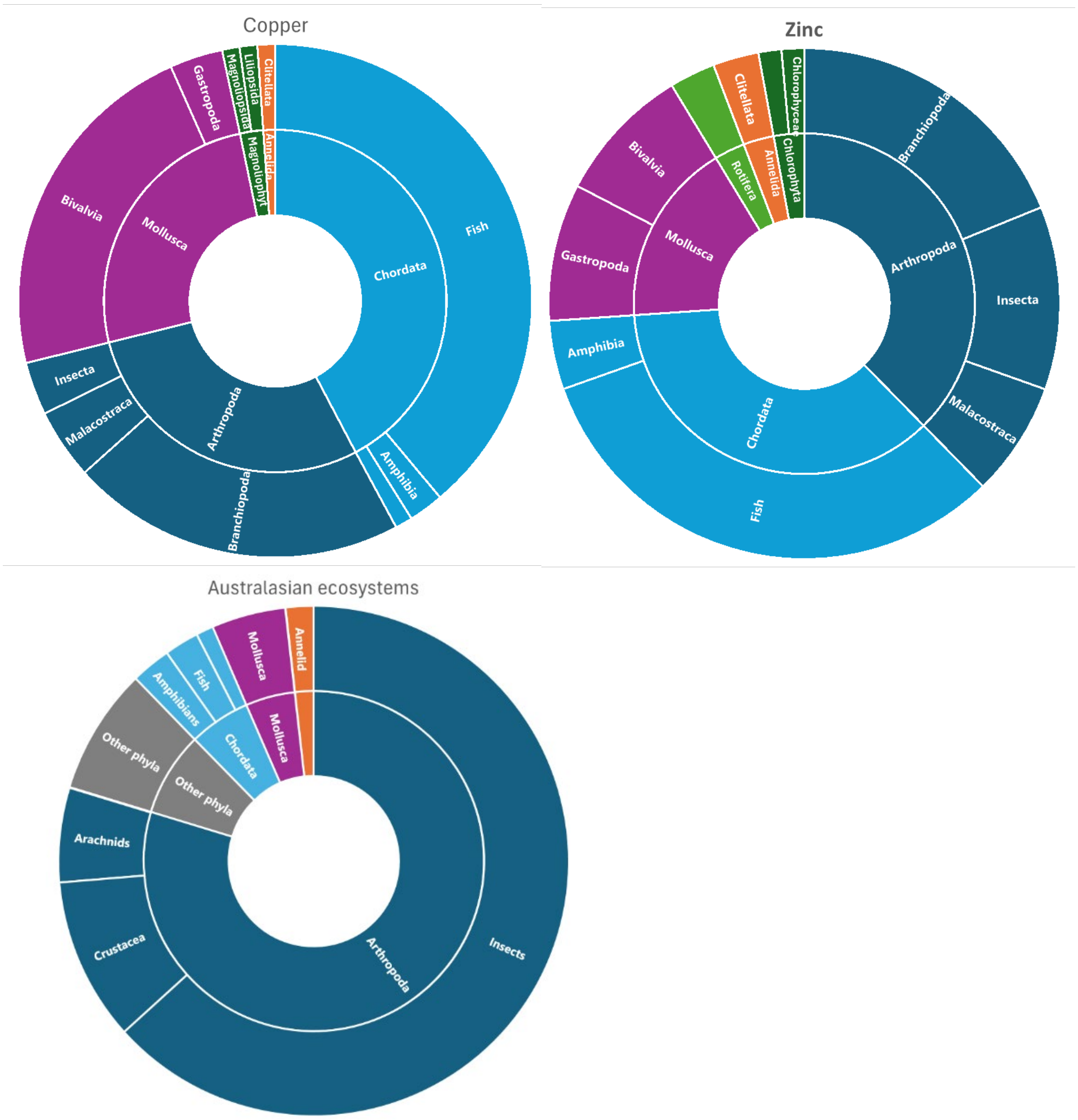


Figure 9.2: Taxonomic composition of data used for deriving **copper** (top) and **zinc** (bottom) acute GVs compared to estimates of diversity in the Australasian region. Information on freshwater ecosystems for Australasia.[173] Aotearoa specific data in the format required has traditionally covered only freshwater fish and/or macroinvertebrates,[174] though diversity data that includes all taxonomic groups is becoming available through eDNA testing.[175]

results of this acute exposure assessment were not included in this acute GV derivation because of the lack of chemical validation of exposure concentrations.

The taxonomic groups included in the acute guideline derivation are not necessarily representative of freshwater ecosystems in Aotearoa, though this is a common weakness for toxicity guideline values, as not all species present in an ecosystem can be used in laboratory toxicity testing. Experimentally this shortcoming has been addressed by using microcosms and mesocosms – simulating standing and flowing water environments – which include an "ecosystem" of species and are often much longer duration experiments which complement chronic testing of chemical exposures (including pulsed

[173] EV Balian et al., 2008. The Freshwater Animal Diversity Assessment: an overview of the results. *Hydrobiologia* 595, 1: 627-37.
[174] M Joy and R Death, 2013. Freshwater Biodiversity, in *Ecosystem Services in New Zealand: Conditions and Trends*, ed. JR Dymond (Lincoln, New Zealand: Manaaki Whenua Press; reprint).
[175] SP Wilkinson et al., 2024. TICI: a taxon-independent community index for eDNA-based ecological health assessment. *PeerJ* 12: e16963.

exposures). Generally, such complex systems are not amenable to application to acute GV derivations based on single short-term exposures because of the level of effort needed to get statistically robust endpoints for the community. Such systems are, however, suitable for validating water quality guidelines for environments such as stormwater-exposed streams and rivers where multiple discharges occur over prolonged periods.

ANZG does not require any specific taxonomic groups to be included when deriving guideline values, as long as four groups are included. By contrast, the US EPA and EU both have specific requirements regarding the inclusion of different taxonomic groups (Table 9.3). These requirements are assessed here to indicate whether the derived acute GVs would meet the standards for those jurisdictions. The US EPA requirements were met for both copper and zinc, but the EU requirements to include *both* algae and higher plants were not met for either metal.

Table 9.3: Assessment of whether taxonomic groups required by US and EU were met with data used for deriving **copper** and **zinc** acute GVs.

US EPA*	EU	Copper	Zinc
Species in the family Salmonidae	Fish	Yes, e.g., *O. mykiss*	Yes, *O. mykiss*
Second family in Class Osteichthytes	Second family in phylum Chordata	Yes, e.g., *P. promelas*	Yes, *P. promelas*
Third family in phylum Chordata		Yes, e.g., *Lithobates catesbeianus*	Yes, e.g., *Bufo gargarizan*
Planktonic crustacean	Crustacean	Yes, e.g., *D. magna*	Yes, e.g., *D. magna*
Insect	Insect	Yes, e.g., *Chironomus decorus*	Yes, e.g., *Rhithrogena* sp.
A family in a phylum other than Arthropoda or Chordata	A family in a phylum other than Arthropoda or Chordata	Yes, molluscs, e.g., *Hyridella depressai*	Yes, molluscs, e.g., *Hyridella depressai*
A family in any order of insect, or any phylum not already represented	A family in any order of insect, or any phylum not already represented	Yes, annelids e.g., *Lumbriculus variegatus*	Yes, annelids e.g., *Limnodrilus hoffmeisteri*
Benthic crustacean		Yes, e.g., *Paracalliope fluviatilis*	Yes, e.g., *Paracalliope fluviatilis*
Algae specifically excluded	Algae	No	Yes, e.g., *R. subcapitata*
Macrophytes specifically excluded	Higher plant	Yes, e.g., *Ceratophyllum demersum*	No

Note: * US EPA data requirements specifically exclude algae and higher plants.

9.4 Inclusion and protection of native species

Data for seven native species were included in deriving the copper acute GVs; and 10 for zinc. These species were generally towards the less sensitive end of the data (top half/highest 50%) used in deriving the GVs (Figure 9.3). This suggests that the GVs would protect these native species. These plots suggest the possibility that the acute GVs are over-protective, given that the native species are all at the less sensitive end. However, there are over 200 aquatic invertebrates in Aotearoa[176] and acute copper and zinc toxicity data for only 3 or 4. We cannot know if the un-tested species are more or less sensitive than those tested–hence conservatism, and a precautionary approach is needed.

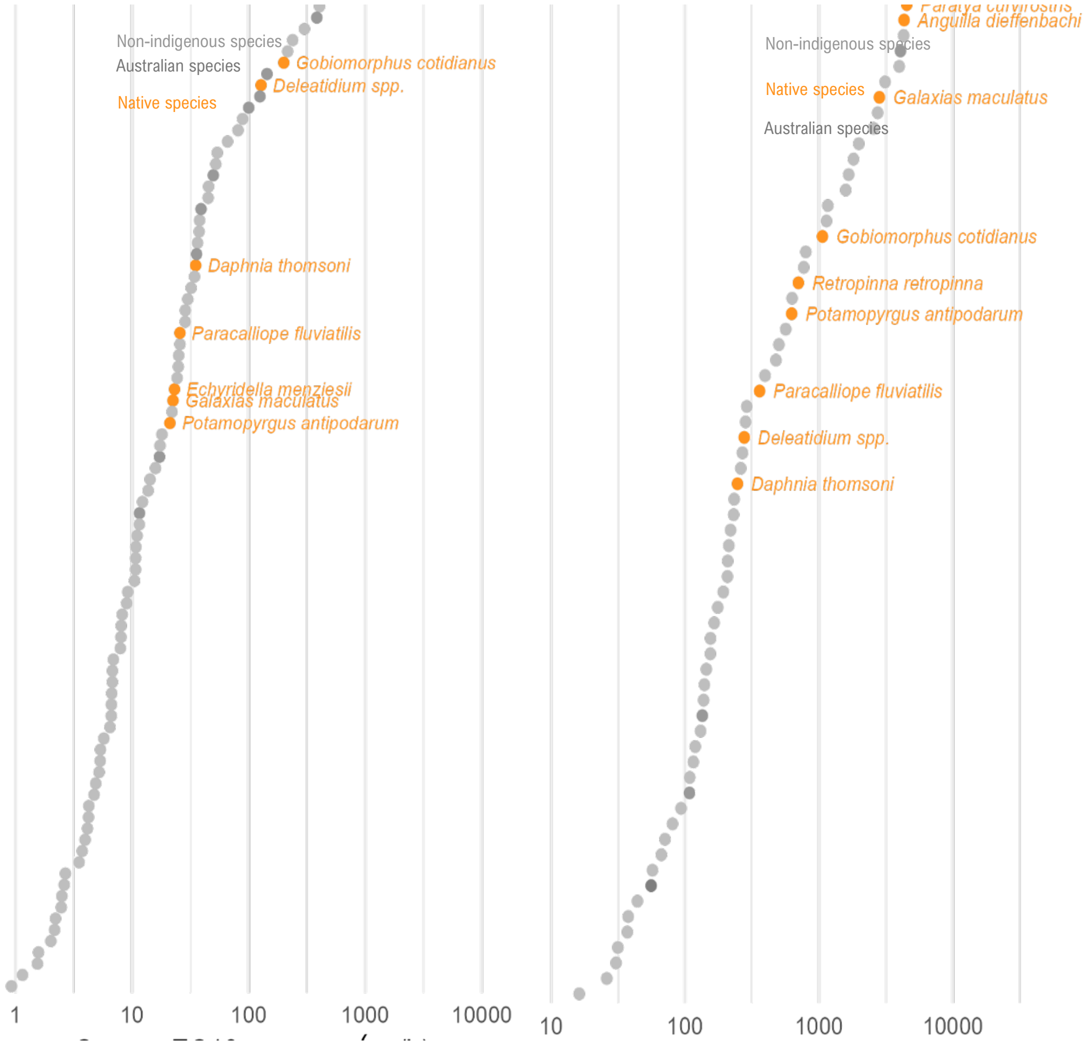


Figure 9.3: Toxicity data (converted EC10s) for native species for **copper** (left) and **zinc** (right). Note these data are the same as that presented in the species-sensitivity distributions (i.e., converted EC10s, normalised to the index condition (pH 7.5, hardness 30 mg/L as $CaCO_3$ and DOC 0.5 mg/L)).

There were also other data available for native species that were not suitable for deriving the GVs.[177] These data can be compared to the SSD data to assess whether that species would have been protected from the reported effect if metal concentrations were below the acute GVs (Table 9.4 and Table 9.5). This assessment indicates the potential risks from copper to the glochidia (larval stage) of native freshwater mussels. This species and life stage is expected to rank around the 5th percentile of most sensitive species.

[176] https://www.doc.govt.nz/nature/native-animals/invertebrates/freshwater/
[177] For example, due to inadequate information on the water chemistry; insufficient number of test concentrations; reporting of non-standard effects such as physiological effects.

It is known that low concentrations of copper can affect the olfactory responses of freshwater fish,[178] and induce avoidance responses that have potential to disrupt migration pathways. One study indicated effects on swimming behaviour when inanga were exposed to 6 μg/L of copper.[179] That concentration would be around the 20th percentile, indicating that if copper concentrations are less than the GV to protect 95% species, there is unlikely to be a disruption of the olfactory response in inanga.

Table 9.4: **Copper** toxicity data for native species, including values not used in the acute GV derivation. Values in bold indicate species that may not be protected by acute GVs, depending on the level of species protection.

