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

Prepared for MBIE Envirolink and Horizons Regional Council

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Disclaimer

This document presents and addresses implementation of default guideline values for copper and zinc. These default guideline values currently exist in draft form as they have not yet completed the publication approval process. While the values are potentially subject to change, it is the expert opinion of the authors that these revised guideline values represent the best available for assessing copper and zinc toxicity in New Zealand waters. These draft guideline values therefore should be used as a replacement for values in ANZECC & ARMCANZ (2000) and reproduced at ANZG (2018). Any changes in the values are expected to be only minor.

This guidance reflects our current best available knowledge and experience in the use of water quality guidelines for toxicants. Guidance may always be improved as new knowledge and experience is gained and we expect to update this document once the default guideline values are finalised and published.

Abbreviations and terms

Word/acronym/ abbreviation/	Description
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. Calculated using the EC50 (or LC50) / Chronic NOEC (or EC10/20) values. Note that the ACR differs between jurisdictions
acute toxicity	A lethal or adverse sub-lethal effect that occurs as the result of a short exposure period to a chemical relative to the organism's life span
ANZECC	Australian and New Zealand Environment and Conservation Council. Water quality guidelines derived using the Australian and New Zealand Environment and Conservation Council risk-based methodology. The last revision of the guidelines was in 2000 but updates (including copper and zinc for freshwaters) are presently being undertaken
ANZG	Australia and New Zealand Governments, publishers of water quality guidelines for fresh and marine waters used in New Zealand
ARMCANZ	Agricultural and Resource Management Council of Australia and New Zealand
average	Arithmetic mean value calculated for a measured (or modelled) variable or parameter
bioavailable Cu or bioavailable Zn	The measured concentration of copper (Cu) or zinc (Zn) adjusted based on the appropriate TMF concentrations and response slopes. The bioavailable Cu or Zn concentration is compared directly with the copper and zinc tier 1 DGV
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
catchment	The land area providing surface water hydraulic inputs to streams and rivers
CCC	Criterion Continuous Concentration. Term used by the US EPA for acute guideline values
CCME	Canadian Council of Ministers for the Environment, publishers of water quality guidelines for fresh and marine waters used across Canada
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
CMC	Criterion Maximum Concentration. Term used by the US EPA for acute guideline values
criteria	Term used by the US EPA for their guideline derivations
CSIRO	Commonwealth Scientific and Industrial Research Organisation of Australia
Cu	Copper
CUSUM chart	Chart of the cumulative sum of deviations. A statistical method of monitoring change over time, by plotting over time the deviation from a target value
default guideline value (DGV)	A 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
DGT	Diffusive Gradient in Thin-Film – devices that absorb selected analytes (e.g., metals) from sediment, soil or water, which can then be measured in the laboratory
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 – a generic term for all forms of organic material in a filtered water sample
DTA	Direct toxicity assessment
EC	Electrical Conductivity (units µS/cm or mS/m)
ECx	The concentration of a substance in water or sediment that is estimated to produce an x% change in the response being measured or a certain effect in x% of the test organisms, under specified conditions
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
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)
EPT	Macroinvertebrate species in the orders Ephemeroptera (mayflies), Plecoptera (stoneflies) and Trichoptera (caddisflies)
fDOM	Fluorescence measurement of DOC
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
humic	Humic acids are natural organic material which result in brown colouration and reduced pH in natural waters. They derive from leaf-litter breakdown and leaching from soils
index condition	A suite of toxicity modifying factors (TMFs) used to normalise toxicity data and for DGV calculation. The index condition parameters differ depending on the metal: Copper – DOC 0.5 mg/L; Zinc pH 7.5, hardness 30 mg/L and DOC 0.5 mg/L
ICx	The concentration of a substance in water or sediment that is estimated to produce an x% inhibition of the response being measured in test organisms relative to the control response, under specified conditions
LCx	The concentration of a substance in water or sediment that is estimated to be lethal to x% of a group of test organisms under specified conditions
LC50 (median lethal concentration)	The concentration of a substance in water or sediment that is estimated to be lethal to 50% of a group of test organisms, relative to the control response, under specified conditions
Levels A to D	Levels A to D are recommended approaches to implementation of these bioavailability-adjusted DGVs. Level A uses site- & sample-specific information and will provide the most accurate indication of potential toxicity. Level D uses generic information and provides a conservative indication of potential toxicity.
lowest observed effect concentration (LOEC)	The lowest concentration of a material used in a toxicity test that has a statistically significant adverse effect on the exposed population of test organisms as compared with the controls
MfE	Ministry for the Environment, New Zealand
MLR	Multiple linear regression – a type of model increasingly used to assess metal bioavailability
NEMS	National Environmental Monitoring Standards (https://www.nems.org.nz/)
Ni	Nickel
no observed effect concentration (NOEC)	The highest concentration of a material used in a toxicity test that has no statistically significant adverse effect on the exposed population of test organisms as compared with the controls
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
ppt	Parts per thousand (i.e., g/L). Measure of concentration used for salinity

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
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
standard	A water quality guideline which has a statutory promulgation (e.g., NPS-FM compliance conditions, regional plans)
TAC	Time-averaged concentration. Usually calculated as an arithmetic mean over the time period of interest
Tier 1 DGV	The tier 1 DGVs are DGVs under conditions of high bioavailability. They can be used for screening in a tiered assessment. The tier 1 DGV for copper is equal to the index condition, however the tier 1 DGV for zinc has not yet been established.
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
type I error	Probability of rejecting a null hypothesis that is actually true (false positive). In water quality management, the probability of concluding a guideline value has been exceeded when in fact it has not
type II error	Probability of accepted a null hypothesis that is not true (false negative). In water quality management, the probability of incorrectly concluding a guideline value has NOT been exceeded, when in fact it has
US EPA	United States Environmental Protection Agency
UV	Ultraviolet light
Zn	Zinc

An important note on terminology

The ANZECC & ARMCANZ (2000)[1] Australian and New Zealand guidelines for fresh and marine water quality were replaced in 2018 (ANZG 2018)[2]. The new guidelines can be referred to as the ANZG guidelines, while the website is referred to as ANZG (2018). ANZG an abbreviation for Australian and New Zealand Governments and Australian state and territory governments.

While ANZECC & ARMCANZ (2000) referred to “trigger values” which would “trigger” some action if exceeded, the ANZG guidelines now refer to “guideline values” or **GVs**. This is more consistent with international terminology. There are two types of GVs: site-specific GVs and default GVs (DGVs). Site-specific GVs are relevant to local conditions or situations and may have been developed by local authorities. These are not provided on the ANZG (2018) website.

DGVs, where they have been developed, **are** provided on the ANZG (2018) website. They are recommended for generic application in the absence of site-specific GVs. In some cases, DGVs are developed to be more relevant to local conditions (such as the DGVs for physico-chemical stressors which are specific to River Environment Classification (REC) classes), or can be subsequently tailored to local conditions (e.g., by adjusting for local water chemistry). Many DGVs have been carried across from ANZECC & ARMCANZ (2000) into the new ANZG (2018) website with no updates, such as DGVs for cadmium and lead. These should also be referred to as DGVs (rather than trigger values), but, to reflect their origins, are referenced as ANZECC & ARMCANZ (2000).

This guidance covers the use of the draft updates for copper and zinc **DGVs** for fresh waters (and to a minor extent marine waters). Except for the zinc marine DGVs, these DGVs can be tailored to specific local water quality conditions. These are referred to as DGVs throughout this document. As these DGVs have not yet been published by the Australian and New Zealand governments as finalised DGVs, they are referred to as **draft DGVs**. When guideline values from other countries, developed using different methods (e.g., for short-term exposures), or site-specific guideline values are discussed in this document, these are referred to as **GVs**.

[1] ANZECC/ARMCANZ (2000). Australian and New Zealand guidelines for fresh and marine water quality. Canberra, Australia, National Water Quality Management Strategy Paper No. 4, Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand.

[2] ANZG (2018). Australian and New Zealand guidelines for fresh and marine water quality. Australian and New Zealand Governments.

About the guidance

What are bioavailability-based guideline values?

Water quality guideline values for metals are widely used in Aotearoa New Zealand (NZ) to support management of fresh and marine waters. Since the introduction of the risk-based trigger values in ANZECC & ARMCANZ (2000), copper and zinc toxicity guideline values have been widely used, particularly within the context of monitoring and managing urban waterbodies and stormwater quality.

The existing DGVs for copper and zinc toxicity in fresh waters, published under the ANZG (2018) Guidelines for fresh and marine water quality were reproduced from the ANZECC & ARMCANZ (2000) guidelines. New DGVs are currently being finalised to replace these trigger values that reflect our improved understanding of the influence of water chemistry on the speciation and bioavailability of copper and zinc[3]. Bioavailability (in this context) refers to the availability and uptake of metals into biological organisms, whereby the metals may cause toxic effects. Bioavailability is an important consideration in deriving and applying metal guideline values. Use of a single guideline value in locations where bioavailability is low may indicate a need for changes in water management (including costly restrictions), even in the absence of adverse effects. Conversely, in locations of high bioavailability, ecosystems may degrade if guideline values that are not sufficiently protective are used. The new bioavailability-based DGVs allow for the guideline values to be adjusted for the water chemistry of the location at which they are applied. This is important because water chemistry varies widely between different locations.

The draft copper DGVs include dissolved organic carbon (DOC) concentration in the water column as the only factor that affects bioavailability (i.e., a toxicity modifying factor). The draft zinc DGVs are more complex and are adjusted for three factors: water hardness, DOC and pH. These both differ from the ANZECC & ARMCANZ (2000) trigger values that included water hardness as the sole toxicity modifying factor.

Why is this implementation guidance important?

The draft copper and zinc DGVs will replace the existing ANZECC & ARMCANZ (2000) DGVs once they have been approved for publication in (likely) early to mid 2024. While the ANZG (2018) website[4] provides extensive information on the use of DGVs, including those for the toxicants copper and zinc, there is minimal information on how to adjust them to take bioavailability into account.

This guidance provides information to support the implementation of the new (but currently still draft) copper and zinc DGVs in NZ, particularly around how to adjust the DGVs for bioavailability. This guidance aims to minimise inconsistencies in their application throughout NZ.

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[3] The copper and zinc toxicity trigger values published by ANZECC & ARMCANZ used an adjustment based on water hardness. When the copper DGVs were republished on the ANZG (2018) website, the recommendation to adjust for hardness was removed. 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. August 2015 - updated October 2018. Canberra.

[4] https://www.waterquality.gov.au/anz-guidelines

Copper and zinc have also been considered as potential attributes within the National Objective Framework (NOF) under the [National Policy Statement for Freshwater Management 2020 (NPS-FM)][5]. While these attributes have not progressed at a national level, some regions have identified copper and/or zinc as additional attributes relevant to managing the mandatory national freshwater value of ecosystem health. Inclusion of copper and zinc as attributes for freshwater management is complicated by the need to consider bioavailability in developing numeric attribute states. While each region can choose to develop attribute state tables as they wish, this document provides guidance to support the use of the draft copper and zinc DGVs as regional attributes, considering the complexity involved with accounting for bioavailability.

Because the copper and zinc DGVs have not yet been approved, and there is ongoing work in NZ and Australia regarding their implementation, this document represents *interim guidance* to assist those users that need information right away. This guidance is intended to be a “living” document and is expected to be updated once the DGVs have been published.

Scope

This guidance focuses on the implementation of the draft copper and zinc DGVs within river and stream environments, addressing the need for more guidance in these dynamic environments. However, much of the information is also relevant to lakes and ponds and, in some cases, estuarine and coastal waters. In addition, parts of the guidance may be relevant to other metals with bioavailability-based DGVs, such as nickel. However, expert guidance should be sought before applying the recommendations to other metals.

Who should use this guidance?

We expect this guidance to be useful for:

- regional and unitary council staff processing resource consent applications, or monitoring compliance with consents, for stormwater or other contaminant discharges to water,
- environmental consultants and resource consent holders using water quality guidelines to assess the environmental effects of contaminant discharges to water,
- council science staff designing, managing and reporting on water quality monitoring programmes, and
- council staff involved in managing waterbodies under the framework of the NPS-FM.

[5] New Zealand Government (2023). National Policy Statement for Freshwater Management 2020. February 2023. Minister for the Environment, Wellington, New Zealand. https://environment.govt.nz/publications/national-policy-statement-for-freshwater-management-2020-amended-february-2023/

How to use this guidance

This guidance should be used together with the information provided by ANZG (2018) and in the individual toxicant DGV derivation technical documents for copper and zinc in fresh water (and in marine waters where relevant). It is assumed that the reader of this document has some experience in the use of the ANZG guidelines.