Taxonomic group	Species (common name)	Test details	Reported EC50 values	Normalised EC50$	Converted EC10	Included in GV or not	Percentile rank from SSD (0-100)*
Crustacea	*Daphnia thomsoni* (*water flea*)	48-h mortality	14-600	57	35	Y	72
	Ceriodaphnia dubia (water flea, wild collected in NZ)	48-h mortality	21-24	11†	6.1	N	25
	Paracalliope fluviatilis (amphipod)	96-h mortality	61	41	26	Y	65
	Paracalliope fluviatilis (amphipod)	96-h morbidity	70-629	115	71	N	85
	Paranephrops planifrons (kōura)	96-h mortality	>447	>509	>316	N	>94
Insecta	*Deleatidium* spp.	96-h mortality	86	206	128	Y	90
Mollusca	*Echyridella menziesii* (kākahi, freshwater mussel)	48-h juvenile survival	33	37	23	Y	60
	***Echyridella menziesii* (kākahi, freshwater mussel)**	**24-h glochidia survival**	**2.9-4.2**	**2.8‡**	**1.8**	**N**	**3-4**
		24-h glochidia survival	**2.9-4.2**	**1.8&**	**1.1**	**N**	**0-1**
	P. antipodarum (mud snail)	96-h morbidity / mortality	14-110	34	21	Y	57
Fish	*Galaxias maculatus* (inanga)	96-h mortality	59	41	22	Y	58
	Galaxias maculatus (inanga)	48-h sodium influx changes	200 #	317 #	174 #	N	91-92
	Galaxias maculatus (inanga)	48-h changes in ammonia excretion rate	50 #	79 #	44#	N	79
	Galaxias maculatus (inanga)	16-h olfactory responses	6 #	9	5	N	20-21
	Gobiomorphus cotidianus (common bully)	96-h mortality	124-1000	412	407	Y	93

Note: $EC50 values normalised to index condition: pH 7.5, hardness 30 mg/L and DOC 0.5 mg/L. *Percentile rank (from 0 to 100) of EC10 values used in SSD; for species/data not included in the SSD, the rank is estimated based on the normalised & estimated EC10 value. † Based on an estimated DOC of 0.5 mg/L ‡Assuming a DOC of 0.5 mg/L, not the DOC of 2.3 mg/L reported (which was due to contamination of the water by resins). &Assuming a DOC of 1 mg/L, not the DOC of 2.3 mg/L reported (which was due to contamination of the water by resins). # Reported values were not EC50 values, but levels at which effects occurred. Used here as an estimate.

[178] JA Hansen et al., 1999. Differences in neurobehavioral responses of chinook salmon (*Oncorhynchus tshawytscha*) and rainbow trout (*Oncorhynchus mykiss*) exposed to copper and cobalt: Behavioral avoidance. *Environmental Toxicology and Chemistry* 18, 9: 1972-78; JK McIntyre et al., 2008. Chemosensory deprivation in juvenile coho salmon exposed to dissolved copper under varying water chemistry conditions. *Environmental Science & Technology* 42, 4: 1352-58.

[179] ORB Thomas et al., 2016. Smell no evil: Copper disrupts the alarm chemical response in a diadromous fish, *Galaxias maculatus*. *Environmental Toxicology and Chemistry* 35, 9: 2209-14.

For zinc, the toxicity data for additional species (Table 9.5) did not demonstrate that any of those species were highly sensitive to zinc, with no values within the 20% most sensitive (which is within the range of the acute GVs depending on the level of species protection).

Table 9.5: **Zinc** toxicity data for native species, including values not used in the acute GV derivation..

Taxonomic group	Species (common name)	Test details	Reported EC50 values	Normal-ised EC50$	Converted EC10	Included in GV or not	Percentile rank from SSD (0-100)*
Crustacea	*Daphnia thomsoni* (water flea)	48-h mortality	274-466	447	246	Y	49
Crustacea	*Paracalliope fluviatilis* (amphipod)	96-h morbidity	293-823	660	360	Y	57
	Paratya curvirostris (shrimp)	96-h mortality	14,000	8200	4500	Y	94
Crustacea	*Paranephrops planifrons* (kōura)	96-h mortality	>450	450	230	N	59-60
Insecta	*Deleatidium* spp.	96-h mortality	570	505	277	Y	53
	Olinga feredayi (caddisfly)	48-h mortality	>10,000	8900	4600	N	94-95
	Pycnocentria evecta (caddisfly)	48-h mortality	>10,000	8900	4600	N	94-95
Mollusca	*Echyridella menziesii* (kākahi, freshwater mussel)	24-h glochidia survival	202-557	345 ‡	180	N	37-38
		24-h glochidia survival	202-557	320 &	160	N	34-35
	P. antipodarum (mud snail)	96-h morbidity/ mortality	446-11200	1100	626	Y	65
Fish	*Galaxias maculatus* (inanga)	96-h mortality	5500-13700	5500	2800	Y	85
	Galaxias maculatus (inanga)	48-h sodium influx changes	1000 #	640 #	320 #	N	35-37
	Galaxias maculatus (inanga)	48-h oxidative stress	1000 #	640 #	320 #	N	35-37
	Gobiomorphus cotidianus (common bully)	96-h mortality	2270	2070	1060	Y	72
	Anguilla australis (shortfin eel)	96-h mortality	11130	10500	5400	Y	96
	Anguilla dieffenbachii (longfin eel)	96-h mortality	8920	8430	4320	Y	93
	Retropinna retropinna (smelt)	96-h mortality	1450	1370	700	Y	68

Note: $EC50 values normalised to index condition: pH 7.5, hardness 30 mg/L and DOC 0.5 mg/L. *Percentile rank (from 0 to 100) of EC10 values used in SSD; for species/data not included in the SSD, the rank is estimated based on the normalised & estimated EC10 value. †Based on an estimated DOC of 0.5 mg/L ‡Assuming a DOC of 0.5 mg/L, not the DOC of 2.3 mg/L reported (which was due to contamination of the water by resins). &Assuming a DOC of 1 mg/L, not the DOC of 2.3 mg/L reported (which was due to contamination of the water by resins). #Reported values were not EC50 values, but levels at which effects occurred. Used here as an estimate.

9.5 Sensitivity testing

9.5.1 Description of options assessed

In this sensitivity testing, the following options were assessed:

- Using only primary quality data, where metals, pH, hardness and DOC were measured (or in the case of DOC estimated from other studies)
- Using only primary or secondary quality data for native species (tertiary data were included in as described in section 7.9 if not primary or secondary data available for a species),
- Using a different value for DOC in laboratory waters made from deionised water (0.5 mg/L instead of 0.3 mg/L)
- Using different factors for the conversion of EC50 values to EC10 values.

The results of this analysis are reported first for copper, and secondly for zinc, to enable comparisons between the GVs calculated for each metal.

9.5.2 Results for copper sensitivity analysis

With several of the tested options there is minimal change in the copper acute GVs (Table 9.6) compared to those recommended in section 8.6. There was minimal difference in the GVs when only high quality (primary ranked) data were used for GV derivation, and/or when tertiary data were not accepted for native species. This is likely due to the extensive acute toxicity dataset for copper, which offers robustness against inclusion and exclusion of a few data points. The most significant change with these options is that there are fewer native species included in the derivation (2-3 vs 7). While this may make little difference to the numeric calculation of copper GVs, this would reduce the confidence in protecting the species that are present in Aotearoa, especially when the entire SSD is used for risk assessment purposes.

When a higher DOC is assumed for the laboratory waters (0.5 mg/L instead of 0.3 mg/L), the copper GVs at the index condition are slightly, but not substantially lower. The limited effect of this change on the copper GVs may be because DOC was measured and reported in a large proportion of the dataset (see section 9.2).

Using the default ratio of five (as recommended by Warne et al. for data conversions[180]) to convert from EC50 to EC10 values has the most marked effect on the GVs, reducing the GVs by around a factor of 3.

[180] Warne et al., 2018.

Table 9.6: Comparison of data included and the **copper** acute GVs with different toxicity datasets, DOC assumptions and EC10 conversion options.

	Recommended	Primary data only	Primary and secondary for native species	Higher DOC in water	Different EC50:EC10 ratio
No. taxonomic groups	7	5	7	7	7
No. species	90	67	87	90	90
No. native species	7	2	3	7	7
Minimum and maximum of EC10 values	0.9 – 12,400	0.9 – 12,400	0.9 – 12,400	0.9 – 12,400	0.3-4,500
Acute GVs at index condition					
99% protection	1.1 (0.6-1.7)	1.1 (0.3-1.8)	1.1 (0.7-1.7)	1.0 (0.3-1.5)	0.4 (0.2-0.5)
95% protection	2.0 (1.4-2.8)	2.0 (1.3—2.9)	2.0 (1.4—2.8)	1.8 (1.2-2.6)	0.7 (0.5-0.9)
90% protection	2.8 (2.2-3.8)	2.8 (2.1-3.9)	2.7 (2.0-3.8)	2.6 (1.9-3.6)	0.9 (0.7-1.3)
80% protection	4.5 (3.5-6.1)	4.4 (3.3-6.0)	4.3 (3.3-5.9)	4.2 (3.3-5.7)	1.5 (1.2-2)

9.5.3 Results for zinc sensitivity analysis

Compared to copper, there were more significant changes between the zinc acute GVs recommended in Section 8.6 and those calculated for the sensitivity analysis (Table 9.7). When only primary quality data were included, the GV for 95% species protection was 27 μg/L compared with 35 μg/L with inclusion of secondary data (where no primary data were available for that species) and tertiary data (accepted for native species only). There was also a large reduction in the number of species—from 69 species to 22 species, due to the large number of species with only secondary quality data available (Figure 9.4).

Table 9.7: Comparison of data included and the **zinc** acute GVs with different toxicity datasets, DOC assumptions and EC10 conversion options.

	Recom-mended	Primary data only	Primary + secondary for native species	Higher DOC in water	Different EC50:EC10 ratio	Including all data for lowest mayfly	Excl. highest mayfly
No. taxonomic groups	8	5	8	8	8	8	8
No. species	69	22	61	69	69	68	68
No. native species	11	2	3	11	11	11	11
Minimum & maximum EC10 values	16-23,800	16-1165	16-23,800	16-23,800	5.9-8700	8.5-23,800	16-16,400
Acute GVs (at index condition)							
99% protection	16 (4-32)	10 (2-34)	17 (5-31)	16 (4-33)	6 (2-12)	11 (3-28)	15 (4-33)
95% protection	35 (17-56)	27 (9-59)	33 (19-52)	35 (17-56)	13 (7-21)	29 (15-52)	34 (17-57)
90% protection	52 (33-79)	41 (18-78)	48 (32-72)	52 (34-79)	20 (13-30)	48 (26-77)	52 (33-80)
80% protection	89 (64-133)	66 (36-115)	79 (57-116)	89 (64-133)	33 (24-50)	88 (59-138)	89 (63-132)

Many of the native species toxicity data values were of lower (tertiary) quality – based on nominal concentrations and estimates of hardness or DOC. The GVs calculated when those were excluded are close to the GVs calculated with them included (33 vs 35 µg/L). This is because there are many species in both options (69 when included, 61 if excluded) and none of the native species are at the very top or bottom of the species sensitivity distribution (hence their removal does not result in a major shift in the model fit).

As with copper, the most significant change with these options is that there are far fewer native species included in the derivation: reducing from 11 to 2 or 3 species only. As stated for copper, this would reduce the confidence in the species protection for Aotearoa.

Changing the assumed DOC for the laboratory waters (0.5 mg/L instead of 0.3 mg/L) did not result in any change to the zinc acute GVs at the index condition. This is likely because DOC was measured and reported in a large proportion of the dataset (see section 9.2) and may also be because the species geometric means at the top and bottom of the distribution were based on reported DOC values.

Using the default ratio of five to convert from EC50 to EC10 values has the most marked effect on the zinc acute GVs, reducing the GVs by around a factor of 2.7.

The most sensitive species was the mayfly *N. triangulifer*. There were additional data for that species, that were excluded from the derivation as the tests were in very hard water (315-377 mg $CaCO_3$/L) with alkaline pH (8.4-8.5).[181] These were excluded after analysis of draft GVs, as the resulting estimated EC10 was over three-fold lower than that of the next most sensitive species, prompting further analysis of this species. Overall, the data for this species were not well-predicted with the pooled fish/invertebrate MLR (section 6.2) and as described by the authors, hardness did not exert a protective effect on zinc toxicity for this species, suggesting it would be inappropriate to use a hardness correction. Furthermore, hardness of >300 mg/L is rare in Aotearoa streams (see Figure 9.6).

If the tests with very high hardness are included, the estimated EC10 value for this species is 8.5 µg/L, based on reported EC50 values of 42-84 µg/L. This results in significantly lower GVs for the 99% and 95% protection levels, though the difference is less at 90% or 80% species protection.

There was some uncertainty regarding the least sensitive species in the SSD dataset, as the DOC in the water was estimated by the authors based on their previous measurements of DOC in the same water source. However, removing this value did not substantively alter the zinc acute GVs.

[181] Besser et al., 2021.. Data for two other tests were excluded as they were conducted in high DOC water (29-41 mg/L), outside the range of the pooled MLR model.

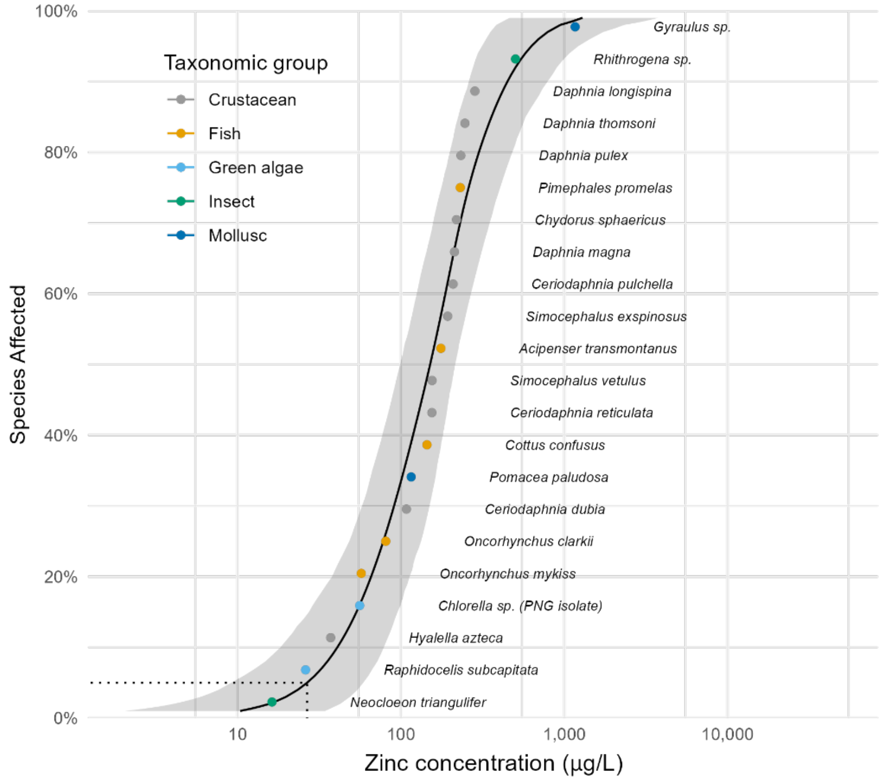


Figure 9.4: **Zinc** species sensitivity distribution (toxicity data normalised to index condition, converted to EC10s) when using only primary quality data.

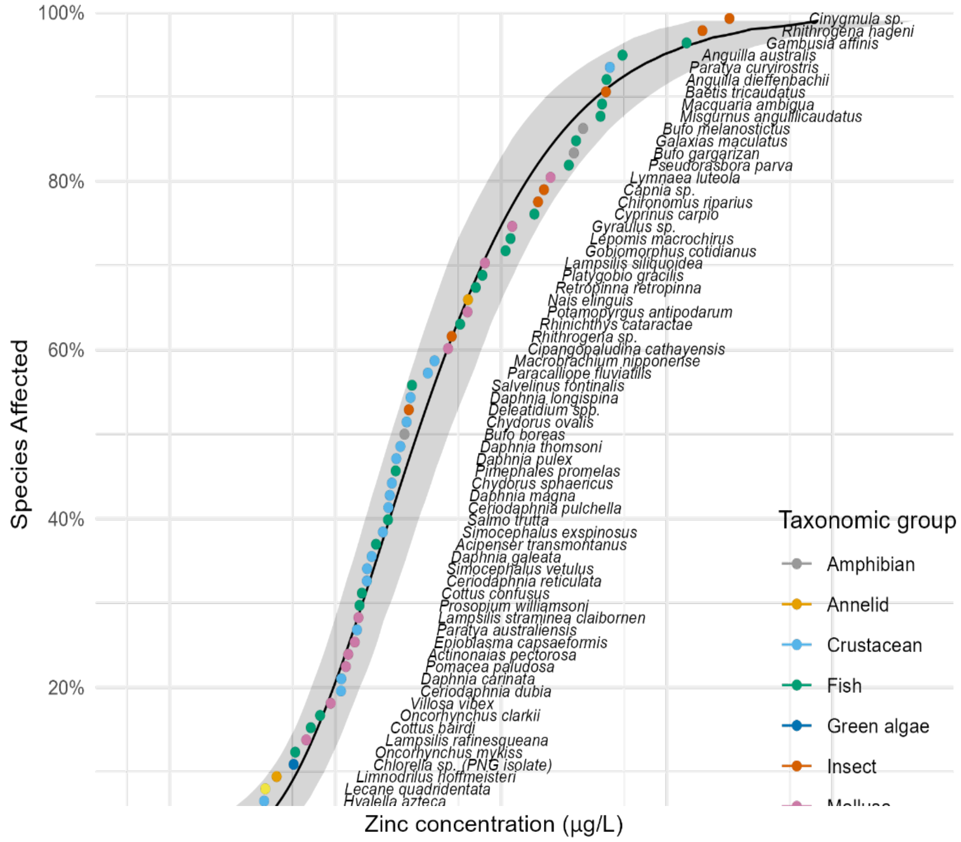


Figure 9.5: **Zinc** species sensitivity distribution (toxicity data normalised to index condition, converted to EC10s) when all data are included for the mayfly *Neocloeon triangulifer*. Note distance between that value and the next most sensitive.

9.5.4 Conclusions

Overall, the sensitivity testing suggested that the derived acute GVs are relatively robust to the inclusion or exclusion of lower quality data and the assumed DOC concentration of 0.3 mg/L in deionised waters. Using the standard conversion factor ratio of five as recommended by Warne et al.[182] to convert from EC50 to EC10 concentrations would result in substantially lower acute GVs and is not recommended.

9.6 Water chemistry covered by the GVs

For acute GVs to have high uptake and widespread use, they must be applicable to waters with a broad range in water chemistries. Their applicability depends on both the bioavailability models used and the toxicity data (these are compared to natural waters of Aotearoa in Figure 9.6). The models and the toxicity data used encompass most of the range of the water chemistries in natural waters, with a few limitations. There are several waters where the pH is <5 where neither the copper nor zinc GVs would be appropriate for application. Additionally, the zinc model (and toxicity data) does not extend to very low hardness waters (e.g., 2-14 mg $CaCO_3$/L), where zinc bioavailability is likely to be high. The zinc model also does not cover waters with DOC >22 mg/L, though in these waters bioavailability is expected to be lower, and an acute GV based on the upper limit of 22 mg/L DOC could be used.

Table 9.8: Median and range of the key toxicity modifying factors in the toxicity datasets used for acute guideline value derivation.

Metal	pH (unitless)	Hardness (mg/L as $CaCO_3$)	DOC (mg/L)
Copper	7.8 (5-8.8)	83 (3.9-898)	2.2 (0.07-30)
Zinc	7.5 (5.4-8.5)	52 (14-411)	0.6 (0.1-20)

[182] Warne et al., 2018.

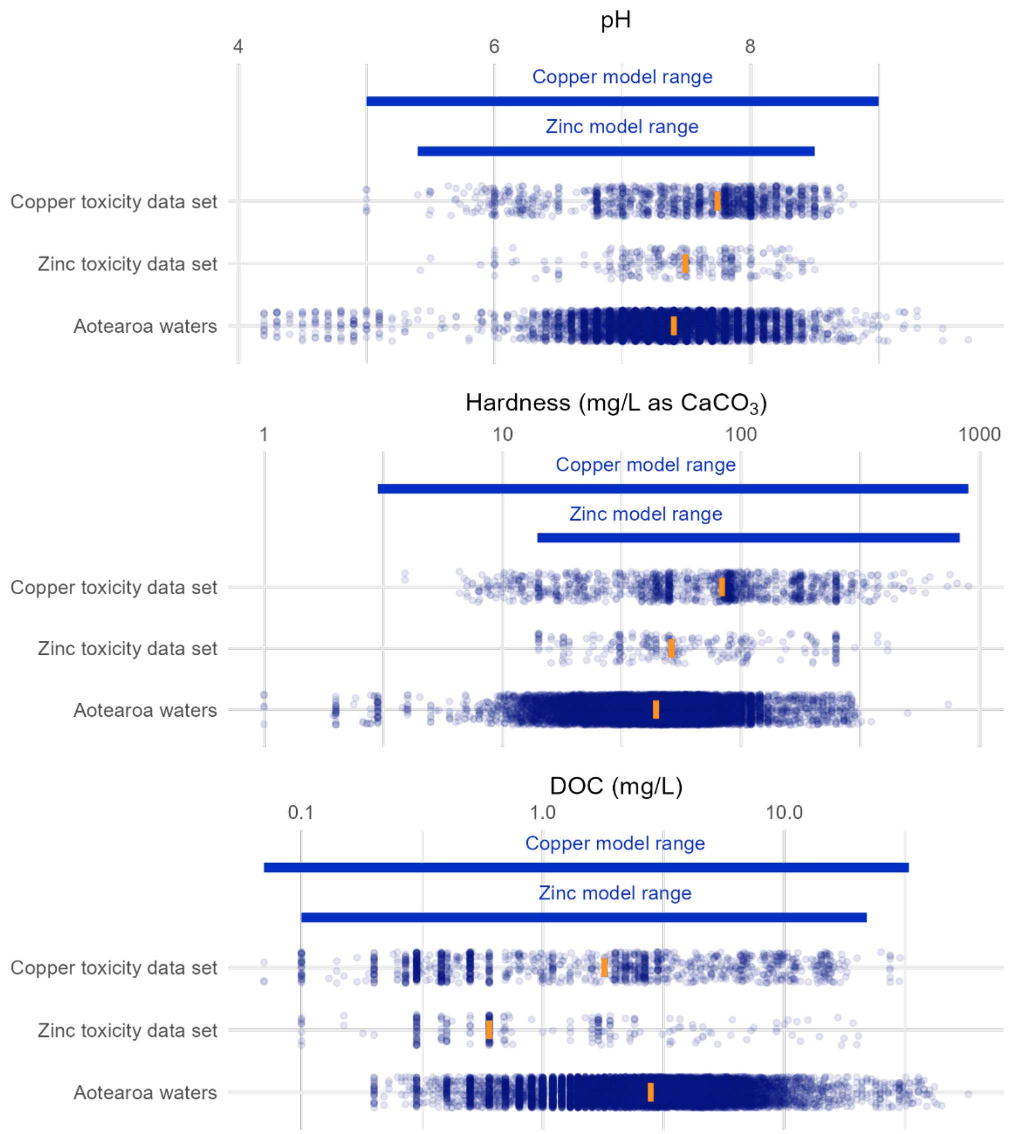


Figure 9.6: TMF range of the models and toxicity dataset compared to the range in monitored waters of Aotearoa. [183] Orange bar indicates median of that dataset. Geothermally influenced waters have lower pH (data not included here).

9.7 Summary of acute GV evaluation

The copper and zinc acute GVs are based on a high quality toxicity dataset, where pH was reported for almost all values. Hardness and DOC were also reported for most of the data; though estimates were required for some species toxicity data, particularly native species. The dataset used in the SSD includes a large number of species—easily enough to satisfy statistical requirements for model fitting and for coverage of different taxonomic groups. Inclusion of data for many native species increases the ecosystem protection for Aotearoa. The key limitations of these GVs are the lack of algae (copper) and plants (zinc) included in their derivation.

The sensitivity analysis indicated generally minor changes to the acute GVs based on different choices related to the data included, and more difference related to the choice of EC50 to EC10 conversion factors.

[183] Data provided by ANZG/MERA.

The conversion factor used was based on metal toxicity data and is therefore considered a more robust option than a “rule-of-thumb” factor.

Based on the available TMF data for Aotearoa, the acute GVs should be widely applicable, though there may be samples where hardness is low (i.e., <14 mg/L as $CaCO_3$) where the zinc GVs would not be applicable.

The next section, which provides guidance on the use of the acute GVs, includes comparisons of measured copper and zinc concentrations to the acute GVs, to indicate where these GVs could be useful in water management.

10 Applying the acute guideline values

10.1 Introduction

This section of the report provides guidance around the application of these acute GVs for water management in Aotearoa. This covers:

- a recommended tiered implementation approach.
- methods to adjust the GVs for the pH, hardness and DOC of waters, what to do in the absence of these TMF data or where TMFs are outside the applicable range for these GVs.
- the timeframe that acute GVs are applicable to and the types of monitoring that could be used to assess acute toxicity.
- methods to measure dissolved copper, zinc and the required TMFs in water samples.

Use of the acute GVs in a tiered approach is demonstrated with case studies.

10.2 Recommended implementation approach

The recommended implementation approach for these acute GVs is analogous to advice for the Australian and New Zealand chronic DGVs.[184] We recommend using a tiered approach for implementing these acute GVs (Figure 10.1). In tier 1 of this approach measurements of dissolved copper and zinc are first compared to tier 1 acute GVs. If metal concentrations exceed those acute GVs, then the assessment progresses to tier 2, where acute GVs are calculated for the water chemistry of interest. If there is no water chemistry information (i.e. measurement of TMFs), the assessment can stop at tier 1, however this would be a precautionary and conservative assessment of toxicity risk.

Tier 1 acute GVs should represent conditions where bioavailability is high, to minimise false negatives (instances where there is a risk of toxicity, but the assessment finds there is low risk). There is currently work being undertaken to develop tier 1 chronic DGVs for copper and zinc for Aotearoa, based on analysis of water chemistry data. However, that process is not yet finalised, and the chronic DGVs are also not yet finalised. Ideally, the tier 1 acute GVs would be calculated using the same method.

In the interim, tier 1 acute GVs (

Table 10.1) are calculated for water chemistry conditions that represent generally high bioavailability (but not extreme conditions). These were based on the 10th percentile of hardness and DOC measurements in Aotearoa (17 mg/L $CaCO_3$ and 0.7 mg/L respectively); and for copper the 10th percentile for pH (7.0) and for zinc the 95th percentile for pH (8.2). The difference in pH is because copper GVs are lower at lower pH, whereas zinc GVs are lower at higher pH. The use of the 10th percentile is a pragmatic decision, to provide Tier 1 GVs that are protective in the waters where these acute GVs are most likely to be applied (e.g., lowland streams). 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 replacements can be developed using a more robust process. Note these interim tier 1 acute GVs are different to the acute GVs presented and evaluated in earlier sections, which were at the index (standard) water chemistry to enable comparisons between copper and zinc GVs.