The guidance is set out in three sections:

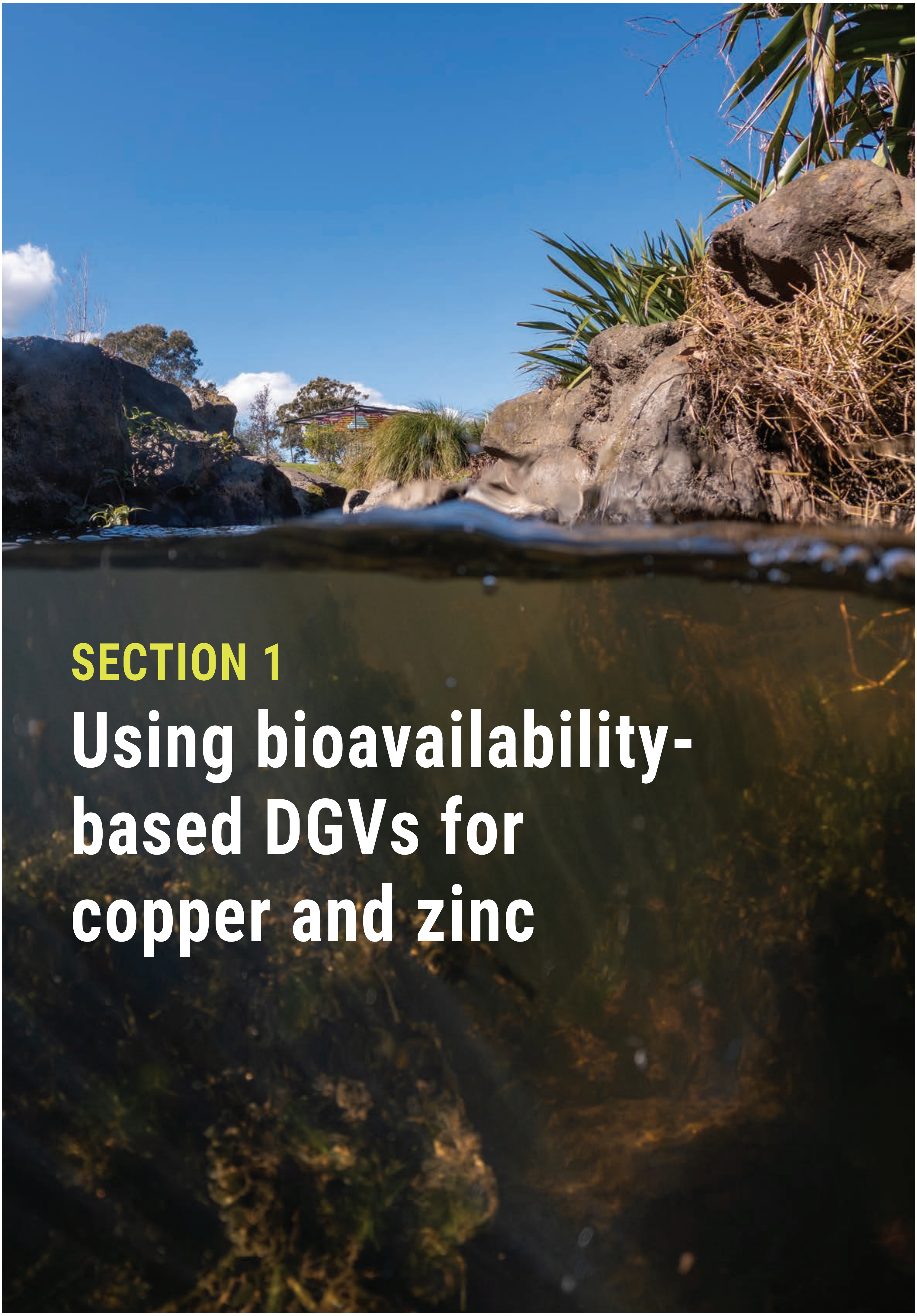
- "Section 1: Using bioavailability-based DGVs for copper and zinc" – outlines how to adjust the DGVs for different water chemistry and recommends a best-practise approach for that adjustment.
- "Section 2: Applying ANZG toxicant DGVs" – sets the context for using the draft DGVs for copper and zinc toxicity, including where and when they can be used to assess environmental data, and what to do to assess acute toxicity risks.
- "Section 3: Copper and zinc attributes under the NPS-FM 2020" – provides recommended attribute tables for copper and zinc as toxicants, data requirements for assessing attribute state (e.g., number of samples and timeframe for sampling) and a discussion of the available evidence to support these attributes.

Within each of these three sections, we provide:

- an overview of the issues related to implementation of the copper and zinc DGVs.
- answers to specific questions related to DGV use (as supplied by council staff), and,
- case studies to demonstrate different approaches to adjusting DGVs for bioavailability and comparing monitoring data with these DGVs.

The guidance includes many footnotes with links to additional information, and these are collated in a bibliography at the end of the document.

A detailed list of abbreviations and terms is included at the front of this document.



SECTION 1
Using bioavailability-based DGVs for copper and zinc

Section 1: Using bioavailability-based DGVs for copper and zinc

1.1 The draft copper and zinc freshwater DGVs – a primer

KEY POINTS:

- **UPDATED DGVS FOR DISSOLVED COPPER AND ZINC TOXICITY ARE CURRENTLY AVAILABLE AS DRAFTS AND WHEN APPROVED WILL BE PUBLISHED ON THE ANZG WEBSITE (LIKELY IN 2024)**
- **THE DRAFT DGVS AT THE INDEX CONDITION[6] ARE LOWER (I.E. MORE CONSERVATIVE) THAN THE CURRENT DGVS DERIVED UNDER ANZECC & ARMCANZ (2000) – ADJUSTMENT FOR LOCAL WATER CHEMISTRY IS HIGHLY RECOMMENDED**
- **THE DRAFT DGVS ARE BIOAVAILABILITY-BASED; THEY ARE ADJUSTED DEPENDING ON THE WATER'S DOC CONCENTRATION (COPPER) OR DOC, HARDNESS AND PH (ZINC), REFLECTING IMPROVED UNDERSTANDING OF THE FACTORS THAT AFFECT COPPER AND ZINC TOXICITY**
- **EQUATIONS, LOOK-UP TABLES, R CODE AND R SHINY APPS CAN BE USED TO ADJUST THE DGVS AND/OR CALCULATE BIOAVAILABLE COPPER AND ZINC CONCENTRATIONS**

All ANZG toxicant default guideline values (DGVs) are risk-based GVs derived from laboratory-based toxicity test data. DGVs are provided for different levels of species protection, appropriate to different levels of ecosystem condition and/or community objectives[6]. ANZG (2018) recommend the 99% species protection DGVs for use in high conservation value ecosystems, and the 80% or 90% species protection DGVs in highly modified (disturbed) systems. The most commonly applied DGVs are those for protection of 95% of species, as recommended for slightly to moderately disturbed systems [7]. The existing ANZG 95% protection level DGVs for fresh water (uplifted from the ANZECC & ARMCANZ (2000) trigger values) are 1.4 µg/L for copper and 8 µg/L (at a hardness of 30 mg/L as $CaCO_3$) for zinc.

Updated toxicant DGVs have been drafted for copper and zinc (dissolved, see Question 1.2) in fresh waters (see Appendix A). The draft DGVs outlined in this section are provided or, alternatively, can be calculated, for different receiving water chemistries (based on dissolved organic carbon (DOC) only for copper, and DOC, pH and hardness for zinc (see below for more details)). These draft DGVs at a water chemistry index condition[8] are provided in Table 1-1. Once the final review and approval process for the draft DGVs is completed, the DGVs will replace the existing values and be published on the ANZG website:

https://www.waterquality.gov.au/anz-guidelines/guideline-values/default/water-quality-toxicants/search

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[6] https://www.waterquality.gov.au/anz-guidelines/resources/key-concepts/level-of-protection

[7] https://www.waterquality.gov.au/anz-guidelines/resources/key-concepts/level-of-protection

[8] The index condition is a specific combination of water chemistry variables, usually representing relatively high metal bioavailability conditions. For the derivation of nickel water quality DGVs, the index condition for Australia and New Zealand was agreed to by a panel of project advisors to be pH 7.5, hardness of ~30 mg CaCO3/L, and 0.5 mg/L DOC, see 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)*: 100-112. The same index condition has been adopted for the zinc DGVs.

Table 1-1: Draft default guideline values (DGVs) for (dissolved) copper and zinc in fresh waters. Although still to be finalised and published, these DGVs have already been through extensive review and any further changes are expected to be minor. Therefore, the authors consider that these values represent the best available GVs for assessing copper and zinc toxicity in Australia and NZ at the current time.

Level of species protection (%)	DGV for dissolved copper (µg/L) at DOC ≤0.5 mg/L	DGV for dissolved zinc (µg/L) at pH 7.5, hardness 30 mg/L and DOC 0.5 mg/L
99	0.2	1.5
95	0.47	4.1
90	0.73	6.8
80	1.3	12

In comparison to the ANZECC & ARMCANZ (2000) DGVs, these draft copper and zinc DGVs are derived from larger toxicity datasets including more recent studies. The updated datasets for the freshwater DGVs include data for sensitive species such as freshwater molluscs, early life stages such as embryos, and species native to Australia and NZ (21 and 12 native species for copper and zinc, respectively, see Question 1.1 for additional details). The draft DGVs use negligible effect concentration data (such as EC_{10}[9] values and NOECs[10]). Unlike the ANZECC & ARMCANZ (2000) DGVs, the draft DGVs do not include any converted toxicity data; that is data from LOEC[11] or EC50[12] values adjusted to negligible effect values based on an adjustment factor. As these draft DGVs are based on large datasets of chronic negligible effect data and the species sensitivity distribution (SSD) models fitted to the data have a good fit, the DGVs are classified as having "very high reliability"[13].

The draft DGVs for copper and zinc in fresh waters consider different toxicity modifying factors (TMFs) than the ANZECC & ARMCANZ (2000) DGVs. These changes reflect improvements in understanding of the influence of water chemistry on the speciation and bioavailability of copper and zinc. The TMF used for the draft copper DGVs is dissolved organic carbon (**DOC**) as copper binds strongly to DOC, reducing its availability for uptake by aquatic organisms. The draft copper DGVs can be adjusted based on the concentration of dissolved organic carbon (DOC) in the water using Equation 1, analogous to the hardness adjustment used in the ANZECC & ARMCANZ (2000) guideline

9 EC10 values are effect concentrations (ECs) estimated to produce a 10% change in the response being measured, or an effect in 10% of the test organisms.

10 No observed effect concentrations are concentrations that have no statistically significant adverse effect on the exposed population of test organisms as compared with the controls.

11 Lowest concentration that has a statistically significant adverse effect on the exposed population of test organisms as compared with the controls.

12 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.

13 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. August 2015 - updated October 2018. Canberra.

values. Hardness[14] was removed as a TMF for copper[15] as multiple studies showed that the hardness adjustment was not protective for several aquatic species native to Australia and/or NZ[16].

$$DOC\ adjusted\ DGV = DGV_{0.5} \times \left(\frac{DOC}{0.5}\right)^{0.977}$$ **Equation 1**

In the above equation, $DGV_{0.5}$ is the DGV (at a selected level of protection, e.g., 95%, in µg/L) at 0.5 mg/L of DOC; and DOC is the concentration of DOC in the water, measured in mg/L, the DOC adjusted DGV is in µg/L.

The TMFs considered in the draft zinc DGVs are **hardness, pH and DOC** concentration. This reflects the binding of zinc by DOC in the water, competition for biological uptake by calcium and magnesium (measured together as hardness), and the influence of hydrogen ions (measured as pH), which can alter the speciation of zinc and compete with zinc for uptake.

The draft zinc DGVs use multiple linear regression (MLR) bioavailability models developed to account for the influence of pH, hardness and DOC on the toxicity of dissolved zinc (see Appendix C). The effect of pH, hardness and DOC on zinc toxicity can differ between taxonomic groups, therefore, a suite of species and trophic level-specific models are used in the draft zinc DGV derivation. This means that there is no simple equation to adjust the DGVs for different hardness, DOC and pH. Instead, multiple equations for different types of organisms are used to adjust the toxicity data before the DGVs (at differing levels of protection) are derived for each combination of pH, hardness and DOC. To make this easier for guideline users, look-up tables of DGVs for different combinations of pH, hardness, and DOC are provided in the draft DGVs technical briefs that will be published by ANZG (see examples Table 1-2, Table 1-3, Table 1.4), and it is expected that R code will be made available for this adjustment via the Envirolink website.

Table 1-2 illustrates how copper DGVs vary at different concentrations of DOC and Table 1-3 and 1.4 show variations in zinc DGVs with different DOC, hardness and pH. The copper DGV for 95% species protection at 0.5 mg/L of DOC or less is low compared to dissolved copper concentrations in many streams, however the DGVs approximately double as the DOC concentration in the water doubles, reflecting the change in copper bioavailability. In contrast, DOC has less effect on the zinc DGVs. However, as those DGVs do change with hardness, pH and DOC, increases in all three can also result in substantial changes to the DGV. For example, the zinc DGV changes from 4.1 µg/L at the index condition to 8.8 µg/L at a hardness of 60 mg/L and DOC of 2 mg/L – these hardness and DOC concentrations could be found in many waters around NZ. Use of the DGVs at the index condition may be unnecessarily restrictive (i.e., conservative), and adjustment for local water chemistry is highly recommended.

[14] Hardness relates to both calcium and magnesium cations and is strictly termed as “total hardness”. This is commonly referred to as “hardness” for brevity (including in previous ANZG and ANZECC & ARMCANZ documents), and that terminology is also used throughout this guidance.

[15] 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. August 2015 - updated October 2018. Canberra.

[16] Markich, et al. (2005). Hardness corrections for copper are inappropriate for protecting sensitive freshwater biota. *Chemosphere 60*: 1-8; Markich, et al. (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)*: 1791-1800.

Table 1-2: Draft copper DGVs at different DOC concentrations.

DOC concentration (mg/L)	DGV for dissolved copper in fresh water, 95% level of species protection (μg/L)
0.5	0.47
1	0.93
2	1.8
4	3.6
8	7.1
12	10
20	17
25	21
30	26

Table 1-3: Draft zinc DGVs at different hardness and DOC concentrations. Based on a pH of 7.5. DGV at index condition shaded grey.

		DGV for dissolved zinc in fresh water, 95% level of species protection (μg/L)							
	Hardness (mg/L as $CaCO_3$)	**20**	**30**	**60**	**90**	**120**	**180**	**300**	**440**
DOC (mg/L)	**0.5**	3.5	4.1	5.3	6.1	6.8	7.9	8.8	9.6
	1	4.5	5.3	6.8	7.9	8.8	10	11	12
	2	5.9	6.9	8.8	10	11	13	15	16
	5	8.3	9.7	12	14	16	18	20	22
	10	11	13	16	18	20	24	26	28
	15	13	15	19	21	24	27	30	33

Table 1-4: Draft zinc DGVs at different pH and hardness concentrations. Based on a DOC of 0.5 mg/L. DGV at index condition shaded grey.

		DGV for dissolved zinc in fresh water, 95% level of species protection (μg/L)							
	Hardness (mg/L as $CaCO_3$)	**20**	**30**	**60**	**90**	**120**	**180**	**300**	**440**
pH	**6.2**	7.9	9.2	12	13	15	17	19	21
	6.5	6.5	7.6	9.7	11	12	14	16	17
	7.0	4.8	5.6	7.2	8.3	9.2	11	12	13
	7.5	3.5	4.1	5.3	6.1	6.8	7.9	8.8	9.6
	8.0	2.5	3.0	3.9	4.5	5.1	5.9	6.6	7.2
	8.2	2.1	2.5	3.3	3.8	4.2	5.0	5.5	6.0

The draft DGVs for copper and zinc apply in fresh waters where the pH, hardness and DOC are within the ranges shown in Table 1-5. Where fresh waters are outside this range the bioavailability models may not adequately predict toxicity risks (i.e., GVs may be either over- or under-protective). This is addressed further in Question 1.7 and section 1.9.