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[184] J Gadd et al., 2023. *Implementing bioavailability-based toxicity guideline values for copper and zinc in Aotearoa New Zealand. Interim technical guidance for scientists and practitioners, focusing on freshwater applications*, National Institute for Water and Atmospheric Research (Auckland, NZ, September 2023), https://www.envirolink.govt.nz/assets/Envirolink/2307-HZLC166-Implementing-bioavailability-based-toxicity-guideline-values-for-Cu-and-Zn.pdf. and upcoming publications for ANZG.

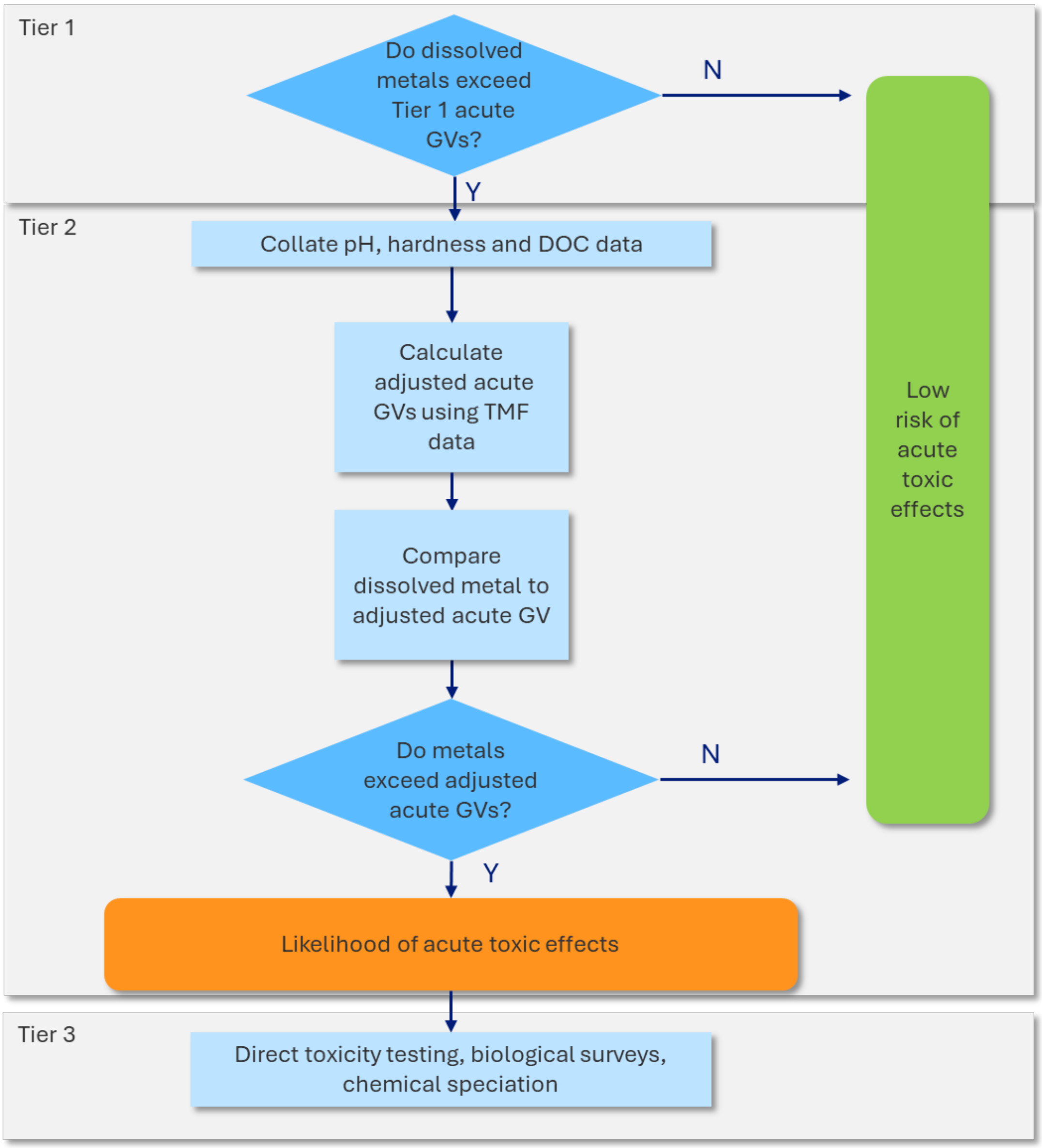


Figure 10.1: Tiered approach recommended for using **copper** and **zinc** acute GVs. Tier 1 is a conservative assessment. Equations are provided for calculating adjusted acute GVs in section 10.3.

Table 10.1: Interim Tier 1 acute GVs for **copper** and **zinc** (μg/L). Copper GVs at pH 7.0, hardness 17 mg $CaCO_3$/L and DOC 0.7 mg/L; zinc GVs at pH 8.2, hardness 17 mg $CaCO_3$/L and DOC 0.7 mg/L. The pH values are different because of the different effect of pH on copper toxicity and zinc toxicity.

	Level of species protection			
	99%	**95%**	**90%**	**80%**
Copper interim Tier 1 acute GV	0.7	1.3	1.7	2.9
Zinc interim Tier 1 acute GV	11	24	36	59

In Tier 2, TMF data are required to provide a toxicity assessment with greater certainty. Bioavailability-adjusted acute GVs can be calculated for each sample using measurements of pH, hardness and DOC for comparison to the dissolved metals. If dissolved metals exceed the adjusted acute GVs, then there is a high likelihood for acute toxicity to occur.[185]

A Tier 3 step can be used, which could include further investigations such as acute toxicity testing of the water samples and/or looking at other lines of evidence such as the presence or absence of sensitive species.

An example of this tiered approach is shown in Figure 10.2. Tier 1 acute GVs are compared to copper and zinc data from monitoring of four Auckland streams during rain events. All samples exceeded the tier 1 GVs for the highest level of protection (99%) for copper, and many for zinc. In addition, many values also exceeded the GVs for the lowest level of protection (80%) for copper in Oakley Creek and for zinc in Motions Creek suggesting the potential for acute toxicity in these streams. This preliminary (tier 1) assessment suggests that the risks should be further investigated, particularly for copper (all streams) and for zinc in Meola and Motions Creeks. This would involve collecting TMF data for these streams, and then comparing metal concentrations (collected at the same time) with adjusted GVs to provide more certainty around the acute toxicity risks.

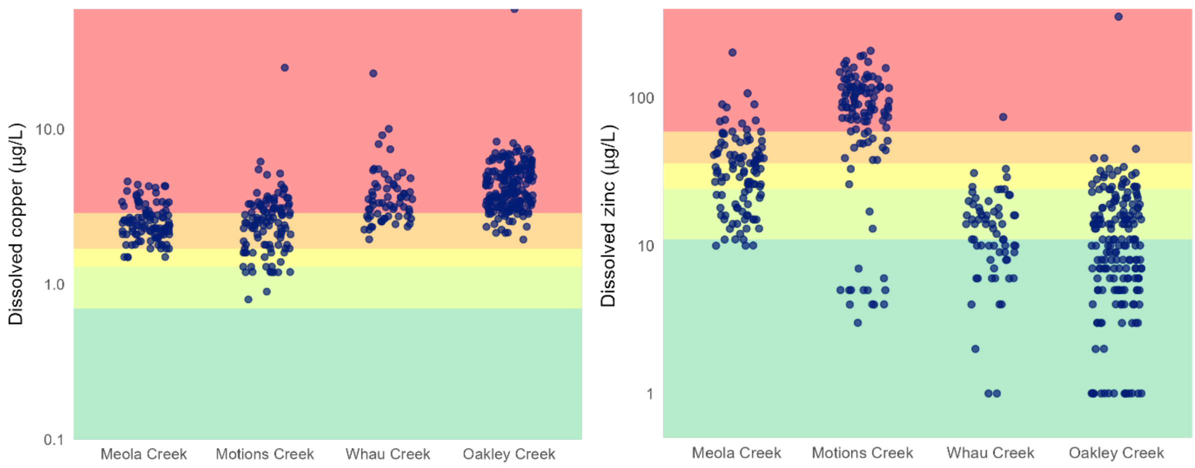
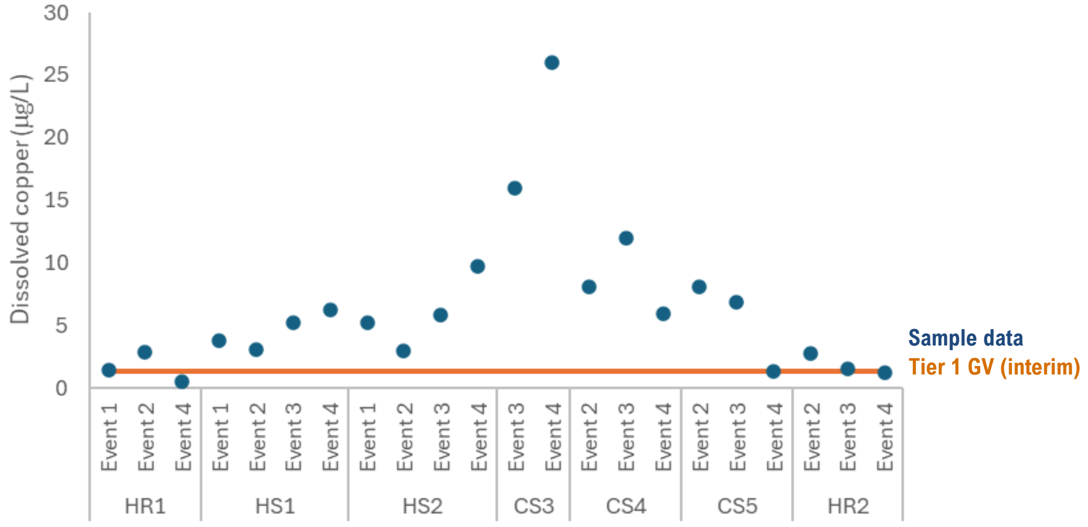


Figure 10.2: Dissolved **copper** (left) and dissolved **zinc** (right) concentrations during storm events compared to interim tier 1 acute GVs for varying levels of protection. GVs shown as background shading for various species protection (99%, 95%, 90% and 80%). Green shading indicates values below the interim tier 1 99% protection GV; red shading indicates values above the interim tier 1 80% protection GV.

For tier 2, where there are TMF data available, the acute GVs should be calculated for the site-specific or sample-specific water chemistry (pH, DOC and hardness). The method for this is outlined in the section 10.3, and an example of this approach is shown in Figure 10.3. In the first plot, the measured dissolved copper concentrations are all compared to the tier 1 acute GV of 0.9 µg/L. All but one value (95% samples) exceeded the interim tier 1 GV, including at least one sample at each site, indicating potential risks of acute toxicity are widespread. Hardness, DOC and pH values for each sample were then used to calculate tier 2 GVs (bottom plot). At this tier, 50% of samples were below the acute GVs, and there were two sites where all samples were below the tier 2 GVs, indicating low risks in these locations, but high likelihood of acute toxicity at other locations.

[185] When Tier 1 GVs are established using a robust method, TMFs can also be used to estimate the bioavailable metal concentrations, which can then be compared to the interim Tier 1 GV.



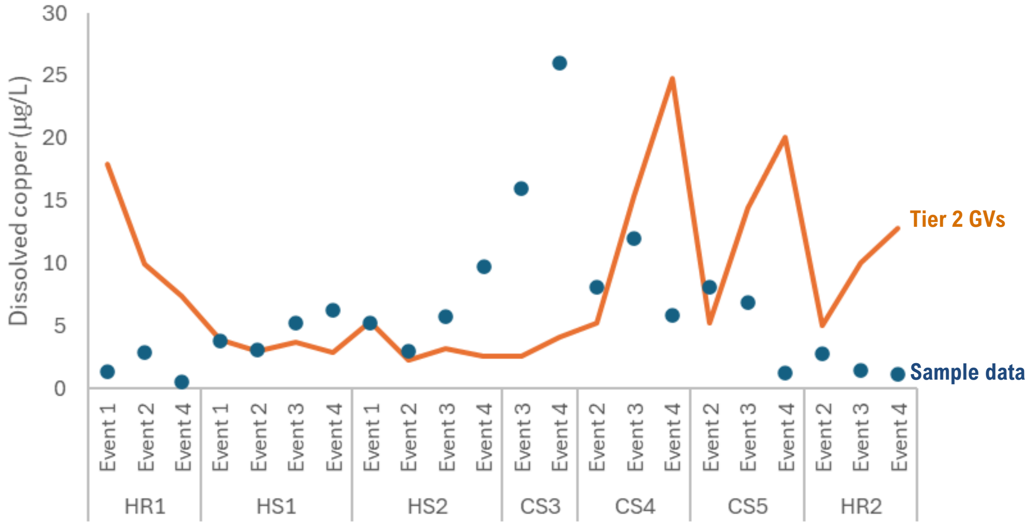


Figure 10.3: Dissolved **copper** concentrations during storm events compared to interim Tier 1 (top) and Tier 2 (bottom) acute GVs. Acute GVs for 95% species protection, shown as orange line. Data provided by Christchurch City Council from sampling with autosamplers during rainfall events; however, data use here is to demonstrate use of tiered approach only and does not necessarily indicate acute risks in the locations shown.