Table 1-5: Applicable range of TMFs for use of dissolved copper and zinc freshwater DGVs.

	Copper	**Zinc**
pH	6 – 8.5	6.2 – 8.3
Hardness (as mg/L $CaCO_3$)	Not limited	20 – 440
DOC (mg/L)	<0.5 – 30	<0.5 – 15

1.1.1 Further work planned

As the draft copper and zinc DGVs still need to be finalised and published, it is possible that there may be some changes to the DGVs. However, any such changes are expected to be minor changes that will not change TMFs included in their derivation and the need to adjust DGVs based on local water chemistry.

Furthermore, it is likely that, in the future, “tier 1” DGVs will also be included. Tier 1 DGVs represent DGVs at high bioavailability conditions and can be used as the first step in a tiered approach to assessing risk. In a tiered approach, the first tier requires less information and represents a “screening” assessment, to reduce the number of sites for further assessment. That further assessment (as described in section 1.3) requires additional information but will provide more certainty in the assessment of toxicity.

The tier 1 DGV for copper is that at DOC of 0.5 mg/L or less, as shown in Table 1-1. These DGVs can be used to screen sites for further assessment. If measured dissolved copper concentrations are below the DGV (e.g., for 95% protection), no further information is required. However, if concentrations are above that tier 1 DGV, then the assessment should proceed as outlined in Figure 1-1.

The tier 1 DGV for zinc is yet to be determined. A tier 1 DGV should not be based on the highest bioavailability condition for each of hardness, DOC and pH (i.e., low hardness and DOC, and high pH) as that combination (especially low hardness and higher pH) is unlikely to actually occur in the environment, and screening on the basis of an unrealistic DGV is not helpful for prioritising sites for further assessment. The intention is therefore to base a tier 1 DGV on water chemistry data collected across Australia and NZ. This will ensure that the pH, water hardness and DOC data used to calculate the DGV are found in the environment in that combination. The zinc DGVs shown in Table 1-1 are indicative of high bioavailability conditions but may be different to the tier 1 DGVs. Selection of the tier 1 DGV will also enable “bioavailable zinc” concentrations to be estimated (see section 1.2).

1.2 Calculating "bioavailable metals" based on TMFs instead of adjusting DGVs

KEY POINTS:

- **THE "BIOAVAILABLE" COPPER CONCENTRATION IN A SAMPLE CAN BE CALCULATED TO COMPARE WITH A CONSTANT HIGH BIOAVAILABILITY (TIER 1) DGV**
- **AN EQUIVALENT OPTION FOR ZINC REQUIRES SELECTION OF A TIER 1 DGV TO ENABLE CALCULATION OF BIOAVAILABILITY FACTORS. THIS OPTION MAY BECOME AVAILABLE IN 2024**

For practitioners who prefer to have a constant (non-varying) DGV, it is possible to adjust the measured dissolved metal concentrations to reflect bioavailability and compare this fraction of the dissolved metal concentration (hereafter the bioavailable copper concentration) with a high bioavailability DGV. Calculating and presenting bioavailable metal concentrations against a single GV may be easier for communicating to the general public or for graphical comparisons between sites, especially when demonstrating time-series data (see Case Study 1).

This is currently only possible for copper, where the tier 1 "high bioavailability" DGV applies to fresh waters with a DOC concentration of 0.5 mg/L or less. Equation 2 below can be used to calculate the bioavailable fraction from dissolved copper concentrations. The "bioavailable copper" concentration should then be compared with the tier 1 DGV: at 0.5 mg/L of DOC (i.e., 0.47 µg/L for the 95% level of species protection). When using the equation in this manner, the copper concentration reported by the laboratory should not be adjusted if the DOC concentration is 0.5 mg/L or less.

$$Bioavailable\ Cu = Dissolved\ Cu \div \left(\frac{DOC}{0.5}\right)^{0.977}$$ **Equation 2**

In the above equation, Cu is the concentration of copper (in µg/L) and DOC is the concentration of DOC in the water, measured in mg/L.

An approach to calculate "bioavailable zinc" will also be possible when a tier 1 "high bioavailability" DGV has been established, but will require the use of an Rscript or R-Shiny tool to facilitate calculation of the bioavailable zinc concentration. The index condition DGVs for zinc can be used as interim "high bioavailability" DGVs (until Australia/NZ or country-specific tier 1 DGVs can be provided), but we do not recommend using the index condition TMF values to calculate the "bioavailable zinc" fraction. This may under-estimate the bioavailable fraction and therefore result in a misleading assessment of toxicity risk.

1.3 Recommended approach for implementing bioavailability-based GVs

KEY POINTS:

- **IF TMF DATA ARE AVAILABLE FOR EVERY SITE/SAMPLING EVENT, ADJUST THE DGV FOR EVERY SITE/SAMPLING EVENT**
- **IF TMF DATA ARE NOT AVAILABLE FOR A SAMPLING EVENT, TMFS COULD BE ESTIMATED FOR THAT SAMPLE FROM EXISTING DATA, USING A CONSERVATIVE PERCENTILE (E.G., 25TH PERCENTILE). USE OF DGVS CALCULATED FROM ESTIMATED TMF VALUES SHOULD BE CONSIDERED A "SCREENING LEVEL ASSESSMENT" AND THE RATIONALE FOR TMF VALUE SELECTION SHOULD BE CLEARLY DOCUMENTED.**
- **IF THERE ARE NO TMF DATA FOR THAT SITE, TMFS COULD BE ESTIMATED FROM EXISTING DATA FROM OTHER SITES, USING A VERY CONSERVATIVE PERCENTILE (E.G., 10TH PERCENTILE). USE OF DGVS CALCULATED FROM ESTIMATED TMF VALUES SHOULD BE CONSIDERED A "SCREENING LEVEL ASSESSMENT" AND THE RATIONALE FOR TMF VALUE SELECTION SHOULD BE CLEARLY DOCUMENTED.**
- **IF THERE ARE NO TMF DATA, A HIGH BIOAVAILABILITY DGV (E.G., TIER 1 OR INDEX CONDITION) DGV CAN BE USED FOR SCREENING BUT THIS WILL LIKELY PROVIDE A HIGHLY CONSERVATIVE ASSESSMENT OF TOXICITY**

The approach set out in this section aims to provide the most robust assessment of toxicity possible, depending on the information available. There are four options, referred to as Levels A to D, for implementing the bioavailability-based DGVs. Each option has a different level of information required (particularly the amount and type of TMF data) and provides a different level of confidence in the assessment of toxicity. This approach is outlined in the flow chart (Figure 1-1) and described below.

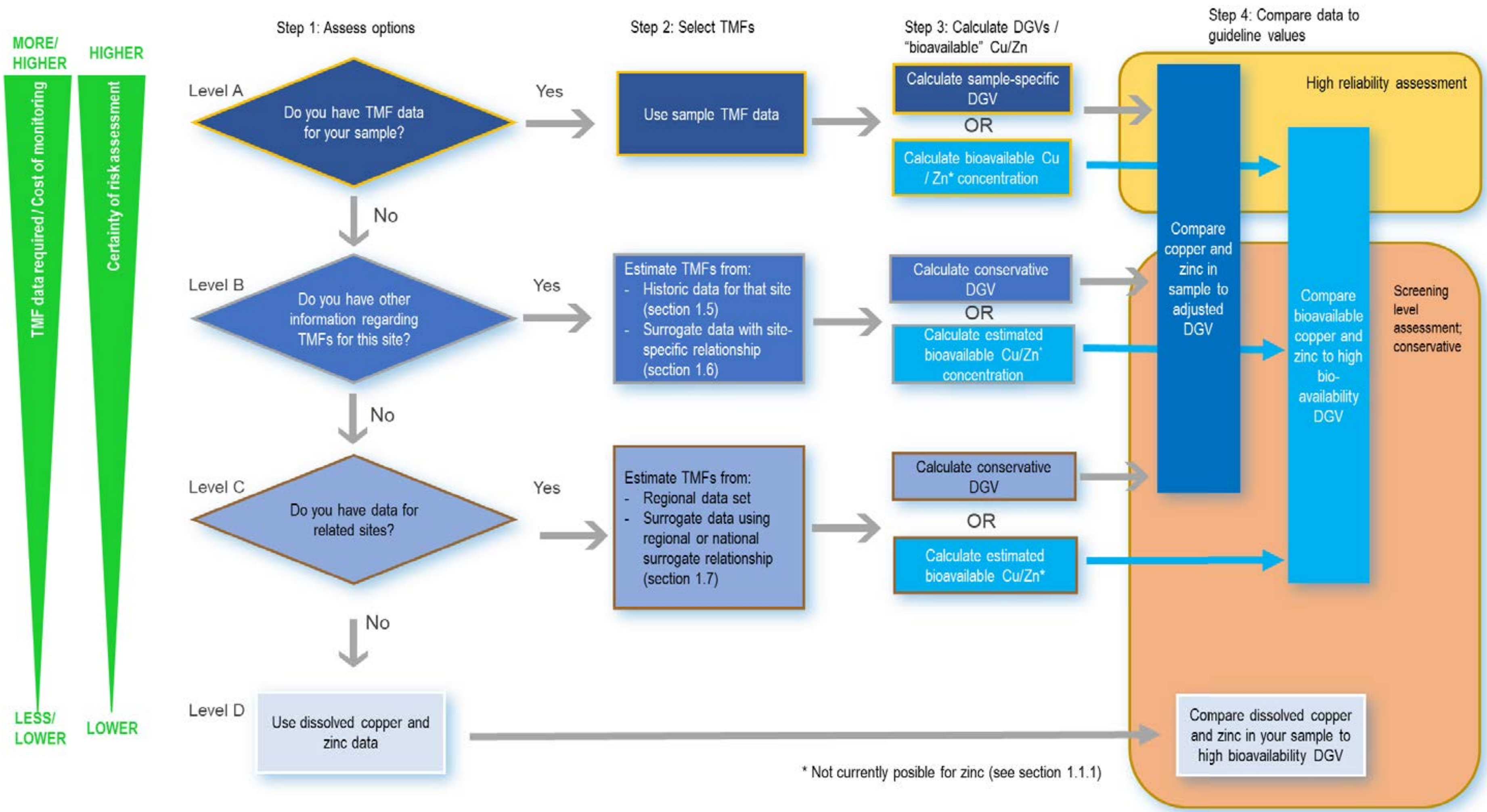

Figure 1-1: Flow chart for application of dissolved copper and zinc draft DGVs. DGV at index condition currently recommended as "high bioavailability DGV" at level D.

Level A

If there are TMF data available for every metal sample calculate a sample-specific DGV for every measurement value in space and time (**Level A** in Figure 1-1). **This approach will provide the most robust assessment of toxicity risk as TMF data are matched to metal data.** However, this method requires that TMF data are available for every data point used in the analysis.

If no TMF data are available for a given water sampling event other options must be used (levels B to D in Figure 1-1) and the assessment should be considered a screening level assessment only. Levels B to D are hierarchical, where, for example, Level B should be used over Level C or Level D, where possible.

Level B

If there are historical TMF data available for the site of interest, there are two options to estimate the TMFs for an individual sample (**Level B**, Figure 1-1):

Option 1: Use historical data for TMFs from samples collected at or near the site of interest to estimate the TMF values for adjusting the DGVs. We recommend using a conservative percentile for this - the 25th percentile for hardness and DOC from that data set, and the 75th percentile for pH (because higher pH results in higher bioavailability/lower DGVs). In addition, the data set used to calculate that percentile should be from samples collected under similar conditions to the sample collected for metals collected for metals (e.g., when calculating a DGV for a sample collected at high flow, the data set used to calculate a TMF percentile should be from samples collected at high flow, see section 1.4 for rationale). Larger datasets will provide more accurate estimates of these percentiles[17]. The estimated TMFs are then used to calculate a conservative DGV for a screening-level assessment.

Option 2: Use a site-specific surrogate relationship to estimate the TMFs (section 1.5). For example, measurements of conductivity may be useful for estimating hardness. When TMFs are estimated from surrogate relationships, use a conservative percentile value (e.g., a 25th percentile). These estimated TMFs are then used to calculate a conservative DGV for a screening-level assessment.

Level C

If no TMF data are available for the site of interest the TMFs can be estimated (**Level C**, Figure 1-1) with the assessment considered a screening level assessment only. Because there is increased uncertainty around the TMF values for the site (in the absence of supporting data), these TMF estimates should be very conservative (i.e., based on a 10th percentile of existing data).

As with level B, there are two possible approaches:

Option 1: Use data from nearby sites to estimate the TMF values for adjusting the DGVs (see section 1.6). Here we recommend using the 10th percentile for hardness and DOC from that data set, and the 90th percentile for pH (because higher pH results in

[17] McBride (2005). Using statistical methods for water quality management: issues, problems and solutions. Wiley Series In Statistics In Practice. New Jersey, John Wiley & Sons Inc.

higher bioavailability/lower DGVs). In addition, where possible, the data set used to calculate that percentile should be from samples collected from similar streams and under similar conditions to the sample collected for metals (see section 1.6 for further details). The estimated TMFs are then used to calculate a conservative DGV for a screening-level assessment.

Option 2: Estimate the TMFs from surrogate data using a surrogate relationship developed for the region or based on national data (section 0). When this approach is adopted, a very conservative percentile value (e.g., a 10th percentile) should be used.

Level D

If no sample-specific data are available (Level A), no historical TMF data are available for the site of interest (Level B), and there is no information from nearby sites or on surrogates (Level C), then the last option is to use a “high bioavailability” or “tier 1” DGV (**Level D**). This is a DGV that represents conditions of high bioavailability – low DOC, low hardness and slightly alkaline pH. Such a DGV is likely to be lower – and therefore more stringent – than a bioavailability-adjusted DGV based on sample-specific TMF data. As this represents a conservative approach, it is best reserved for screening-level assessments only. In some cases, it may not be useful for making decisions related to water management because it may (incorrectly) indicate high proportions of GV exceedance at many sites.