A third example of the use of the tiered approach is shown in Figure 10.4 for a single site, where measured dissolved copper and zinc concentrations are compared to both the interim Tier 1 acute GVs and bioavailability-adjusted acute GVs. Although all samples exceeded the interim Tier 1 copper acute GV, none exceeded the bioavailability-adjusted acute GVs. On the other hand, though fewer zinc samples exceeded the interim Tier 1 GV (around half the samples), three of those also exceeded the bioavailability-adjusted acute GVs for zinc. This demonstrates the greater effect of water chemistry in modifying copper bioavailability, compared to zinc bioavailability.

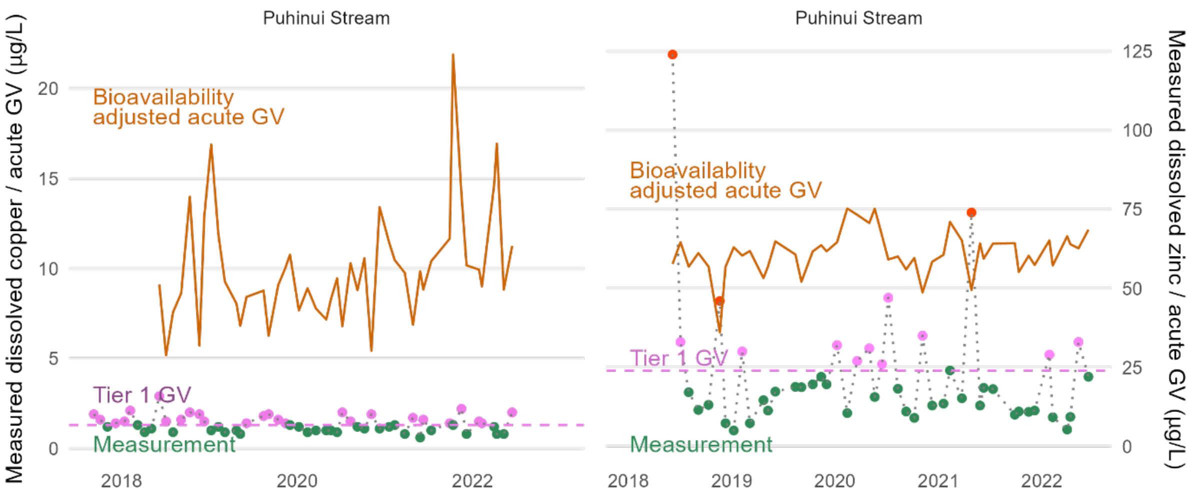


Figure 10.4: Dissolved **copper** (left) and **zinc** (right) concentrations measured in Puhinui Stream during monthly monitoring compared to a tier 1 acute GV (pink dashed line) and to bioavailability-adjusted acute GVs (dark orange line) for 95% species protection. Metal concentrations (connected by dotted line) below the tier 1 GVs are shown in green, those above the tier 1 GV are shown in pink and those above the bioavailability-adjusted GVs are shown in orange. This indicates that dissolved copper concentrations in all samples exceeded the interim Tier 1 GVs but were consistently below the adjusted acute GVs; many values for dissolved zinc exceeded the interim Tier 1 acute GVs and two also exceeded adjusted acute GVs. Monitoring data provided by Auckland Council.

10.3 Calculating bioavailability-adjusted acute GVs

In tier 2, where dissolved copper and zinc concentrations exceed the interim Tier 1 acute GVs, bioavailability-adjusted acute GVs should be calculated, using equations provided in section 8.7 and repeated below for 95% species protection.

$$Copper\ acute\ GV_{95} = \exp^{(-6.6 + 0.78\, pH + 0.58 \times \log(hardness) + 0.70 \times \log(DOC)} \qquad \text{Equation 10.1}$$

$$Zinc\ acute\ GV_{95} = \exp^{(2.5 - 0.12 \times pH + 0.6 \times \log(hardness) + 0.13 \times \log(DOC)} \qquad \text{Equation 10.2}$$

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.

The effect of pH, DOC and hardness on the copper and zinc acute GVs for 95% species protection is shown in Table 10.2 and Table 10.3. The copper acute GVs increase with increasing pH, hardness and DOC; though the effect of the latter two factors is minor at low pH. The zinc acute GVs decrease as pH increases, though the effect of both pH and DOC are smaller than the effect of hardness, based on the range of data shown.

Table 10.2: **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.

		Hardness (mg $CaCO_3$/L)				
pH	**DOC (mg/L)**	**15**	**30**	**60**	**120**	**240**
6.5	**0.3**	0.4	0.6	1.0	1.4	2.1
7.5	**0.3**	0.9	1.4	2.1	3.1	4.6
8.5	**0.3**	2.0	3.0	4.5	6.8	10
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	11.6	17
7.5	**6**	7.6	11	17	25	38
8.5	**6**	17	25	37	55	82

Table 10.3: **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.

		Hardness (mg $CaCO_3$/L)				
pH	**DOC (mg/L)**	**15**	**30**	**60**	**120**	**240**
6.5	**0.3**	24	37	56	84	128
7.5	**0.3**	21	33	49	75	113
8.5	**0.3**	19	29	44	66	100
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

10.4 TMF data requirements

The recommended method for use of these GVs is to adjust the acute GV for every site or sampling event, based on the site- or sample-specific measurements of pH, hardness and DOC (Table 10.4). If those TMF data are not available for a specific sampling event, then TMFs could be estimated for that sample from other data (if available), following the advice previously provided for chronic copper and zinc DGVs.[186] Alternatively, Tier 1 acute GVs can be used for screening in the absence of any TMF information, though that assessment would be conservative and should be considered preliminary.

Table 10.4: Recommended implementation approach for acute GVs. Adopted from implementation advice for chronic copper and zinc DGVs for Aotearoa/New Zealand. [186]

	TMF data	Action
Level A (most robust assessment of toxicity risk)	Sample- or site- specific	Calculate a sample-specific GV for every measurement value in space and time
Level B	Available for same site (from other monitoring) or from surrogates	Use other TMF data from that site to calculate GV. Recommend 25th percentile values from that data for hardness and DOC, 25th percentile for pH for copper GVs and 75th percentile for pH for zinc GVs †
Level C	Available for other sites/ related sites	Use other TMF data from other sites to calculate GV. Recommend 10th ‡ percentile values from that data for hardness and DOC, 10th percentile for pH for copper GVs and 90th percentile for pH for zinc GVs†
Level D (least robust, screening-level, conservative assessment)	None available	Use tier 1 GVs

Note: † A 75th/90th percentile is recommended for pH for calculating zinc acute GVs, as zinc GVs are lower with *higher* values for pH.
‡ Lower percentile value recommended to provide more conservative assessment as TMF data are estimates for this site.

10.5 Applicable water chemistries

The guideline values should be used within the range shown in Table 10.5. These ranges are based on the MLR models used for the adjustments and based on the toxicity data used in the derivation. Use of the acute GVs outside of this range may result in an over-estimate or under-estimate of risk. GVs should NOT be calculated using TMF values that are outside of the ranges specified (e.g., for a DOC >30 mg/L) because the models have not been verified outside of that range and the toxicity dataset used may not be relevant for those conditions.

Table 10.5: Applicable range in water chemistry TMFs for using the acute GVs.

Metal	pH	Hardness	DOC
Copper	5.0-8.8	3.9-898	0.1-30
Zinc	5.4-8.5	14-411	0.1-20

When the TMF values are generally within the applicable range for the GVs, but only occasionally outside, GVs calculated at an appropriate TMF value can be used with some caveats (Table 10.6). When a GV is calculated this way, that should be documented in any reporting. There is additional uncertainty if more than one TMF is outside the applicability range.

186 Gadd et al., 2023.

Table 10.6: Strategies to calculate acute GVs when measured TMFs are outside the suitable range for application to **copper** and **zinc** acute GV calculations.

Scenario	Action	Effect on metal bioavailability	Interpretation
Hardness exceeds upper limit	Use GV calculated at maximum applicable hardness for that metal	Metal bioavailability may be lower than at upper limit.	Copper and zinc acute GVs may be conservative.
Hardness less than lower limit	Use GV calculated at minimum applicable hardness for that metal	Metal bioavailability may be higher than at lower limit; Different species (those adapted to low ionic conditions) may be present than those used in deriving the guideline values, and these acute GVs may be not applicable.	Acute GV may not be protective – use with caution.
pH less than lower limit	Use GV calculated at minimum applicable pH for that metal	Copper bioavailability may be higher than at lower limit, whereas zinc bioavailability may be lower. Different species (those adapted to low pH conditions) may be present than those used in deriving the guideline values, and these acute GVs may be not applicable.	Use both copper and zinc GVs with caution.
pH exceeds upper limit	Use GV calculated at maximum applicable pH for that metal.	Copper bioavailability may be lower than at lower upper, whereas zinc bioavailability may be higher.	Copper acute GV may be conservative. Zinc acute GV may not be protective – use with caution.
DOC less than lower limit	Use GV calculated at minimum applicable DOC for that metal.	Metal bioavailability may be higher than at lower limit, bioavailability may be higher than in the toxicity dataset used in the derivation.	Acute GV may not be protective – use with caution.
DOC exceeds upper limit for copper and/or zinc	Use GV calculated at maximum applicable DOC for that metal.	Metal bioavailability may be lower than at upper limit.	Copper and/or zinc acute GV may be conservative; though use of upper limit DOC likely provides a good estimation of risk.

These acute GVs are designed for use in freshwater environments, that is, those where salinity is less than 1 ppt.[187] Acute GVs should be adjusted for the hardness of saline waters before use–e.g., around 190 mg/L as $CaCO_3$ for salinity of 1 ppt. There are no acute GVs for copper or zinc in marine waters. While the advice for chronic copper and zinc DGVs was that freshwater DGVs would likely be conservative if applied to saline waters,[188] this may not be the case for these acute GVs. Such advice would require an assessment of whether species present in marine waters are more, or less acutely sensitive to copper and/or zinc than freshwater species – this was not in the scope for this project.

10.6 Applicable exposure durations

Acute GVs are designed to assess effects of short-term exposures. The toxicity data used to derive the GVs were predominantly from 48 hour and 96 hour exposure duration tests (and for zinc, some 24 hour tests with algae). This means the acute GVs are most appropriate for a timeframe of around 48 hours. Acute GVs are also relevant to exposures that are shorter than the duration of an acute toxicity test–for example, in a 96 hour test, the initial 48 hours of exposure may result in toxicity, though mortality may not be observed until 72-96 hours after exposure began.

The acute GVs may over-estimate toxicity risks when used for much shorter exposures (e.g., minutes or hours). However, this use could be used as a screening level assessment to indicate potential for toxicity–if

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188 Gadd et al., 2023.

metal concentrations in samples that represent exposures of minutes to hours (for example, sampling during storm events) do not exceed the acute GVs, this is high confidence that the ecosystem is being protected from acute effects. On the other hand, if those concentrations exceed the GVs, this indicates **potential** for acute toxicity-this does not imply that an adverse effect will occur. This depends also on the magnitude of that exceedance, as well as its duration.

Acute GVs may under-estimate risks of toxicity when used for longer exposures–in the order of a week or more. Chronic DGVs are more appropriate for that timeframe. Monthly monitoring programmes routinely used by councils would generally be expected to represent the long-term exposures and do not provide the data that would be applicable to assessing risks from short-term exposures (i.e., using the acute GVs). However, if there are samples collected from those programmes that exceed acute GVs, this clearly indicates potential for acute toxicity. In that case, further action should be taken. That could include more frequent sampling to assess the duration of an exceedance. Alternatively, if such a sample was collected under high flows, then targeted sampling may be useful to investigate whether that exceedance was a rare occurrence, or whether acute GVs are regularly exceeded during high flows.

Multiple short-term exposures may result in harmful effects may occur even if concentrations are below these acute GVs because of the repeated nature of the exposures.[189] Toxicity assessments are particularly challenging when exposure concentrations vary over time.

[189] JS Bearr et al., 2006. Effects of pulsed copper exposures on early life-stage *Pimephales promelas*. *Environmental Toxicology and Chemistry* 25, 5: 1376-82; BM Angel et al., 2015. Time-averaged copper concentrations from continuous exposures predicts pulsed exposure toxicity to the marine diatom, *Phaeodactylum tricornutum*: Importance of uptake and elimination. *Aquatic Toxicology* 164: 1-9; TC Hoang et al., 2007. Toxicity of two pulsed metal exposures to *Daphnia magna*: Relative effects of pulsed duration-concentration and influence of interpulse period. *Archives Environmental Contamination and Toxicology* 53, 4: 579-89.

10.7 Protocols for measurement

Dissolved copper and zinc and the toxicity modifying factors in the water column of streams, rivers and lakes should be measured using prescribed technical standards (refer to NEMS[190]). Particular attention should be given to the recommended methods for DOC when requesting this analysis from a laboratory. An alternative method for DOC, based on measuring total carbon (TC, after filtration) then total inorganic carbon (TIC) and subtracting these to give organic carbon can result in poor resolution for the DOC measurement when both TC and TIC are high.[191] The method recommended by NEMS (DNPOC, Table 10.7) is the preferred method for use with metal guideline values (acute and chronic).

Table 10.7: Recommended methods for sample handling and measurement for **copper**, **zinc** and toxicity modifying factors (TMFs). Adapted from NEMS [190] with additional information from Hill Laboratories [191].