The “high bioavailability” DGVs for copper are those at DOC of 0.5 mg/L or less, as shown in Table 1-1. As stated in section 1.1, the “tier 1” DGV for zinc has not yet been determined. **As an interim measure, we recommend using the dissolved zinc draft DGVs for the index condition** (as in Table 1-1), based on DOC of 0.5 mg/L, hardness of 30 mg/L as CaCO3 and pH of 7.5. Although this TMF combination represents relatively high zinc bioavailability conditions, it may not be protective in all waters. For example, care should be used in applying this TMF combination to alpine rivers, which are typically characterised by low hardness and DOC. Note the TMF conditions (i.e., combination of TMF values) under which zinc is most bioavailable may be different to copper (or nickel or other metals for which bioavailability-based DGVs are derived in the future) as TMFs can affect the toxicity of each metal differently (i.e., to different magnitudes and directions).

Other situations

It is possible that a **combination of Levels A to D** could be applied. For example, guideline users may have sample-specific data for pH, some historical data for hardness but no data for DOC. In cases like this, the available data should always be used in calculating DGVs (i.e., sample-specific pH data) along with estimates for the other TMFs, and this would be considered a screening-level assessment. That is, the hardness used for the DGV calculation should be the 25th percentile from the historical data set, and a value of 0.5 mg/L used for DOC.

1.4 Rationale for the recommended implementation approach

Key points:

- **Hardness, DOC and pH vary across space and time and are not easily predicted based on current knowledge**
- **Metals and TMFs may not vary in the same way over time or with respect to flow. Use of median values is not a conservative approach (i.e., sufficiently conservative to indicate whether an ecosystem is protected from toxicity)**
- **Estimating TMFs from medians of measurements at other sites is not conservative for a screening level assessment**

Calculating a DGV based on the TMFs measured along with the metals provides a robust assessment of toxicity. This is particularly important for the zinc DGVs as each of the TMFs (pH, hardness and DOC) may vary in different directions in relation to flow and season. The measured (dissolved) metal concentration can be compared to the sample-specific DGV to assess whether it meets (i.e., is below) the DGV (see Figure 1-2). Summary statistics can also be calculated from the sample-by-sample comparison to assess whether more than 95% of the samples meet their corresponding DGV. This method provides more information than calculating a 95th percentile alone from the measured data and comparing that to a single DGV[18]. For example, the proportion of samples that exceed the DGVs can be compared between sites (Figure 1-3). Alternatively, the TMF data for each sample can be used to estimate the bioavailable copper and/or zinc concentration, which can then be compared to a tier 1 DGV (see Case Study 1).

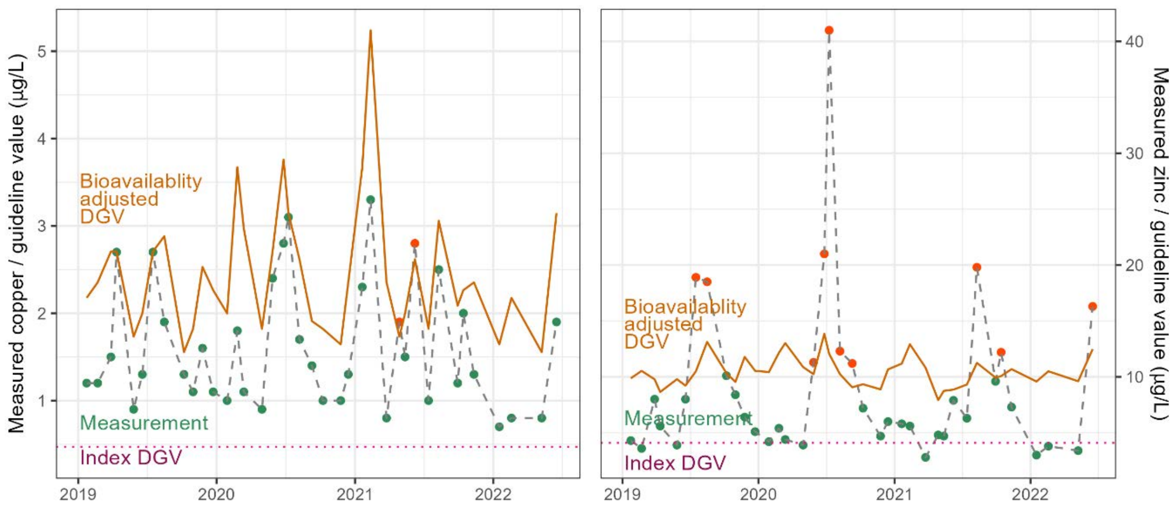

Figure 1-2: Comparison of monthly measurements of dissolved copper (left) and zinc (right) concentrations in Oakley Creek (Auckland) against bioavailability-adjusted DGVs (95% protection) that reflect changing DOC only (copper) or DOC, hardness and pH (zinc). Metal concentrations above and below the bioavailability-adjusted DGV are shown in red and green, respectively, with measurements connected by a dashed line. Bioavailability-adjusted DGVs are shown as a solid line in dark orange. The index DGVs are also

[18] Furthermore, with bioavailability-based DGVs, it would not be clear what that single DGV should be. An index condition DGV is likely too conservative, and calculating a DGV based on a median DOC / pH / hardness is not recommended. See section 1.4 for further discussion.

shown for comparison (purple dashed line) and indicate that dissolved copper concentrations in all samples and dissolved zinc concentrations in most samples exceed index DGVs. Monitoring data provided by Auckland Council.

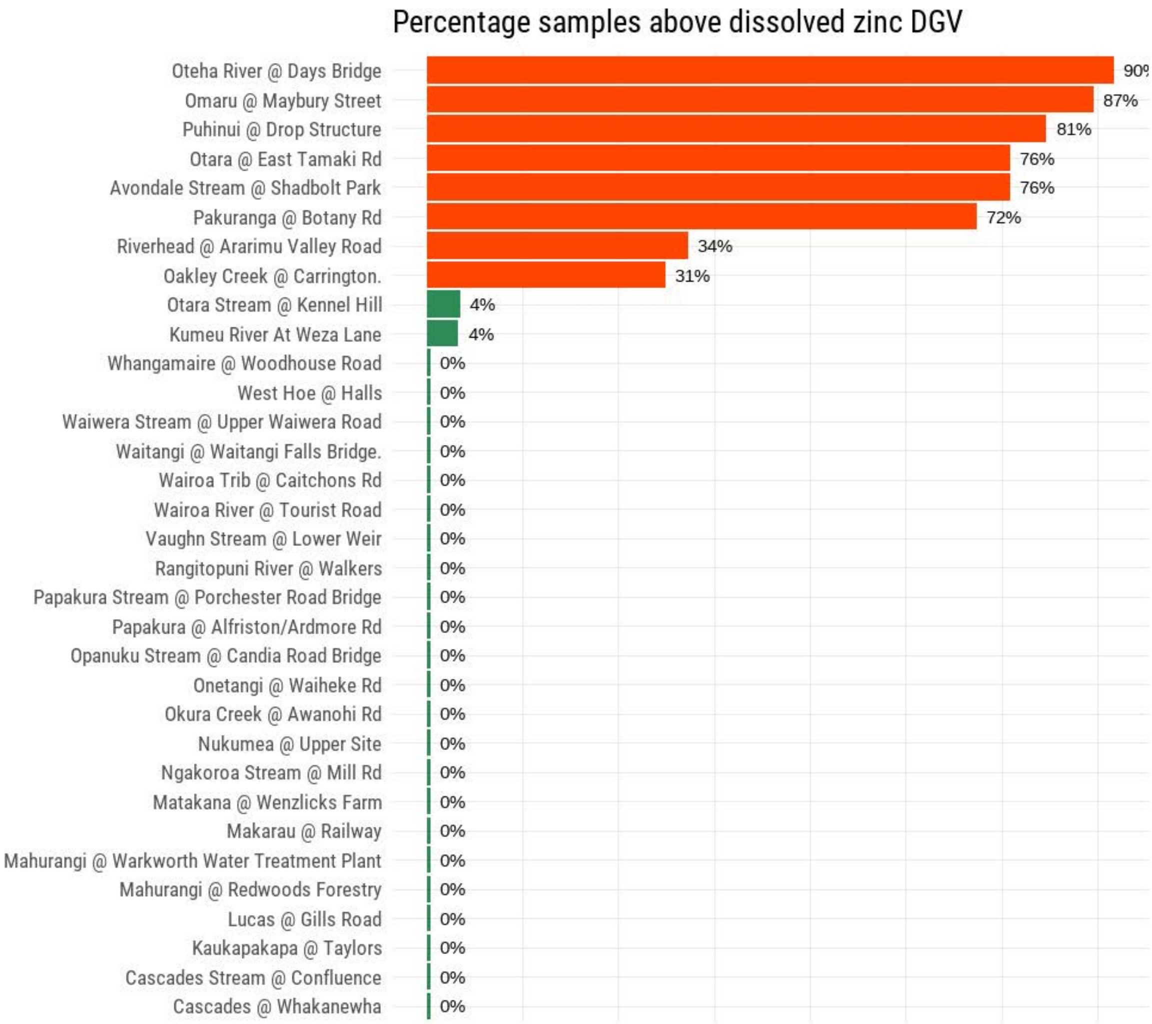

Figure 1-3: Comparing the percentage exceedance of zinc DGVs across multiple stream monitoring sites in Auckland when using a bioavailability-adjusted DGV. The percentage exceedance can be calculated for any desired timeframe and then compared across all sites. Here the bars coloured orange indicate sites where more than 5% of samples exceeded the DGV (<95% of samples are below the DGVs). Based on monthly monitoring of dissolved zinc over the period January 2018 to December 2022. Data provided by Auckland Council.

Case Study 1: Calculating bioavailable copper concentrations for comparing to Tier 1 DGVs

In Figure 1-2, Auckland Council water column copper and zinc concentrations measured at a site on Oakley Creek were compared to varying DGVs, based on measured DOC, hardness and pH for each sample (figure for copper reproduced in left panel of Figure 1-4 below). The same data can be used to calculate "bioavailable" copper from the measured metal concentrations, using the tier 1 copper DGV. "Bioavailable copper" concentrations are calculated using Equation 2. This is not currently possible for zinc as the tier 1 DGV has not yet been determined.

Table 1-6: Measured dissolved copper and estimated bioavailable copper concentrations based on DOC at the Oakley Creek at Carrington site. Data supplied by Auckland Council.

Date	Dissolved copper (µg/L)	DOC (mg/L)	"Bioavailable copper" (µg/L)
25-03-2021	0.8	2.6	0.15
28-04-2021	1.9	1.9	0.51
13-05-2021	1.5	2.2	0.35
08-06-2021	2.8	2.9	0.50

The bioavailable copper concentrations are then compared with the tier 1 DGV – here the 95% level of species protection is used: 0.47 µg/L. Table 1-6 and Figure 1-4 indicate that copper concentrations exceeded their corresponding GV on 28th April and 8th June 2021, regardless of the method used.

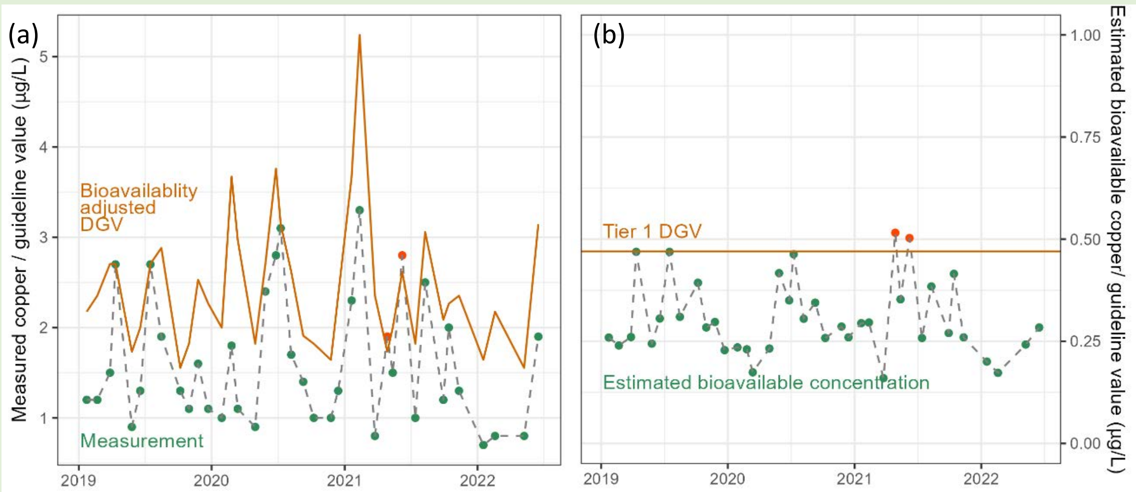

Figure 1-4: Comparison of a) dissolved copper concentrations to varying bioavailability-adjusted DGVs (as shown in Figure 1-2) and b) bioavailable copper concentrations to a stable tier 1 copper DGV. Either method may be used to compare measured copper concentrations to copper DGVs. Concentrations above and below the DGVs are shown in red and green, respectively (note two measurements shown as at the DGV were very slightly below the DGV). Measurements connected by dashed line. DGV shown as a solid

dark orange line. Dissolved copper and DOC data provided by Auckland Council.

In the past, many users of the hardness-based metal DGVs (e.g., ANZECC & ARMCANZ (2000)) have calculated DGVs based on the median (or mean, or some other percentile) hardness at a site, even if hardness is measured in each sample. **This method is NOT recommended**. All TMFs can vary substantially over time at any given site with a factor of two variation common for hardness and DOC, though greater variation can be observed at some sites (Figure 1-5, Figure 1-6). A two-fold variation in DOC can change copper DGVs by a factor of two. Similarly, two-fold changes in DOC and hardness change zinc DGVs by approximately 1.5-fold – these changes to the DGVs imply that a precautionary approach is needed.

A copper DGV based on a median DOC concentration would be higher than the copper DGVs based on sample-specific DOC concentrations for 50% of samples. Use of a median is therefore not conservative for assessing potential metal toxicity. Where TMF data are not available for a sample, but there are some data available for the site (i.e. Level B assessment), we recommend using a 25th percentile of the available TMF data (see section 1.3 for details). This is more precautionary than a median (with DGVs lower than this in only 25% samples) without being extreme. The use of a 25th percentile is consistent with EU guidance for implementing bioavailability-based metal guidelines[19], which was based on analysis of risks to waterbodies in the UK[20].