Metal	Storage and handling	Measurement/test method	Recommended (minimum) limit of detection (µg/L)
Dissolved copper	Unpreserved HDPE bottle filled with no air gap; sample kept cool (<10°C). Samples should be filtered within 36 hours of collection.	Filtration (0.45 µm filter*), then analysis by ICP-MS (APHA 3125 B)	0.5
Dissolved zinc			1
pH	Measured in the field or in a laboratory on a sample; collected in an unpreserved HDPE bottle filled with no air gap; sample kept cool (<10°C).	Analysis with pH meter after warming to room temperature, APHA 4500-H+ B	± 0.1†
Hardness	(see below for calcium and magnesium)	Calculated from Ca and Mg (APHA 2340 B)	1000 (1 mg/L)
Dissolved calcium	As for dissolved copper and zinc	Filtration (0.45 µm filter), then analysis by ICP-MS (APHA 3125 B) or ICP-AES (APHA 3120 B)	50
Dissolved magnesium	As for dissolved copper and zinc		20
DOC (as DNPOC)	Unpreserved and furnaced brown/amber glass bottle filled with no air gap; sample kept cool (<10°C). Plastic bottles should not be used as plasticisers may leach into the sample. Samples should be filtered within 36 hours of collection.	Filtration (using inert filters), then purging to remove inorganic carbon followed by oxidation of carbon by either persulfate-heat or UV-oxidation then analysis by IR detection (APHA 5310 C) DOC should NOT be measured by subtraction (i.e., as total carbon – inorganic carbon) as the error in the measurement is generally too high for natural waters	300 (0.3 mg/L)

Notes: * Glass fibre filters should not be used in filtering or for prefiltering as these have high zinc content which can leach into samples. Filters should be tested for metal contamination before using. † Represents a measurement resolution rather than a detection limit.

Field filtration for metals should be considered when there is a long delay between sampling and analysis (>36 hours). As the acute GVs for zinc are somewhat higher than background concentrations, there is a lower risk of accidentally contaminating samples through poor sample handling. In spite of that lower risk, field staff should be trained in the field filtration methods prior to their use, and field blanks should be tested alongside the samples. Field filtration may be particularly useful where there are high concentrations of particulates in the samples that have potential to either adsorb, or release metals during storage and transport. Measurements of copper and zinc without filtration (i.e., total copper and total zinc) can also be used with these acute GVs, however this would provide a conservative estimate of toxicity.

[190] NEMS, 2019. *Water Quality Part 2 of 4: Sampling, Measuring, Processing and Archiving of Discrete River Water Quality Data*, https://www.nems.org.nz/documents/water-quality-part-2-rivers/.
[191] This method does remove volatile organics such as some light hydrocarbons but these are not relevant to the measurement of DOC for adjustment 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

11 Using acute GVs within NPS-FM context

A potential application of the GVs is to define attributes including potentially national attributes that could be added to the National Policy Statement for Freshwater Management; NPS-FM) or attributes that are adopted by a regional council (RC) or territorial local authority (TLA) as part of its own management of water quality. An attribute has a different management purpose than a GV and it is important to understand the role and requirements of attributes when considering adopting GVs as attributes. The following subsections broadly discuss the purpose and requirements of attributes and the extent to which these can be met for attributes for copper and zinc. This section concludes with some recommended steps when considering whether to adopt GVs (or adapted values thereof) as attributes.

11.1 Purpose and requirements of attributes

The purpose of attributes, as defined by the NPS-FM, is to support and sustain the values of freshwater environments at an acceptable level by robustly and justifiably:

1. defining target states for freshwater and,
2. defining limits and management actions that are needed to achieve those targets (Figure 11.1).

The existing NPS-FM attributes are associated with 'aspects to be managed' that represent nationally important freshwater management issues, including trophic state, toxicity status and human pathogens.

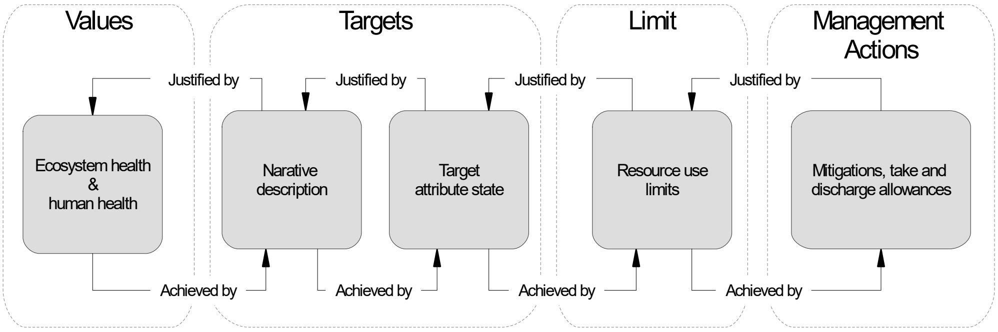

Figure 11.1: Generalised diagram of the links between values, targets, limits and management actions. Adapted from MfE (2018).[192]

To achieve this purpose, MfE indicate that the NPS-FM attributes need to comply with the following five principles or requirements:

1. Link to the value
    - The attribute represents an aspect of the freshwater environments that needs to be managed to support the value.
2. Measurable attribute state
    - There must be protocols that define attribute states including:
        - established analytical methods for analysis of the instream concentrations associated with monitoring observations.

[192] Ministry for the Environment, 2018. *A Guide to Attributes In Appendix 2 of the National Policy Statement for Freshwater Management (as amended 2017)*, Ministry for the Environment (Wellington).

- narrative descriptions and associated numeric thresholds that define a graduated range of levels of support for values that are referred to in the NPSFM as attribute states (i.e., A, B, C and D bands).
- summary statistics of the measured concentrations that are compared to the thresholds to assess the attribute state

3. Relationship to limits and management

- We know where there are likely to be significant issues with achieving the target attribute state
- We know what to do to manage the state of this attribute in freshwater bodies.
- There are quantitative relationships that link the attribute state to resource use limits and/or management interventions.

4. Evaluation of current state of the attribute

- We have existing data of sufficient quality, quantity, and representativeness to adequately assess the current state of the attribute at relevant locations.
- We can assess the location, extent and magnitude of failures to achieve a proposed target attribute state at relevant locations (including on a national scale if the intent is to include the attribute in a national regulation).

5. Implications of including the attribute in the NOF.

- We can assess the socio-economic impacts of implementing the attribute at a national scale.

The above requirements are appropriate considerations if copper and zinc attributes were to be added to the National Policy Statement for Freshwater Management; NPS-FM) or if they were to be implemented by territorial local authority (TLA) as part of its own management of water quality. The following sections consider if these requirements can be met.

11.2 Could copper and zinc attributes meet these requirements?

11.2.1 Link to the value

The NPS identifies four compulsory national values that apply to all freshwater bodies—ecosystem health, human contact, mahinga kai, and threatened species. Toxicity is among the aspects of freshwater environments that need to be managed to support and sustain these compulsory values. The metals copper and zinc are among the most ubiquitous toxicants in the environment and can be present at toxic concentrations in streams and rivers.

Appendix 2 of the Freshwater NPS defines attributes that must be used to set target states. However, Appendix 2 of the NPS only explicitly provides for some of the aspects and attributes that need to be managed to sustain the compulsory values. For example, there are only two attributes that are related to toxicity (nitrate and ammoniacal nitrogen). The NPS recognises that the Appendix 2 attributes will not be sufficient on their own to sustain the compulsory values and that other attributes may be identified and used to set targets and management actions. Copper and zinc are relevant because they are linked to compulsory values and are aspects of freshwater environments that need to be managed to support those values. This means that even if they are not implemented as Appendix 2 attributes, RCs and TLAs should consider setting targets for copper and zinc.

11.2.2 Measurement and band thresholds

Measurement

There are established methods for the sampling and analysis (see section 10.7) of copper and zinc concentrations in streams and rivers. Observations of these metals can be made as part of routine monitoring using prescribed standards for grab sampling.[193] Methods to sample under storm flow conditions are also well-established with best-practice guidance and standards available.[194]

Band thresholds

Previous proposed attribute tables have set out narrative descriptions and thresholds (see Table 11.1) that are broadly analogous to two existing NPS-FM Appendix 2 toxicity attributes (nitrate and ammoniacal nitrogen). In those tables, the narrative descriptions of attribute states (i.e., A, B, C and D bands) are related to the proportion of species for which effects can be anticipated (i.e., the levels of species protection) based on chronic guideline values. Similar narrative descriptions could be used for copper and zinc attributes as the GVs are based on the same SSD modelling approach, which provides different levels of species protection. For the band A/B and B/C thresholds, both median and 95th percentile concentrations are compared to chronic DGVs. Those chronic DGVs are more stringent than the acute GVs (even at 99% species protection), ensuring protection from both chronic and acute effects. Acute GVs are not included in the nitrate and ammonia tables, but could be used as the C/D threshold for copper and zinc to protect values from acute effects.

Table 11.1: Previously suggested attribute bands and narrative descriptions for copper and zinc attributes. Table originally developed for Auckland Council.[195]

		How you meet this, using copper and zinc toxic guideline values	
Attribute band and description	**What would that mean in terms of toxicity?**	**Median**	**95th percentile**
A Pristine, minimal/no significant effect	Low likelihood of toxic effects (either acute or chronic) on even the most sensitive species	<GV99 (chronic)	<GV95 (chronic)
B Associated with good water quality and minor stress	Possible toxic effects (either acute or chronic) on the most sensitive species, but low likelihood of toxic effects on most (~90%) species	<GV95 (chronic)	<GV90 (chronic)
C Moderate likelihood of effects, which could include effects on of the 20% most sensitive species (site-specific)	Possible toxic effects (chronic) on sensitive species (20% most sensitive), but low likelihood of toxic effects (chronic) on most species Possible toxic effects (acute) on the most sensitive of species (5% most sensitive), but low likelihood of toxic effects (acute) on most species	<GV80 (chronic)	<GV95 (acute)
D Poor quality/poor conditions. High likelihood of adverse effects on multiple species (site-specific)	Toxic effects (chronic or acute) are possible on sensitive and insensitive species	>GV80 (chronic)	>GV95 (acute)

* The ambient concentration could be represented by a median of long-term monitoring. The maximum concentration could be represented by a maximum or a 95th percentile where monitoring is at high frequency (i.e., including sub-daily monitoring).

Populating Table 11.1 with the draft chronic DGVs and acute GVs derived in this report indicates some issues with the outlined table (Table 11.2). The tier 1 acute GV at 95% species protection is lower than the draft chronic DGV for 80% species protection. This causes a conflict with the definition of the C band. This may or

[193] NEMS, 2019.
[194] EA Fassman, 2010. *Sampling Requirements and Reporting Statistics for the Proprietary Devices Evaluation Protocol Development. Prepared by UniServices for Auckland Regional Council*, Auckland Regional Council (Auckland, February 2010); J Gadd, A Semadeni-Davies, and J Moores, 2014. *Design of Stormwater Monitoring Programmes*, Environment Southland (February); *Water quality — Sampling — Part 1: Guidance on the design of sampling programmes and sampling techniques*, (Switzerland: ISO, 2023); DT McCarthy and D Harmel, 2014. Quality assurance /quality control in stormwater sampling, in *Quality Assurance & Quality Control Of Environmental Field Sampling*; DT McCarthy et al., 2018. Assessment of sampling strategies for estimation of site mean concentrations of stormwater pollutants. *Water Research* 129: 297-304; *Water quality — Sampling. Part 1: Guidance on the design of sampling programs, sampling techniques and the preservation and handling of samples,* (Homebush, NSW: AS/NZ, 1998).
[195] J Gadd et al., 2019. *Developing Auckland-Specific Ecosystem Health Attributes for Copper and Zinc: Summary of work to date and identification of future tasks*, Auckland Council (Auckland).

may not change when the chronic DGVs are finalised and tier 1 DGVs are provided. For zinc, the tier 1 acute GV is substantially higher than the chronic DGVs, even at 80% species protection. However, there is also potential for this to change as the zinc DGVs are reviewed and finalised through the ANZG process – those values may become higher and closer to the acute GVs.

Furthermore, copper and zinc GVs are bioavailability-based, and therefore differ with the water chemistry of a site or sample. Ideally the bioavailable fraction of the metal is calculated and compared to the thresholds in the table to simplify matters. However, this is not straight-forward as there are different bioavailability models used for chronic and acute GVs. If the attribute tables included a mixture of chronic and acute GVs for the thresholds, two sets of estimated bioavailable concentrations would be required to assess site grades at the C/D band for each metal, one based on the acute model and a second based on the chronic. There is a possibility that this could result in contradictory grades.

Table 11.2: Example of numeric thresholds for copper and zinc attributes following the outline of Table 11.1 and updated to use the acute GVs derived for Aotearoa, as detailed in this report.

	Bioavailable copper		Bioavailable zinc	
Attribute band and description	**Median**	**95th percentile**	**Median**	**95th percentile**
A Pristine, minimal/no significant effect	<0.2	<0.5	<0.4	<1.3
B Associated with good water quality and minor stress	>0.2 and <0.5	>0.5 and <0.7	>0.4 and <1.6	>1.3 and <2.3
C Moderate likelihood of effects, which could include effects on of the 20% most sensitive species (site-specific)	>0.5 and <1.3	>0.7 and <0.9 †	>1.6 and <4.4	>2.3 and <19 ‡
D Poor quality/poor conditions. High likelihood of adverse effects on multiple species (site-specific)	>1.3	>0.9 †	>4.4	>19 ‡

Notes: † This acute GV (tier 1 GV for 95% species protection) is more stringent than the 80% protection chronic DGV. Table would need to be amended. ‡ This acute GV (tier 1 GV for 95% species protection) is less stringent than the 80% protection chronic DGV. Table could be retained as is.

An assessment of state for copper and zinc should be based on both long-term (chronic) and short-term (acute) exposures. But there is not an objectively correct way to define thresholds that combine protection for both chronic and acute effects. This combined protection is arguably most important for urban environments where metal concentrations during storm events may briefly increase to concentrations that have potential to cause acute toxicity . The ideal attribute table would incorporate both acute and chronic effects across each of the attribute states. The rationale for that is as follows: a site should not be graded "A" (pristine / high quality) if toxic contaminants are generally very low, but there are occasional events that result in extremely high concentrations of a contaminant (sufficient to cause acute toxicity). That would be inconsistent with a narrative attribute description of "pristine". However, it is complicated to incorporate both acute and chronic effects, that operate over different time-frames (short-term and long-term), into a single table. While a 95th percentile could be considered representative of short-term, transient exposures, use of only a median for comparing to the chronic DGVs does not provide the level of protection consistent with the narrative description as this DGV can be exceeded for long periods of time.[196] ANZG recommend that chronic DGVs are assessed using 95th percentiles.[197] It may be that a different time-frame is required for assessing protection from chronic versus acute effects. This is an

[196] A table could use chronic DGVs and acute DGVs at each attribute band to assess protection at both time-frames, with the median concentration (ambient conditions) compared to the chronic DGVs and the 95th percentile (transient spikes) compared to the acute GVs. However, if chronic DGVs only need to be met 50% of the time (i.e., when comparing a median concentration to that threshold) for a certain grading, there is potential that concentrations exceed that chronic DGV and reach levels that affect a high percentage of species (though below the acute GV) for 49% of the time. The numeric thresholds would not be consistent with narratives around the species protection for each band.

[197] Note that ANZG (2018) recommends that a 99% level of species protection is used for sites with high ecological value and 95th percentiles of monitoring data are compared against that DGVs. However, ANZG (2018) does allow for different jurisdictions to provide guidance relevant to the assessment purpose.

aspect of the guideline values (both chronic and acute) that could be addressed in the future to increase clarity in implementation of guideline values.[198]

An assessment of attribute states at monitoring sites involves comparing the numeric thresholds to one or more summary statistics calculated from monitoring observations. For most attributes, including the previously drafted tables for copper and zinc, numeric states are defined by median (50^{th} percentile) and 95^{th} percentile values. Calculated percentiles are compared to the thresholds to determine the attribute state, which can be described as a "grade" (i.e., A, B, C or D).

An important issue associated with the assessment of attribute states is whether the threshold should be compared to percentiles of the sample or percentiles of time.[199] We note the NPSFM is inconsistent and ambiguous about this matter. It is our opinion that the thresholds should be compared to percentiles of time primarily because it is the percentile of time that the compulsory values (e.g., a fish in the stream) experience. However, there is a significant complication that arises because the observations are a statistical sample of the population, and the percentiles of the sample are therefore uncertain estimates of the percentile of time. McBride (2016)[199] discusses the implications of two aspects of this uncertainty. First, rigorous determination of the attribute state should be based on a sample size that achieves a minimum acceptable level of misclassification risk (e.g., assigning a C grade based on the sample when in fact the population grade is D). Second, the misclassification error risk determines the degree to which there may be "state switching" (e.g., determining states A-B-A-B-B in five successive years when in fact the waterbody was always in state B).

McBride describes the theoretical basis for estimating confidence in the attribute state assessments. Conceptually, an appropriate number of samples and therefore an appropriate monitoring programme can be determined by deciding on an acceptable level of misclassification error risk. However, more recently, Milne et al. has pointed out that these theoretical methods do not account for all the uncertainty associated with attribute states assessed from monitoring data.[200] This is because the monitoring site sample (i.e., the observations) are a taken from a population that is non-stationary and seasonal, which violates the assumptions of McBride's theoretical methods. In fact, we do not have methods to rigorously evaluate the uncertainty of percentiles calculated from monitoring data as estimates of attribute state. Milne et al. conclude that assessment of the attribute state will need to involve elements of expert judgement. We also emphasize that ensuring protection from acute effects (if acute thresholds are used in an attribute table) requires a monitoring programme that has considerably higher frequency than the monthly sampling programmes that most regional councils currently operate.

In our opinion, the inability to rigorously evaluate the uncertainty of attribute states for copper and zinc means that we cannot currently provide a complete specification of how these attributes should be monitored and assessed (i.e., how sites would be graded). In addition, the very intensive monitoring that would be required to rigorously evaluate the 95^{th} percentile is likely to be onerous in urban streams with highly variable metal concentrations. We therefore consider that there would need to be a level of pragmatism allowed regarding monitoring and assessment of attribute state. For example, in catchments that are judged as having a low risk of transient exposure to acutely toxic concentrations, we suggest that limited numbers of observations are required. But in high-risk environments such as those dominated by high-density urban, including industrial land uses, much more monitoring effort would be needed to establish attribute states with reasonable levels of confidence, particularly with respect to the estimate of the population 95^{th} percentile value.

The risk of exceedance of target attribute states for copper and zinc is most likely in catchments with appreciable areas of urban land.[201] Other situations where exceedance of target attribute state is possible

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[198] The US EPA provide this additional information with their criteria: acute GVs (termed criterion maximum concentration or CMC) are for a "one-hour average not to be exceeded more than once every three years on average", and the chronic GVs (termed criterion chronic concentration or CCC) are for a "four-day average not to be exceeded more than once every three years on average". However, the provenance of the US EPA timeframes is not clear, does not appear to be evidence-based, and may not be relevant for metals.
[199] G McBride, 2016. *National Objectives Framework: Statistical considerations for design and assessment*, Ministry for the Environment (Wellington, NZ).
[200] J Milne et al., 2023. *Attribute states and uncertainty Preliminary expert commentary on implementation of clause 3.10(4) of the NPS-FM 2020*, National Institute Water and Atmospheric Research (Wellington).
[201] Gadd et al., 2024.

include catchments with mining operations and potentially in rural settings if copper and zinc are included in fungal or herbicide treatments. We suggest that the simple catchment models that predict copper and zinc concentrations as a function of land use composition (see following section) could be used as screening tools to help make decisions about the appropriate level of monitoring effort at individual sites.

11.2.3 Relationship to limits and management

Urban discharges of copper and zinc to freshwater can be managed in multiple ways. Diffuse sources in catchments can be reduced by removing sources, or covering surfaces that include these metals (often referred to as source control). Industrial activities that generate and discharge these metals can be managed differently to reduce the amount of these contaminants from the site. Stormwater can be treated, either near the source (such as with road-side swales instead of kerbs to reduce road runoff) or closer to the bottom of the stormwater catchment, using detention basins and wetlands to reduce copper and zinc before discharge to freshwater.[202]

The concentration of copper and zinc, and therefore the attribute state, must be able to be linked to catchment sources of copper and zinc and management methods to identify and justify limits and actions (Figure 11.1) that may be required to achieve the target state. The specification of target attribute states (TASs) for copper and zinc is consistent with the objectives and limits-based approach prescribed by the NPS-FM but creates a need to explicitly link the concentrations of copper and zinc (i.e., attribute states) to the management of these metals in the upstream catchment (Figure 11.2).

The schematic diagram shown in Figure 11.2 represents what Larned and Snelder refer to as a land-water system model.[203] When viewed from left to right, the model represents a causal chain linking catchment land use to copper and zinc loads and concentrations in receiving water bodies. When viewed from right to left, the model represents the analytical steps that are required to assess how target states for copper and zinc can be achieved and to justify the management actions.

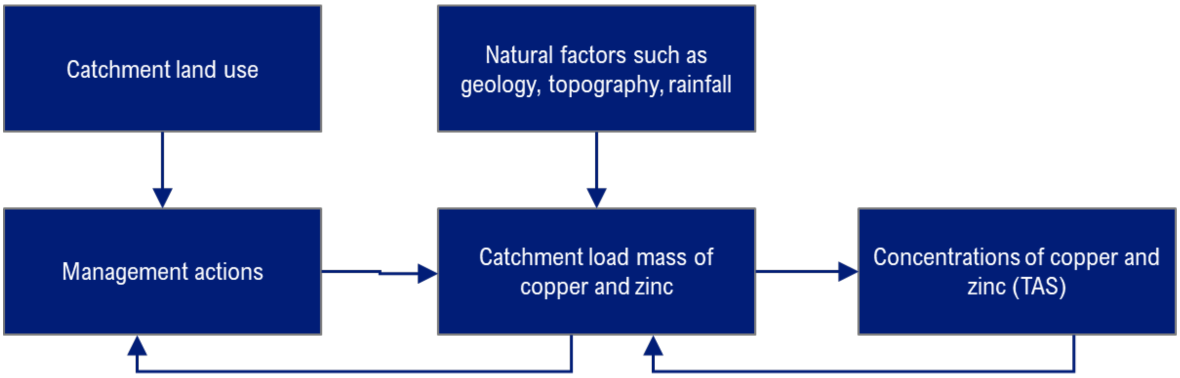

Figure 11.2: Schematic diagram of a land-water system model for **copper** and **zinc**.

The solid arrows represent causal processes that link catchment sources of copper and zinc to instream concentrations (and target attribute states). The dotted arrows represent analytical steps that show how attribute states can be achieved and justify management actions.

Ideally, the land-water system model can be represented by integrating existing appropriate models. The integrated model of the land water system then provides an objective basis for decision makers to select among alternative targets and management actions to achieve these.[204] The process of testing among alternative options is referred to as scenario analysis and is common to the general approach that needs to be taken for the implementation of all NPS-FM attributes.

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[202] See A Cunningham et al., 2017. *Stormwater Management Devices in the Auckland Region*, Auckland Council (Auckland, December 2017).
[203] ST Larned and TH Snelder, 2024. Meeting the growing need for land-water system modelling to assess land management actions. *Environmental Management* 73, 1: 1-18.
[204] Larned and Snelder, 2024.

There are multiple examples of land-water system models that exist for copper and zinc, from simple relationships between loads from land delivered to water, to complex process-based models of contaminant build-up and wash-off integrated with flow models. Examples of these are described further below.

The Metals in Urban Stream Tool (MUST) is an example of a simple integrated land water system model for copper and zinc.[205]. MUST estimates the catchment mean annual loads of copper and zinc based on the composition of land use in the catchment, based on the Contaminant Load Model (CLM) previously developed by Auckland Council.[206] This component of MUST also enables users to select management actions to reduce loads from the catchment such as using source control or installing stormwater treatment devices. MUST estimates in-stream concentrations of copper and zinc (as median and 95th percentile) from the estimated loads. The concentrations are estimated based on empirically derived models of the relationships between loads (expressed as yields [load/catchment area]) and observed median and 95th percentile concentrations. The model is designed to estimate concentrations of copper and zinc in locations with no monitoring data.

More complicated models such as US EPA's Storm Water Management Model (SWMM) and Auckland Council's FWMT[207] similarly include information on the land use in the catchment (and in some cases soils and slope information) and allow users to select different management actions to reduce metals. These models provide a time-series of metal concentrations (e.g., daily or sub-daily). However, such models require a greater level of information, including flow data and metal monitoring data, for model calibration and validation. Further, the resources required to set-up and run such models mean they are not applicable to a national-scale modelling exercise which may be useful for evaluating copper and zinc as attributes.

11.2.4 Evaluation of current state of the attribute

Concentrations of copper and zinc are measured regularly at 159 and 173 sites distributed throughout Aotearoa but focused on catchments with a high proportion of urban land use.[208] As of June 2022, only 100 of these sites had monthly observations over a 5 year period which has been a rule of thumb for assessing the "current state" of the existing Appendix 2 attributes.[209] Gadd et al. evaluated current state for copper and zinc by summarising the distribution of observations at each site by the median and 95th percentiles. "Sufficient data" was defined by five years of monthly monitoring with observations for at least 80% of the years (four out of five years) and at least 80% of the months. If monitoring has continued, it will be now possible to evaluate current state at significantly more than 100 sites. We note that although this rule of thumb for sufficient samples has been used in numerous studies and is consistent with the prescribed monitoring for some Appendix 2 attributes, it is not clear that this achieves an acceptable misclassification error rate and, in our view, is insufficient to robustly assess the population 95th percentile value, or to ensure protection from acute effects.

Gadd et al. show that the likelihood of exceeding any proposed target attribute state thresholds for copper and zinc concentrations rise with increasing proportion of urban land in catchments.[208] Coupling this information with spatial data describing all catchments in New Zealand could provide a basis for estimating where any proposed target attribute state is being exceeded. In addition, the MUST and/or CLM models, or the relationships underlying these models would be sufficient to estimate load reductions that would be necessary to achieve compliance. In our opinion, such analysis is likely to be as robust as that of Snelder et al.[210] and would provide a reasonable assessment of the location, extent and magnitude of failures to achieve proposed target attribute states at relevant locations nationwide. Note that current

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[205] https://shinylabs.niwa.co.nz/wq-must/
[206] Auckland Regional Council, 2010. *Contaminant Load Model User's Manual*, Auckland Regional Council (Auckland).
[207] https://www.epa.gov/water-research/storm-water-management-model-swmm; Auckland Council, 2021. *Freshwater Management Tool: Baseline configuration and performance*, Auckland Council Healthy Waters Department, Paradigm Environmental and Morphum Environmental Ltd (Auckland: Auckland Council).
[208] Gadd et al., 2024.
[209] A Whitehead et al., 2022. *Water quality state and trends in New Zealand rivers: analyses of national data ending in 2020*, Ministry for the Environment (February 2022).
[210] T Snelder et al., 2023. *Nitrogen, phosphorus, sediment and Escherichia coli in New Zealand's aquatic receiving environments: Comparison of current state to national bottom lines*, LWP Ltd (Christchurch, October 2022).

assessments based either existing data or on models would be most relevant to an attribute table based largely on chronic DGVs.