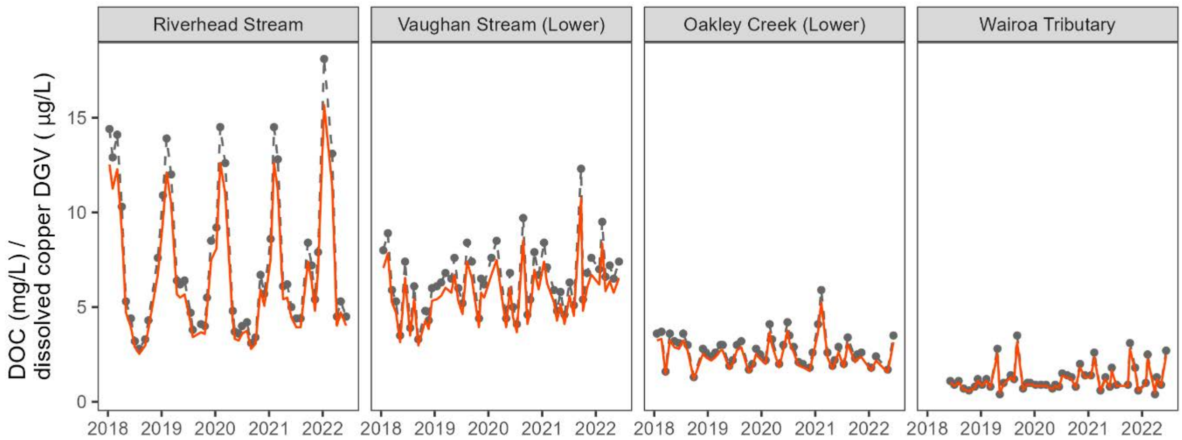

Figure 1-5: Variation in DOC concentrations (grey dots) over time at four stream sites in Auckland and the subsequent variation in copper DGVs (orange line). Data provided by Auckland Council for monthly measurements from SOE monitoring between January 2018 and June 2022.

Seasonal factors may drive DOC production and transport in streams, and flow can also affect DOC, either through transporting DOC to the stream (increasing the concentration) or via dilution

[19] Coquery, et al. (2019). Technical Guidance for implementing Environmental Quality Standards (EQS) for metals. Consideration of metal bioavailability and natural background concentrations in assessing compliance. Draft version European Commission *Common Implementation Strategy for the Water Framework Directive (2000/60/EC)*. 15 November 2019.

[20] Merrington and Peters (2012). The importance of dissolved organic carbon in the assessment of environmental quality standard compliance for copper and zinc. Water Framework Directive - United Kingdom Technical Advisory Group (WFD-UKTAG), Scotland.

(decreasing the concentration) [21]. These relationships between flow and concentration may be site-specific.

Water hardness also varies within a site (Figure 1-6) – and relationships between flow and hardness have been observed in urban streams, with lower hardness during high flows (Figure 1-7). As these higher flow periods are typically those with higher concentrations of metals (delivered via stormwater discharges), this represents a period of higher risk to aquatic ecosystems. **Using a median hardness concentration to calculate DGVs may not be protective to stream life during high flow events.**

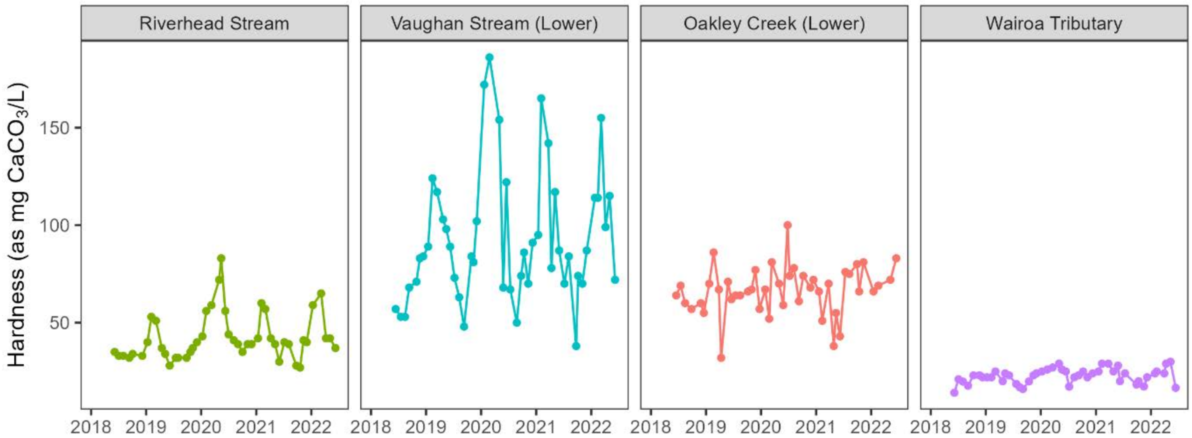

Figure 1-6: Variation in hardness over time at four stream sites in Auckland. Data provided by Auckland Council for monthly measurements from SOE monitoring between June 2018 and June 2022.

[21] Werner, et al. (2019). High-frequency measurements explain quantity and quality of dissolved organic carbon mobilization in a headwater catchment. *Biogeosciences 16(22)*: 4497-4516; Pisani, et al. (2020). Riparian land cover and hydrology influence stream dissolved organic matter composition in an agricultural watershed. *Science of The Total Environment 717*: 137165.

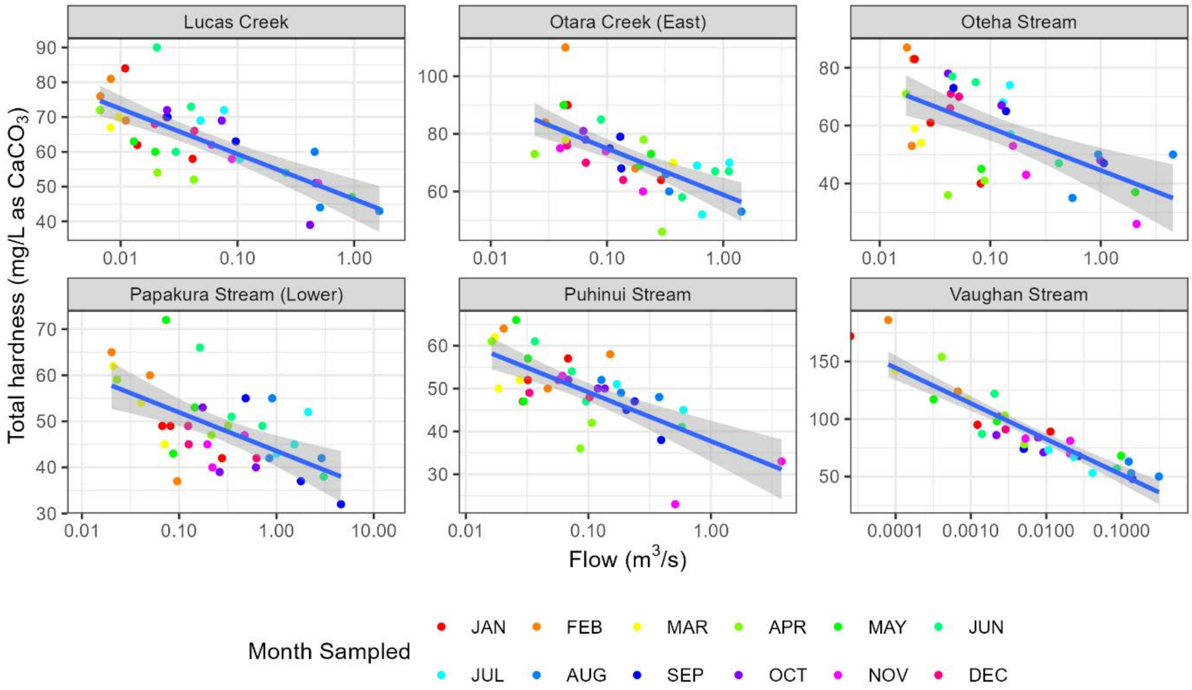

Figure 1-7: Total hardness concentrations versus stream flow for six urban stream sites in Auckland, based on monthly measurements from SOE monitoring between November 2017 and June 2021. Note that the scales of the x-axes (flow) and y-axes (hardness) differ between plots, with a logarithmic scale used for flow. Dots are coloured by the month sampled to indicate within year variation. The blue line indicates linear regression and the grey shaded area indicates the 95% confidence interval around that regression.

Although using DGVs based on TMFs from averages (whether a mean or median) across a number of sites can be considered a screening method, it is possible to overlook locations where DGVs should be lower and where exceedances could occur when using a sample-specific DGV. It is therefore not as conservative as a screening method should be.

Using catchment averages of TMFs can also direct management efforts to the wrong locations. For example, if the DOC concentration is higher at some sites, where metal concentrations are also higher, those metal concentrations may fall below a sample or site-adapted DGV, but not when using a catchment-based average (see Case Study 2). Funding and monitoring resources could be misplaced with poor environmental protection outcomes. With current knowledge it is difficult to predict the DOC (and the chance of over- or under-estimating risks) at any site without measuring it. If DOC is being measured at a site to assess how that site compares to a catchment-wide average for DOC, use that DOC data to calculate a site/sample-specific DGV.

Case Study 2: Comparison of monitoring data to copper DGVs based on catchment-wide median DOC versus site and sample-based DOC measurements

Christchurch City Council measured DOC concentrations in all stream water samples collected for metal analysis during monthly monitoring in 2019. The results indicate that there is considerable variation across sites, even within the single catchment of Ōtākaro/Avon River (Figure 1-8). Christchurch City Council has typically calculated catchment-wide DGVs for zinc, based on the median hardness across each catchment[22].

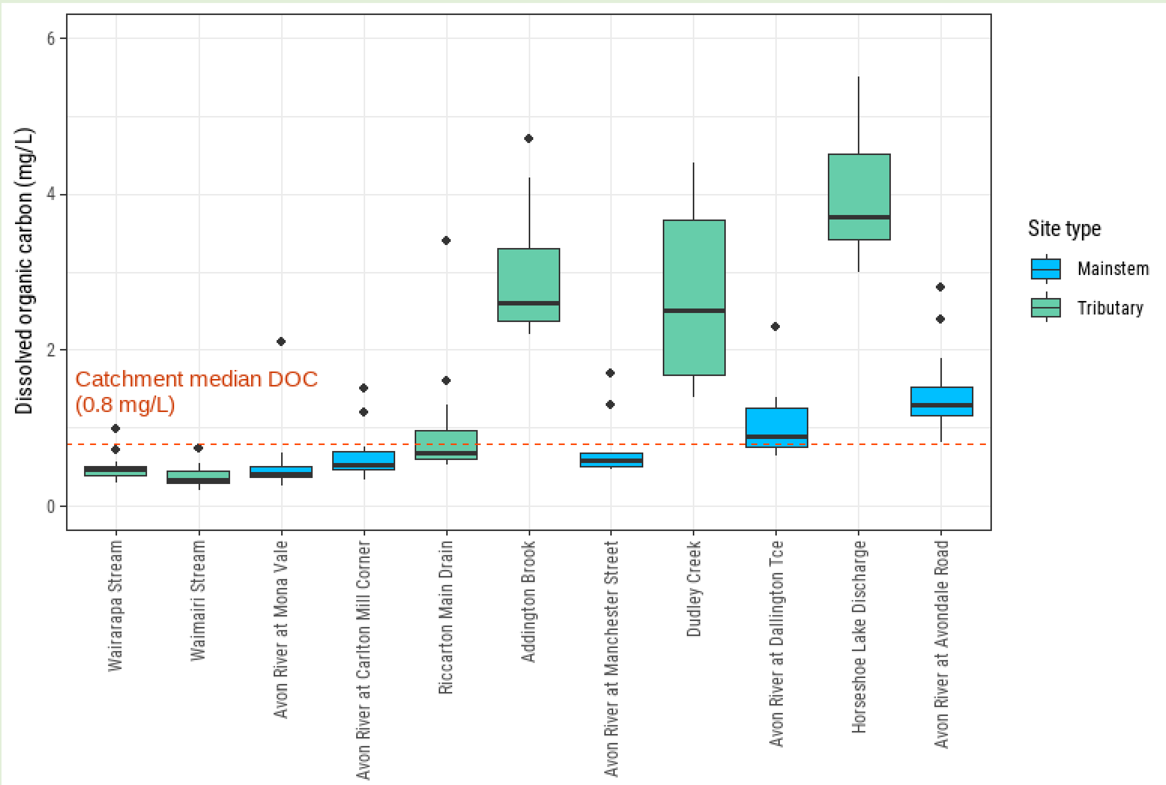

Figure 1-8: Variation in dissolved organic carbon (DOC) concentration between sites within a single Christchurch catchment. Sites on tributaries are coloured green and sites on the mainstem are coloured blue. The median DOC across all sites is 0.8 mg/L. Data from monthly monitoring in 2019; supplied by Christchurch City Council.

[22] For details see Appendix D of Margetts and Poudyal (2022). Christchurch City surface water quality annual report 2021. Prepared to meet the requirements of CRC214226. Christchurch City Council, *Christchurch City Council Report*. Christchurch City Council, Christchurch, New Zealand.

When using this same approach for copper DGVs, based on DOC, all 11 sites in the Avon River catchment had over 5% of samples exceed the catchment-wide DGV. The high percentage of samples from Addington Brook exceeding the DGV at this site (Figure 1-9 (a)) suggests this is a key location for further investigation and potential management.

When adjusting the DGV for each site and sampling occasion, only six sites exceeded the DGVs in more than 5% of samples (Figure 1-9 (b)). At each of those six sites, the DGVs were exceeded in 8% samples (only once in the 12-month period). This is despite the use of more conservative DGVs most of the time for Wairarapa and Waimairi streams; and in the two upper Avon River sites (Mona Vale and Carlton Mill Corner). This second comparison suggests there is an equal need for further investigation or potential management action at each of these six sites.

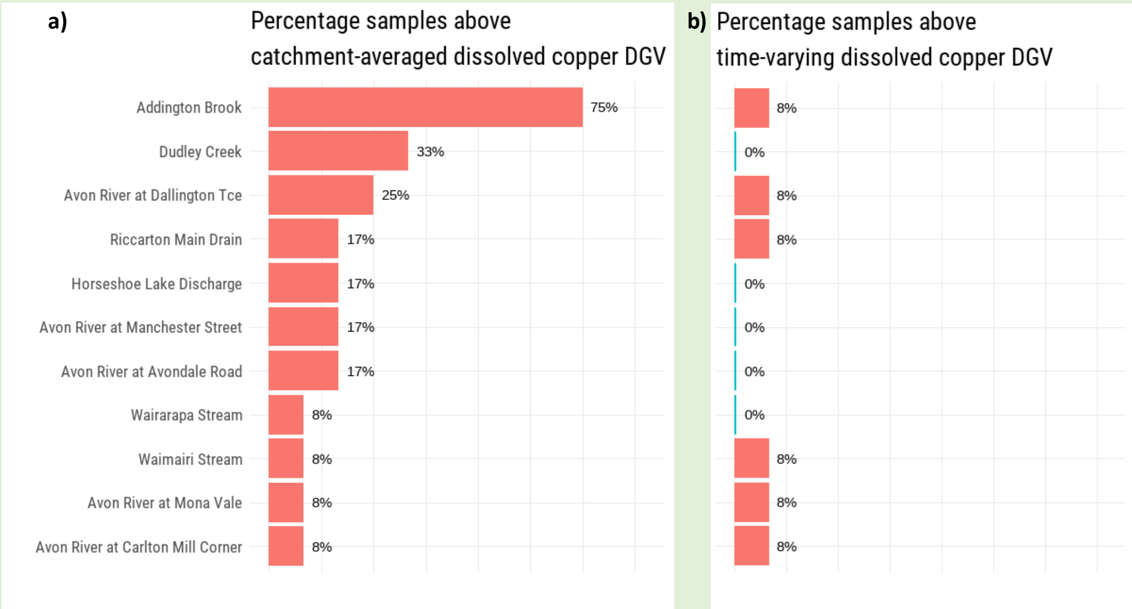

Figure 1-9: Comparing percentage exceedance of dissolved copper DGVs across multiple stream sites when using a) one DGV based on a catchment-average, and b) DGVs varying for each site and date. Copper and DOC data from monthly monitoring between January and December 2019, provided by Christchurch City Council.

1.5 Using surrogates to estimate TMFs

A surrogate is a proxy measure for a variable of true interest that is too difficult or costly to measure directly on a routine basis. Electrical conductivity is a potential surrogate for hardness (Figure 1-10). For DOC, potential surrogates include spectrometric measures of water samples, such as UV absorbance at specific wavelengths, or fluorescence measurements (e.g., fDOM, fluorescence of dissolved organic matter using *in situ* sensors). Dissolved iron has also been suggested as a DOC surrogate in the United Kingdom[23]. These surrogate variables may be cheaper to measure over the long term than hardness or DOC (assuming that samples are already being collected for metals and/or *in situ* sensor data are available), or there may be historical data that could be used to indicate the likely hardness or DOC.

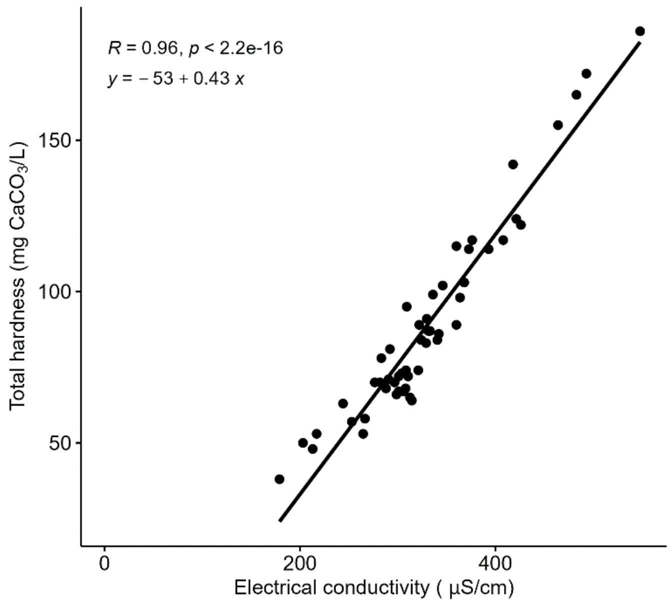

Figure 1-10: Relationship between total hardness and electrical conductivity at a single site. Data provided by Auckland Council.

An issue with the surrogate approach is that relationships are likely to be site-specific, especially for DOC. The sources and the characteristics of DOC (e.g., high in humics from forested catchments or wetlands) influence that relationship. Similarly, fDOM measurements are influenced by site-specific factors such as suspended particles, pH and the presence of metals; different analytical instruments can provide different results; and for *in situ* measurements, sensor positioning and fouling or drift also influence measurements.

Analysis of relationships between absorbance at 340 nm and DOC concentrations shows some sites have strong linear relationships (Figure 1-11), while at other sites, there is little relationship between the two variables. For example, in the Ngaruroro River at Kuripapango, DOC concentrations range from 0.2 to 6.5 mg/L (30-fold range) over a relatively narrow range in UV (2 to 10, 5-fold range); at the Hoteo River at Gubbs site there is no apparent relationship between DOC and A430 (Figure 1-11). Even for sites with a reasonably high correlation such as the Hutt River at Boulcott site (R^2 = 0.82), there are samples that vary from the line of best fit. Overall, given this variability, relationships

[23] Peters, et al. (2011). Effects of iron on benthic macroinvertebrate communities in the field. *Bulletin of Environmental Contamination and Toxicology 86(6)*: 591-595.

between DOC and potential surrogates (such as UV absorbance or fDOM) should be developed for every site, and may not be useful at all sites. If a site-specific relationship is developed, a conservative percentile estimate (e.g., 25th percentile) for DOC is recommended to provide a safety factor in calculating copper and zinc DGVs.

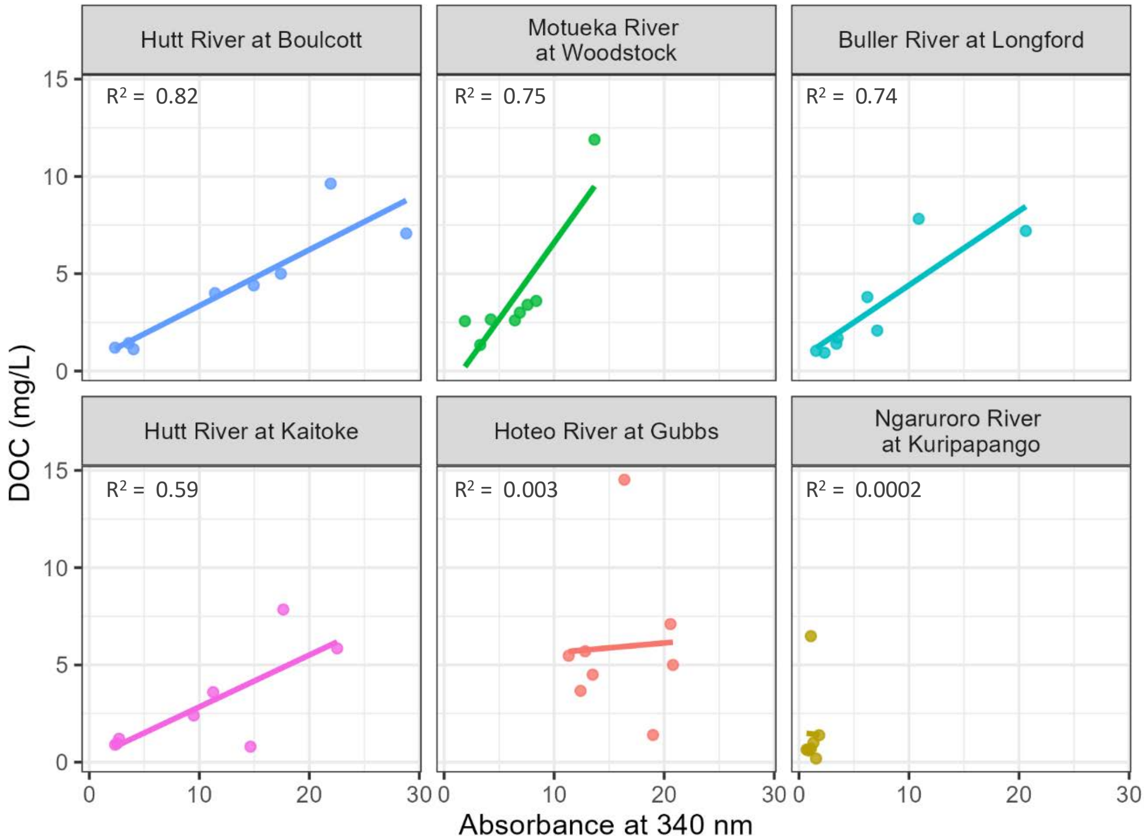

Figure 1-11: Relationship between DOC and UV absorbance at 440 nm at six NZ river sites. Data collected from NIWA's national water quality network and a Landcare Research study of DOC[24].

1.6 Estimating TMF values from data for other sites

As outlined for Level C (section 1.2.3), if no TMF data are available for your site of interest, pH, hardness and/DOC values could be estimated from existing data from other sources. Because there is considerable uncertainty when extrapolating between sites (see rest of this section), a very conservative percentile (e.g., 10th percentile) should be used to select that TMF value and calculate a DGV.

Values for pH, DOC and hardness can vary significantly between sites. While DOC concentrations tend to be low (<~1 mg/L) in spring-fed, rocky-bottomed streams, and high (> 10 mg/L, up to 30 mg/L) in streams that drain wetlands and/or catchments with peat soils, in most streams DOC concentrations can easily range between 1 and 8 mg/L (Figure 1-12).

[24] Scott, et al. (2006). Localized erosion affects national carbon budget. *Geophysical Research Letters 33(1)*.

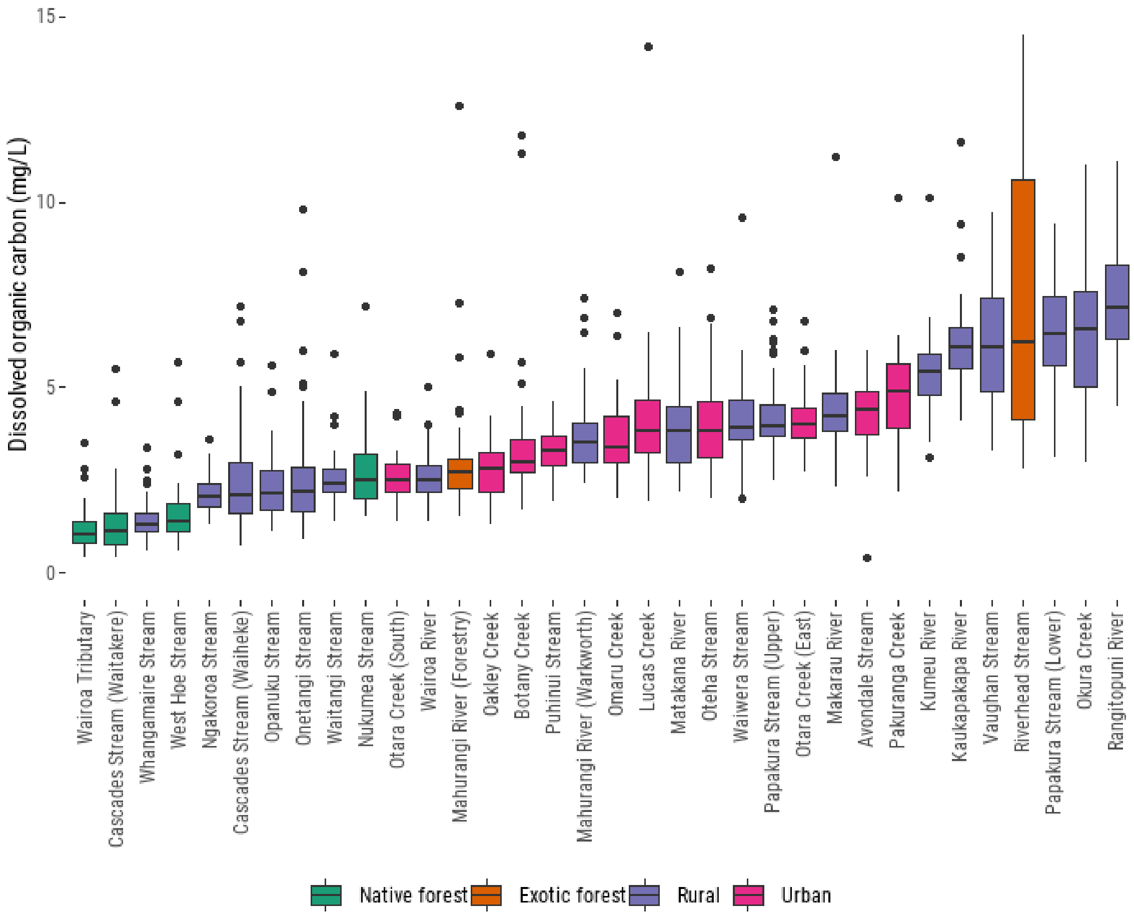

Figure 1-12: Variation in DOC concentrations between and within stream sites in the Auckland region sampled monthly between November 2017 and June 2021. Stream sites are ordered by increasing median concentrations (indicated by the horizontal black line within each box) from left to right and are coloured by land cover category. Data supplied by Auckland Council.

Similarly, water hardness depends on local geology (for example hardness is frequently >200 mg/L in Hawke's Bay streams), and is also influenced by other factors. In some regions, hardness can be lower in forested and rural streams and higher in urban streams where there is substantial contact with concrete surfaces (e.g., bridges, pipes, channelised or stabilised stream beds and banks). For example, hardness tends to be higher in urban streams in the Auckland Region (Figure 1-13), varying more than 2- or 3-fold between sites.

Stream pH can also be related to local geology (for example, being higher in areas with limestone geology and higher hardness) but is also influenced by other factors including catchment vegetation (especially forests) and the presence of photosynthesising organisms. In the monitored streams in the Auckland Region pH followed a similar pattern to hardness, being generally higher in urban streams.