11.2.5 Implications of including the attribute in the NOF

There would be significant implications including economic costs associated with meeting target attribute states for copper and zinc in catchments that were currently non-compliant. The implications and costs associated with implementing any proposed copper and zinc thresholds could be evaluated. This could start with the assessment of the location, extent and magnitude of failures to achieve proposed target attribute states at relevant locations as described above. Once the location, extent and magnitude of failures has been determined, scenario modelling could be used to examine how catchments could be managed to achieve compliance with the target attribute states. Management could comprise a mixture of the methods for managing the discharge of copper and zinc to freshwater that are described above. As well as examining a range of physical measures, it would be important to evaluate the costs so that the most efficient options can be identified.

The costs of stormwater management, including source control methods and installation of devices have been recently assessed for Auckland, and those costs are likely to be applicable in other parts of Aotearoa.[211] In our opinion, evaluation of the implications and costs of adopting target attribute states for metals can be achieved using the available tools and would not be dissimilar to studies of this type that have been undertaken for other contaminants.[212]

11.3 Recommended steps for considering whether to adopt GVs (or adapted values thereof) as attributes

We recommend that any attribute table is protective of both chronic and acute effects. However, we emphasise that there are judgments involved defining that attribute state thresholds particularly because these need to combine protection for both chronic and acute effects and that there is not an objectively correct way to do this. The previously drafted attribute tables, updated with acute GVs for Aotearoa (Table 11.2) can be regarded as an example. However, as mentioned, there are issues with that format, particularly for copper. We recommend that further thought is given to this table particularly with respect to how to combine the consideration of short-term and long-term exposures into a single table, and how these are best represented by summary statistics. While previously drafted tables for copper and zinc are based on other Appendix 2 toxicant attribute tables using both a median and a 95th percentile, there may be better alternatives that we have not considered.

The development of proposed attribute tables for copper and zinc should use existing monitoring data to assess potential issues with the table. For example, data analysis should assess the possibility of contradictory results when using different bioavailability models for acute and chronic GVs.

Alternatively, attribute tables could be developed that are based only on chronic DGVs and used for grading under the NPS-FM. While this would not assess or protect from acute toxicity, this may still be useful for freshwater management. Where there are concerns about acute toxicity, for example, due to intermittent discharges, or transient high concentrations associated with storm events, then those risks could be assessed, though this may not be defined in numeric terms in the attribute table.

We recommend that the thresholds in any attribute table for copper and zinc should, in principle, be compared to percentiles of time. However, if adopted as attributes, we also recommend that there be a high level of discretion around how copper and zinc attribute states are assessed from monitoring data. If an attribute table based on both chronic and acute DGVs is to be used with SOE (monthly grab sampling) data, we suggest that the grading is considered interim in most (but not all) cases. For example, where

[211] S Ira, P Walsh, and C Batstone, 2021. *Freshwater Management Tool: report 9. A total economic valuation approach to understanding costs and benefits of intervention scenarios – Part 1 Urban Devices.* , Prepared by Koru Environmental, Manaaki Whenua Landcare Research and Batstone Associates for Auckland Council (Auckland: Auckland Council); S Ira, 2021. *Freshwater Management Tool: report 10. A total economic valuation approach to understanding costs and benefits of intervention scenarios – Part 2 Urban source control costs.* , Prepared by Koru Environmental for Auckland Council (Auckland: Auckland Council).
[212] T Denne, 2020. *Essential Freshwater Package: Costs Analysis. Report prepared for Ministry for the Environment* (April 2020).

monthly monitoring data indicates that all concentrations (of bioavailable copper) are below the A band thresholds, the grading could be an interim A. The grading is interim because the possibility exists that additional sampling during storms would result in a value (or values) that exceed the maximum threshold. Additional confidence in the interim grade would be obtained through additional monitoring. However, as discussed in section 11.2.2 and by Milne et al., there is not a statistically robust procedure to quantify the confidence in the attribute state estimated from infrequent monitoring data, or to quantify the additional confidence that would be provided with more sampling. A situation where an evaluated grade would not be considered interim is where monthly monitoring data provide a grading of D. In this case, there can be higher confidence that this grade is correctly classified.

12 Summary

Copper and zinc acute GVs are expected to have several uses for water management in Aotearoa and fill a current gap in assessing the potential for toxicity in urban waterways.

The key types of bioavailability models that can be used for deriving metal GVs are linear regression models (including multiple linear regression, MLR) and the BLM. Four different model options were assessed for each of copper and zinc. These were the hardness regression; a pooled fish/invertebrate MLR model; a suite of MLR models, specific to each trophic level (fish, invertebrate, plant/algae); and a BLM. The model evaluation included assessing suitability for species other than those used in model development, suitability for native species, the range in water chemistry that would be covered by the model and the taxonomic coverage of the model. The pooled fish/invertebrate MLR models performed at least as well as the BLM models for both copper and zinc and are easier to use. These models were used to adjust acute toxicity data for copper and zinc to a standard water chemistry, for deriving acute GVs.

Although EC10 values are the preferred statistic to derive protective GVs, few acute studies report these statistics. EC50 values were therefore used and converted to EC10 values after normalisation for water chemistry. That conversion was based on different conversion factors for fish, invertebrates and plants/algae and for each metal. The converted EC10s were summarised to single species values, resulting in 90 species for copper and 69 species for zinc. Those values were used in SSDs with multiple distribution models fitted to the data. A model averaging method was used to calculate acute GVs at various levels of protection. The acute GVs differ depending on the pH, hardness and DOC of the waters. For both copper and zinc, GVs are higher at higher concentrations of DOC and hardness. For copper, the GVs are higher at higher pH. By contrast, for zinc the GVs are lower at higher pH, though the difference is relatively minor compared to the effect of hardness, and to a lesser extent, DOC.

The acute GVs are considered to be robust, based on the large dataset, covering a wide number of species and taxonomic groups. One important limitation relates to the protection of plant and algal species, as there were few acute toxicity data available for those taxonomic groups.

A tiered approach to implementation is recommended, whereby dissolved metal concentrations are first compared to tier 1 acute GVs (screening), which represent conditions of high bioavailability. If concentrations exceed those GVs, then TMFs can be used to adjust the GVs for a tier 2 assessment. When TMF data are not available, the tier 1 screening level will provide a conservative assessment of risk. The highest confidence in the assessment would be obtained where TMFs are measured in the samples being assessed. When TMF data are estimated from other samples, there is less certainty in the assessment.

Interim tier 1 acute GVs are provided, calculated for low percentile estimates of water chemistry in Aotearoa. Tier 1 chronic DGVs are currently being developed in a project for the Australian and New Zealand guidelines. When those tier 1 chronic DGVs are finalised, the interim tier 1 acute GVs could be updated based on that same methodology and replace those provided in Table 12.1.

Table 12.1: Interim Tier 1 acute GVs for **copper** and **zinc** (µg/L). Copper GVs at pH 7.0, hardness 17 mg $CaCO_3$/L and DOC 0.7 mg/L; zinc GVs at pH 8.2, hardness 17 mg $CaCO_3$/L and DOC 0.7 mg/L. The pH values are different because of the different effect of pH on copper toxicity and zinc toxicity.

	Level of protection			
	99%	**95%**	**90%**	**80%**
Copper interim tier 1 acute GV	0.7	1.3	1.7	2.9
Zinc interim tier 1 acute GV	11	24	36	59

Although copper and zinc attributes generally meet the requirements for NPS-FM attributes there are difficulties in developing attribute tables with band thresholds that protect from both acute (short-term) and chronic (long-term) exposures. Further work is required to develop that table and assess its practicality.

13 Glossary, Acronyms and Abbreviations

Word/acronym/ abbreviation	Description
acute toxicity	A lethal or sublethal adverse effect that occurs after exposure to a chemical for a short period of time e.g., hours to days. Termed acute GV in this document.
Adverse effect	A harmful result of some activity. In the RMA, adverse effects may include temporary or permanent effects and cumulative effects that arise over time or in combination with other effects
ACR	Acute-to-chronic-ratio. Acute EC50 value divided by the chronic EC10/NOEC value. A ratio used to convert acute toxicity values to chronic "no effect" toxicity values.
AF	Adjustment factor (or assessment factor). Arbitrary factor used by US EPA and in EU to convert an acute criteria value to a "no effect" guideline value.
ANZG	Australia and New Zealand Governments, publishers of water quality guidelines for fresh and marine waters used in New Zealand
Attribute	Terminology from NPS-FM; something we can measure and monitor that tells us about the state of a river or lake
bioavailable metals	The metal that can be taken up (absorbed) by an organism
BLM	Biotic ligand model, a model or set of models for metal toxicity in aquatic organisms, that account for differing bioavailability of individual metals in waters with differing chemistry (particularly DOC, pH, calcium and magnesium)
bottom line	a term used in the NPS-FM to indicate a level at which sites would be considered degraded, and above which target attribute states must be set
Calculated GV	Acute GVs adjusted to a different set of water chemistry, using the provided equations or tables
CCC	criterion continuous concentration. Term used by US EPA for chronic water quality criteria.
CCME	Canadian Council of Ministers for the Environment, publishers of water quality guidelines for fresh and marine waters used across Canada
CF	Conversion Factor. Ratio of acute EC50 to EC10 values calibrated from a suite of tests from different species and taxa. Used to convert reported EC50 data to "predicted" EC10 values.
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. Long-term, e.g., several days to weeks or months. In addition, chronic toxicity includes adverse effects on a sensitive early life stage – these may occur after exposure for a short-time, hours to days
Concentration units	µg/L = micrograms per litre, parts per billion; mg/L = milligrams per litre, parts per million
Cu	copper
default guideline value (DGV)	A chronic guideline value recommended for generic application in the absence of a more specific guideline value (e.g., site-specific) in the Australian and New Zealand Guidelines for Fresh and Marine Water Quality. Formerly known as 'trigger values'
dissolved metal concentration	Operationally defined as the concentration remaining after filtration through a 0.45 µm pore filter
DOC	Dissolved organic carbon–a measurement of organic matter in solution, based on the carbon content (using a carbon analyser), after passing through a 0.45 µm filter
DOM	Dissolved organic matter
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, 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

Word/acronym/ abbreviation	Description
endemic	Species native to a particular area; originating where it occurs
endpoint	The specific response of an organism that is measured in a toxicity test (e.g., mortality, growth, reproduction, a particular biomarker)
EU	European Union
guideline value (GV)	The concentration of an indicator for a specific community value (such as aquatic ecosystem health) below which there is considered to be a low risk of unacceptable effects. The ANZG framework recommends that GVs for more than one indicator should be used simultaneously in a multiple lines of evidence approach. (Also refer to default guideline value and site-specific guideline value.)
hardness	The sum of the measured concentrations of dissolved calcium and magnesium
HC5	5% hazardous concentration, equivalent to the 95% level of protection used in ANZG
index condition	suite of toxicity modifying factors (TMFs) used to normalise toxicity data and for GV calculation. The index condition parameters for copper and zinc are pH 7.5, hardness 30 mg/L and DOC 0.5 mg/L. The index condition does not relate to the application of the GVs
Interim tier 1 GVs	Provisional guideline values to use in Tier 1, based on high bioavailability waters. These are intended for use only until Tier 1 GVs can be developed using a more robust process. Interim GVs may not be protective in all environments, especially pristine waters, but are designed to be protective in the waters where these acute GVs are most likely to be applied (e.g., lowland streams).
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
Mahinga kai	In the NPS-FM this refers to freshwater species, traditionally used as food, tools or other resources; and to provide this value, kai must be safe to harvest and eat
MfE	Ministry for the Environment, New Zealand
MLR	Multiple linear regression – a type of statistical model increasingly used to assess metal bioavailability
NOF	National Objectives Framework
NPS-FM	National Policy Statement for Freshwater Management. New Zealand legislation which requires regional councils to establish objectives and set limits in their regional plans to manage fresh water
NZ	New Zealand
pH	The intensity of the acidic or basic character of a solution, defined as the negative logarithm of the hydrogen ion concentration of a solution
site-adapted guideline value	A DGV that has been adapted, based on existing knowledge, to make it more relevant to a site of interest (modified from van Dam et al. 2019)
site-specific guideline value	A GV that has been specifically developed to account for relevant chemical, physical and/or ecological conditions that occur at a site of interest (modified from van Dam et al. 2019)
SOE	State of Environment monitoring – regular monitoring undertaken by local authorities to enable them to assess and inform policies
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
Speciation (chemical)	The specific chemical forms of a metal (or other elements) found in water, which includes their redox state
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

Word/acronym/ abbreviation	Description
taxon (taxa)	Any group of organisms considered sufficiently distinct from other such groups to be treated as a separate unit (for example species, genera, families – algae, plants, invertebrates, fish)
Tier 1 GV	Guideline values that represent conditions of high bioavailability and can be used for screening in a tiered assessment. Interim tier 1 acute GVs for copper and zinc are provided in this report
toxicity	The inherent potential or capacity of a material to cause adverse effects in a living organism
TMFs, Toxicity modifying factor(s)	The aspects of water chemistry that influence bioavailability. In this guidance use of the term TMF generally refers only to pH, hardness and DOC, though there are other variables that may influence bioavailability such as water temperature and alkalinity
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
US EPA	United States Environmental Protection Agency
Zn	Zinc

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