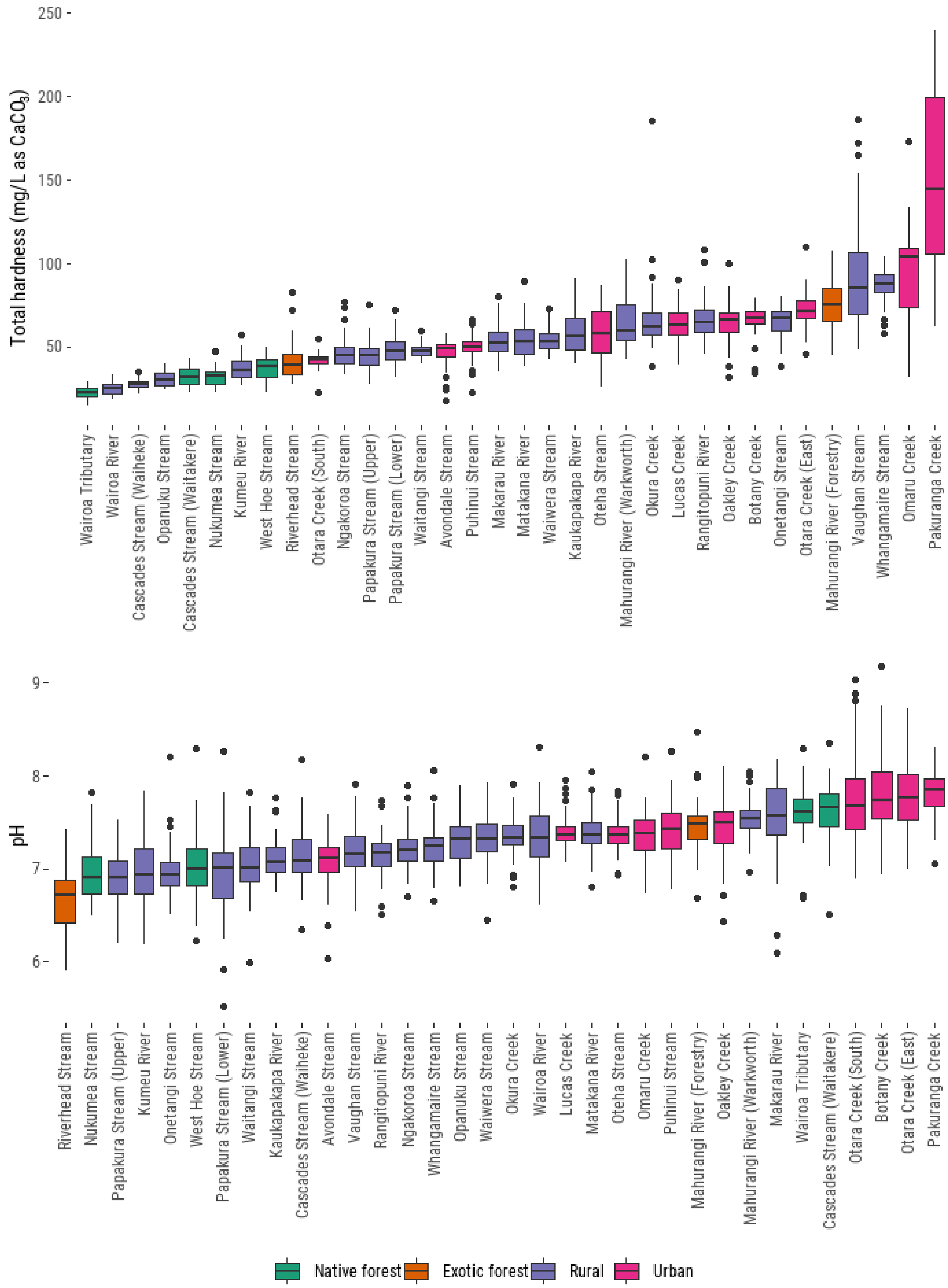

Figure 1-13: Variation in hardness (top) and pH (bottom) between and within stream sites in the Auckland region sampled monthly between November 2017 and June 2021. Stream sites are ordered increasing median values (indicated by the horizontal black line within each box) from left to right and are coloured by land cover category. Data supplied by Auckland Council.

Within the observed DOC range, copper DGVs may range more than 7-fold – from 0.93 to 7.1 µg/L for the DGV for protection of 95% species. The range in hardness of 2- or 3-fold between sites can result in DGVs that are up to 1.5-fold lower or higher. These adjustments can result in a marked difference between measured copper or zinc concentrations being above or below bioavailability-adjusted DGVs. For that reason, a conservative estimate of the TMF is recommended.

The recommended approach for sites with no data is:

- Collate data from sites with characteristics broadly similar to those at the site of application. Consider aspects such as geology, catchment land use and stream order.
- Select data from stream samples collected under similar conditions to the metal sample, in terms of season and flow.
- Calculate the 10th percentile for hardness and/or DOC and the 90th percentile for pH, and use these values to calculate a bioavailability-adjusted DGV. Note that with small data sets there is likely to be high uncertainty around a 10th or 90th percentile.

A 10th percentile (90th for pH) is recommended for this option to provide a conservative DGV. The additional conservatism (compared to the 25th percentile recommended when using data specific to a site) is due to the additional uncertainty when extrapolating TMF measurements across sites. A 10th percentile is also recommended by the US EPA for use in calculating bioavailability-based metal GVs[25].

There remains potential for sites to have lower values for hardness and DOC and higher values for pH than the value selected for DGV adjustment – hence this approach is best used for screening multiple sites to broadly assess risks and identify where further data is required. It is expected that DGVs calculated using this approach will be less conservative than a tier 1 DGV, making it potentially be more useful for screening purposes.

If there are site and sample event data for potential surrogates such as electrical conductivity (EC), then that data could be used to estimate hardness. A relatively strong relationship exists between hardness and electrical conductivity (EC) in most NZ streams (Figure 1-14). In the absence of local hardness data, an estimate of 10th percentile of hardness based on local EC data (using Equation 3) could be used as a conservative estimate.

[25] US EPA (2022). User Manual and Instructions for Metals Aquatic Life Criteria and Chemistry Map (MetALiCC MAP). EPA-822-B-22-001. October 2022. Office of Water, Washington, DC.

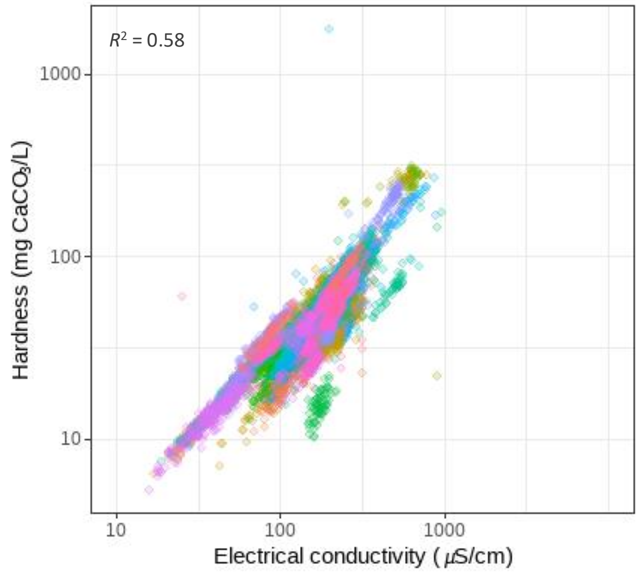

Figure 1-14: Relationship between hardness and electrical conductivity at various sites across NZ. Different colours relate to different sites. Data provided by councils.

$$Estimated\ hardness = 5.5 + 0.15 * \ Electrical\ conductivity \quad \textbf{Equation 3}$$

Hardness in mg $CaCO_3$/L, electrical conductivity in μS/cm

However, there are a number of sites where this relationship is not applicable – with site-specific factors that influence that relationship. For example, rivers close to the coast may have lower hardness for a given EC if EC is influenced by sodium and chloride ions (delivered via rainfall with oceanic influences or via saline groundwater inputs). This is illustrated in Figure 1-14 where, although there is a clear relationship between EC and hardness, there are several sites (lower right, in green) that do not exhibit the same relationship as the bulk of the sites. It is not possible to tell whether a new site would conform to that relationship without measuring hardness and EC. It is therefore recommended that both hardness and EC are measured multiple times to check whether the Equation 3 is applicable.

Where the national relationship is shown to not be applicable, a site-specific relationship would likely need to be derived. The number of samples (and data points) required to derive that relationship would depend on the variability (and range). Our recommended approach is to assess the relationship between hardness and EC as samples are collected, and to continue sampling until a site-specific relationship is developed that a) covers a suitably broad range of values and b) has a correlation with an acceptable degree of certainty.

1.7 Estimating TMFs for toxicity assessments with modelled copper and zinc

There are many possible situations where practitioners or resource managers may wish to compare copper and/or zinc concentrations predicted from a model(s) with DGVs. Examples include assessing the risks associated with metal concentrations downstream of a proposed future discharge and predicting the likely effects of land use change with increased stream metal concentrations. The DGVs can be used with predicted copper and zinc concentrations to assess potential toxicity – however this assessment is complicated by the incorporation of TMFs in the DGVs.

Hardness, pH and DOC may not be easily predicted using the same models as used for predicting copper and zinc (for example, catchment-scale process-based models). Yet, using a "high bioavailability" DGV across all sites (and times) may not be informative, and DGVs adjusted to the water chemistry would be preferable. Other methods, such as statistical methods, may be needed to estimate TMF values to adjust DGVs for a screening level assessment based on predictions of copper and zinc. Regardless of the method used to estimate TMF values (whether statistical or process-based), consideration should be given to factors such as flow conditions, seasons, and differences in land use. TMFs should be selected from a dataset based on samples collected under similar conditions (e.g., for modelling of storm events, using data from samples collected at high flows). The process for selecting TMF values for adjustment of DGVs should be clearly documented along with any assumptions made in that selection.

1.8 Metal and TMF measurement methods

The National Environmental Monitoring Standards (NEMS)[26] for Discrete Water Quality set out standard methods for collecting, storing, transporting and analysing water samples for copper, zinc, pH, hardness and DOC in fresh water [27]. These are reproduced in Table 1-7.

Determination of dissolved copper and zinc requires water samples to be filtered prior to analysis. Laboratory-based filtration is generally more convenient and reduces the risk of contamination introduced in the field (particularly for zinc analyses). However, samples can also be filtered in the field to ensure that the dissolved concentrations do not change during storage (i.e., due to partitioning onto, or dissolution from solids). Field filtration should be considered when there is a long delay between sampling and analysis (>36 hours), where dissolved metal concentrations are expected to be very low and close to the DGVs, and where field staff are trained in the field filtration methods.

[26] https://www.nems.org.nz/

[27] NEMS (2019). Water Quality Part 2 of 4: Sampling, Measuring, Processing and Archiving of Discrete River Water Quality Data. *National Environmental Monitoring Standards*. https://www.nems.org.nz/documents/water-quality-part-2-rivers/

Table 1-7: Summary of NEMS recommended methods for sample handling and measurement for metals and toxicity modifying factors.

	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, then analysis by ICP-MS (APHA 3125 B)	0.5*
Dissolved zinc			1*
Dissolved calcium		Filtration, then analysis by ICP-MS (APHA 3125 B) or ICP-AES (APHA 3120 B)	50
Dissolved magnesium			20
Hardness (as $CaCO_3$)	Not applicable	Calculated from Ca and Mg (APHA 2340 B)	1000
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 †
DOC	Unpreserved and furnaced brown/amber glass bottle filled with no air gap; sample kept cool (<10°C). Samples should be filtered within 36 hours of collection.	Filtration (ideally using glass fibre filter), then purging to remove inorganic carbon followed by analysis via persulfate-heat or UV-oxidation then (APHA 5310 C)	300

Note: * For waters with very high bioavailability (low DOC, low hardness, high pH) DGVs may be slightly lower than these recommended detection limits and lower detection limits (i.e., ultra-trace analyses) may be required for measurements on samples from pristine waters. † Represents a resolution rather than a detection limit.

1.9 Developing site-specific GVs

Where/if the DGVs are not applicable because the TMFs are consistently outside the applicable range (Table 1-5), or the composition of aquatic species is markedly different from those used to derive the DGV, site-specific GVs can be derived. An example where this may be relevant is in West Coast forest streams.

Detailed guidance on deriving site-specific (or site-adapted) GVs is provided in ANZG (2018; https://www.waterquality.gov.au/anz-guidelines/guideline-values/derive) and also in van Dam et al. (2019). There are several examples from Australia where site-specific GVs have been derived (largely within a mining context) where the DOC, hardness or pH is outside the range for DGVs. Recent examples include the site-specific guideline values derived for copper, zinc and uranium for use at the Ranger uranium mine in the Northern Territory[28]. This mine is located in an area of high conservation value (World Heritage site and a Ramsar site) and surface waters have low pH and very low hardness and alkalinity and hence high potential metal bioavailability. The process to derive site-

[28] https://www.dcceew.gov.au/sites/default/files/documents/copper-zinc-surface-water-rehab-standard-ranger-uranium-mine.pdf

specific GVs for this site included undertaking toxicity testing on relevant tropical aquatic species in waters with very low hardness, similar to the receiving waters.

Alternatively, direct toxicity assessment (DTA) can be used to directly assess the toxicity of a discharge/contaminant under local conditions (e.g., local or regionally relevant species in local waters). Guidance on DTA is provided by ANZG.[29]

1.10 Frequently Asked Questions

This section includes key questions asked by councils involved in using water quality guideline values.

Question 1.1 Are the draft copper and zinc DGVs relevant to my location? What native species are included?

The draft DGVs for copper and zinc are **highly relevant** to NZ because they were derived from datasets that include species native to NZ (Table 1-8). Data were also included for numerous species native to Australia, some of which may be related to NZ species, for which we do not have toxicity data. Species from outside of NZ were also used in the DGV derivation to increase the diversity of species included and improve the protection of whole ecosystems. In contrast, water quality GVs from other jurisdictions, particularly North America, may only include species found in those regions and are therefore less applicable to NZ.

Table 1-8: NZ native species included in the draft DGVs for dissolved copper and zinc[30] in fresh water.

	Native species included in the draft DGVs	
Species type	**Copper**	**Zinc**
Fish	Inanga *(Galaxias maculatus)* Common bully *(Gobiomorphus cotidianus)*	None
Crustacea	Water flea (*Ceriodaphnia dubia**) Water flea (*Daphnia thomsoni*) Amphipod *(Paracalliope fluviatilis)* Koura/freshwater crayfish *(Paranephrops planifrons)*	Water flea (*Ceriodaphnia dubia**) Water flea (*Daphnia thomsoni*)
Molluscs	Kākahi *(Echyridella menziesii)*	Kākahi *(Echyridella menziesii)*

[29] ANZG (2023). Guidance on the use of ecosystem receptor indicators for the assessment of water and sediment quality, 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.

[30] Anon (2023). Toxicant default guideline values for aquatic ecosystem protection: Copper in fresh water - DRAFT. Unpublished report under development for Australian and New Zealand Guidelines for Fresh and Marine Water Quality. Submission not intended for public distribution. July 2023. ; Anon (2023). Toxicant default guideline values for aquatic ecosystem protection. Zinc in fresh water - DRAFT. Unpublished report under development for Australian and New Zealand Guidelines for Fresh and Marine Water Quality. Submission not intended for public distribution. April 2023.

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		NZ mud snail *(Potamopyrgus antipodarum)*
Cnidaria	Green hydra *(Hydra viridissima)*	
Green algae	*Chlamydomonas reinhardtii ** *Chlorella* species* *Raphidocelis subcapitata**	*Chlorella* species* *Raphidocelis subcapitata**

Note: *Organisms used in testing overseas may be different sub-species to that found in NZ.

Some of the species that are native to NZ and Australia are found at the sensitive end of the ranked sensitivity of species used in deriving the DGVs (Figure 1-15). However, there are also species found outside of NZ that are as sensitive and native species that are at, or towards the insensitive end of that range. There are no clear differences between species native to NZ and those found elsewhere. This means it is relevant to include species found outside of NZ to increase the number of species included in the DGV derivation.

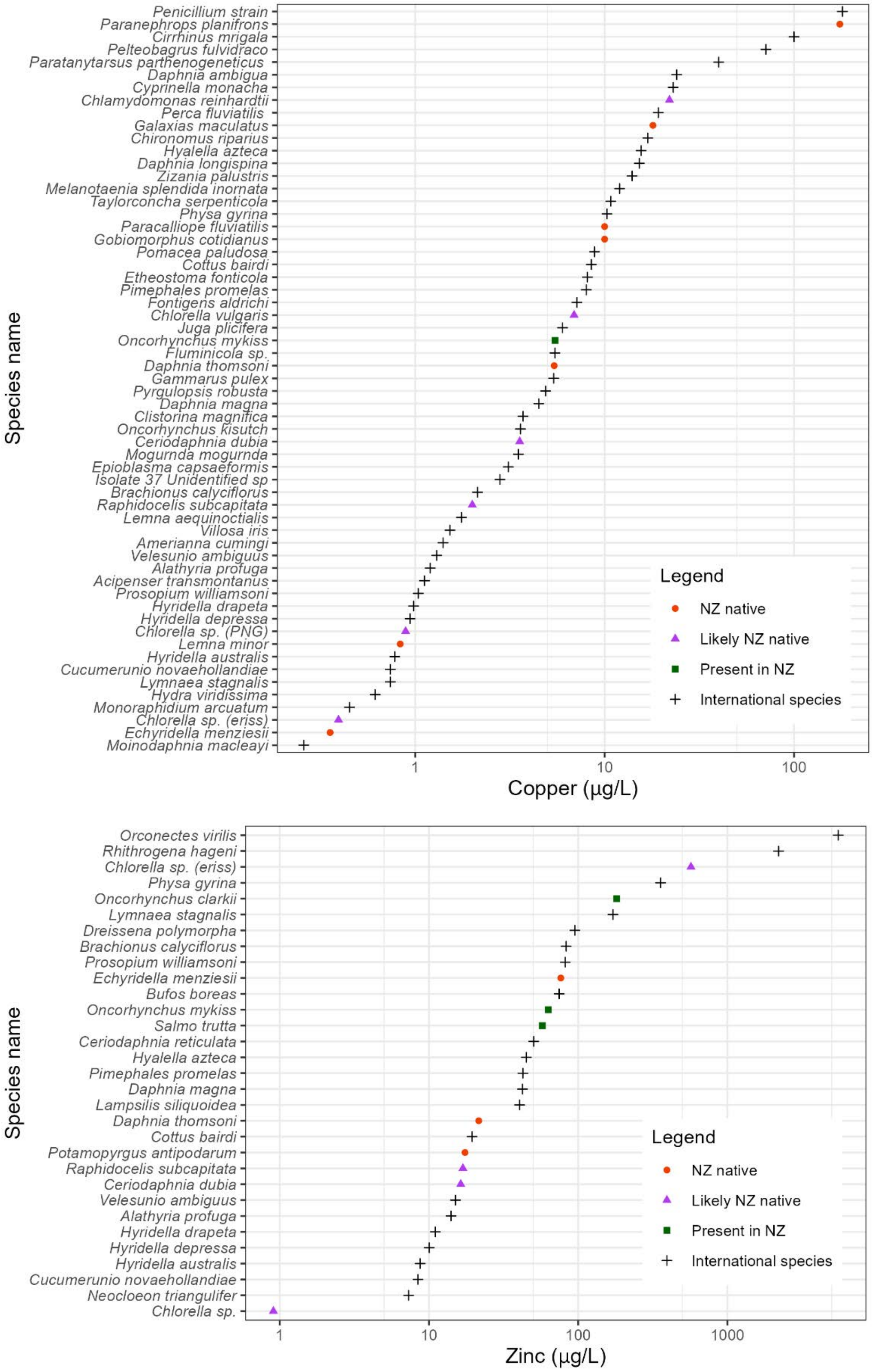


Figure 1-15: Comparison of native and international species' toxicity data used in deriving the draft DGVs for dissolved copper (top) and zinc (bottom) in fresh water.

Question 1.2 What form of copper and zinc should I compare against the DGVs?

The draft copper and zinc DGVs are based on the concentration of **dissolved** metals, defined as the concentration remaining after filtration of the water sample through a 0.45 µm pore filter. It is this fraction that is likely to contain the highest proportion of bioavailable metal.

Acid-soluble, total recoverable and total metal concentrations are typically much higher than dissolved concentrations and are measured by digesting a water sample with acid (ranging from weak to strong acids) without filtration. These measurements therefore include metals that are attached to particulate matter and are less bioavailable to aquatic organisms. Acid-soluble, total recoverable and total metal concentrations can be compared against the DGVs, but exceedance of a DGV is more likely and does not mean there is necessarily a risk of toxicity to aquatic life. This conservative approach could be used where no dissolved metal data are available.

In some cases, different filter pore sizes have been used to determine "dissolved" metals. For example, filtration with glass fibre filters (GF/F) which have a nominal pore size of 0.7 µm, or membrane filters with pore size of 0.22 µm. While measurements made using these different pore sizes would be generally comparable to the water quality DGVs, standardisation to filtering at 0.45 µm is recommended. This is also a NEMS requirement.

The bioavailable fraction of a metal can also be compared with the tier 1 DGVs. This fraction could be established through calculation for copper (as described in section 1.2) and in the future, for zinc; or metal speciation modelling (such as WHAM[31] or MINTEQ[32]). Alternatively, it can be established through measurements, such as the use of DGTs[33] in the field, or by passing the water sample through a Chelex column[34] in the laboratory. Bioavailable metal concentrations should not be compared to adjusted-DGVs – the effect of TMFs is already accounted for by calculating or measuring the bioavailable metal fraction.

Question 1.3 Do you have to measure all TMFs each time copper and zinc are sampled?

The most robust assessment of toxicity requires measurements of pH, hardness and DOC in each sample analysed for copper and zinc because, as already established, these water quality variables tend to vary across time, even at the scale of an individual site. For example, hardness and DOC can vary by a factor of two depending on flow and season respectively. However, alternative approaches are provided where sample-specific TMF data are not yet available (Figure 1-1, and see section 1.3). Also see Question 1.6.

Question 1.4 Do you have to measure TMFs at each monitoring site?

The most robust assessment of toxicity requires measurements of pH, hardness and DOC at each monitoring site because these water quality variables tend to vary between sites (see section 1.6). If

[31] Tipping. (1994). WHAM - a chemical-equilibrium model and computer code for waters, sediments, and soils incorporating a discrete site electrostatic model of ion-binding by humic substances. *Computers & Geosciences 20(6)*: 973-1023.

[32] Brown. (1987). MINTEQA1, Equilibrium metal speciation model; A user's manual. *EPA/600/3-87/012*.

[33] Diffusive gradients in thin films, a type of passive sampler. Davison and Zhang. (1994). In situ speciation measurements of trace components in natural waters using thin-film gels. *Nature 367(6463)*: 546-548.

[34] Bowles, et al. (2006). A rapid Chelex column method for the determination of metal speciation in natural waters. *Analytica Chimica Acta 558(1)*: 237-245.

site-specific data are not available, a conservative estimate of the DGV should be used. Also see Question 1.6.

Question 1.5 What if TMF data are missing on some sampling occasions?

In some circumstances individual TMF data may be missing or were considered unreliable (e.g., a sample bottle broke during transport, or a pH meter failed calibration or validation). In this case, there are three options, each with different implications:

- Compare the copper and zinc concentrations for the affected sampling date to the tier 1 (interim for zinc) DGV. This will likely be very conservative and may result in that sample measurement exceeding the DGV, when it would not have if it had been compared to an adjusted DGV.
- Omit the copper or zinc measurements for dates on which TMF data are missing when assessing compliance with DGV. As this option will reduce the amount of data available for compliance and statistical comparisons, depending on how many samples are affected, it may not be acceptable. With this method there is also a potential risk of data being conveniently "lost" for sampling dates and times where metal concentrations are higher than usual.
- Estimate the TMF value for that sampling date/site. This option would be suitable where there are sufficient data are available to estimate that TMF for that particular site and under similar conditions (season, flow). If this option is used the TMF estimates should be conservative (e.g., a 25th percentile of the previously measured data, as explained in section 1.4) and a note included in the documented assessment that the guideline comparison is based on estimated TMF data and is therefore indicative only.

Where there are few missing data, option 2 is recommended. Option 3 is recommended for most circumstances as this is a middle-of-the-road option that uses the available data.

Question 1.6 Does use of these DGVs mean TMFs must be monitored indefinitely?

Measuring TMFs every month at all sites in a SOE or other long-term monitoring programme increases monitoring costs. A pragmatic approach would be to periodically assess the range in each TMF at each site as monitoring continues. The monitoring period needs to include a range of different stream flow and seasonal conditions to provide a representative data set for the TMFs and how they change over time. In Auckland, a five-year monitoring period has been shown to provide observations that generally represent the flow distribution[35] – this period may also be sufficient in other regions.

If a TMF estimate from an historic data set is to be used in future assessments of copper or zinc toxicity, use a 25th percentile for DOC and hardness and a 75th percentile for pH to provide a sufficiently conservative toxicity assessment. Under this scenario, the comparison would be considered a screening level-assessment. This represents a trade-off, where the monitoring costs are

[35] Snelder and Kerr (2022). Relationships between flow and river water quality monitoring data and recommendations for assessing NPS-FM attribute states and trends. Prepared for Auckland Council by LWP, Land Water People. October 2022.

lower, but the DGV may be more conservative than one derived from sample-specific data, and there is an increased risk of measured concentrations exceeding the DGV.

When upstream catchment (or riparian) characteristics change, it would be prudent to reinstate monitoring for a period of time (e.g., two years), to establish whether the TMFs have changed. If so, the new dataset should be used in future estimates of TMF values for calculating DGVs. Catchment changes that may affect TMFs include changes in land use (e.g., extensive residential infilling resulting in higher impervious surfaces), and cessation (or addition) of point source discharges.

Question 1.7 What do I do when TMFs are out of range of the DGV specifications?

There may be locations where the water chemistry is consistently outside of the range in which the copper and zinc DGVs apply (refer Table 1-5). For example, a humic-stained brown-water West Coast stream may consistently have DOC concentrations above 15 mg/L and a stream affected by acid mine drainage would have a pH less than 6[36]. In such cases, the bioavailability models used to derive the DGVs may not be valid and site-specific GVs may need to be derived (see section 1.9).

When the TMF values are generally within the applicable range for the DGVs, but only occasionally outside, DGVs could be used with some caveats (Table 1-9). DGVs should be adjusted using estimates for the TMFs that are within the applicable range, and should provide a conservative (that is, protective) indication of risk. When TMFs are outside the applicable range and a DGV is calculated this way, that should be documented in any reporting. DGVs should NOT be calculated using TMF values outside of the ranges specified (e.g., for a DOC of 40 mg/L) because it is not possible to verify whether the DGV would be protective outside this range.

Table 1-9: Strategies to calculate GVs when TMFs are outside the suitable range for application of copper and zinc default GVs for fresh water.

Scenario	Action	Interpretation
Hardness exceeds upper limit for zinc	Use DGV calculated from hardness of 440 mg $CaCO_3$/L	DGVs may be conservative
Hardness less than lower limit for zinc	Use DGV calculated from hardness of 20 mg $CaCO_3$/L	DGVs may not be protective – use with caution
DOC exceeds upper limit for copper and/or zinc	Use DGV calculated from DOC of 30 mg/L for copper and 15 mg/L for zinc	DGVs may be conservative
pH is less than lower limit for zinc	Use DGV calculated from pH of 6.2	DGVs may be conservative
pH is more than upper limit for zinc	Use DGV calculated from pH of 8.3	DGVs may not be protective – use with caution
pH is outside the range for copper	Compare copper concentrations to DGV based on DOC	DGVs can be used, but adverse effects may occur as a direct result of the low or high pH

[36] Harding, et al. (2000). Effects of mining and production forestry. *In*: Collier and Winterbourn (eds). New Zealand stream invertebrates: Ecology and implications for management, pp. 230-258. New Zealand Limnological Society, Christchurch.

Question 1.8 What if a measured metal concentration is below the laboratory's method detection limit?

Metal concentrations in waterbodies may be below the limits of detection recommended by NEMS for dissolved copper and zinc (Table 1-7). These values are known as censored data. Further, there can be times when coarser detection limits are used due to sample characteristics (like high salinity), which can also result in censored data. Methods for dealing with censored data (other than methods like substituting the limit of detection or half of the detection limit) are well advanced[37], and have been widely used in NZ in assessing state and trends[38]. While there is less guidance on how to compare censored values to DGVs under these conditions, the assessment is simple when the detection limit is lower than the DGV – it can be concluded that the metal concentrations are below the DGV and there is low risk of toxicity (at the level of protection of the DGV used).

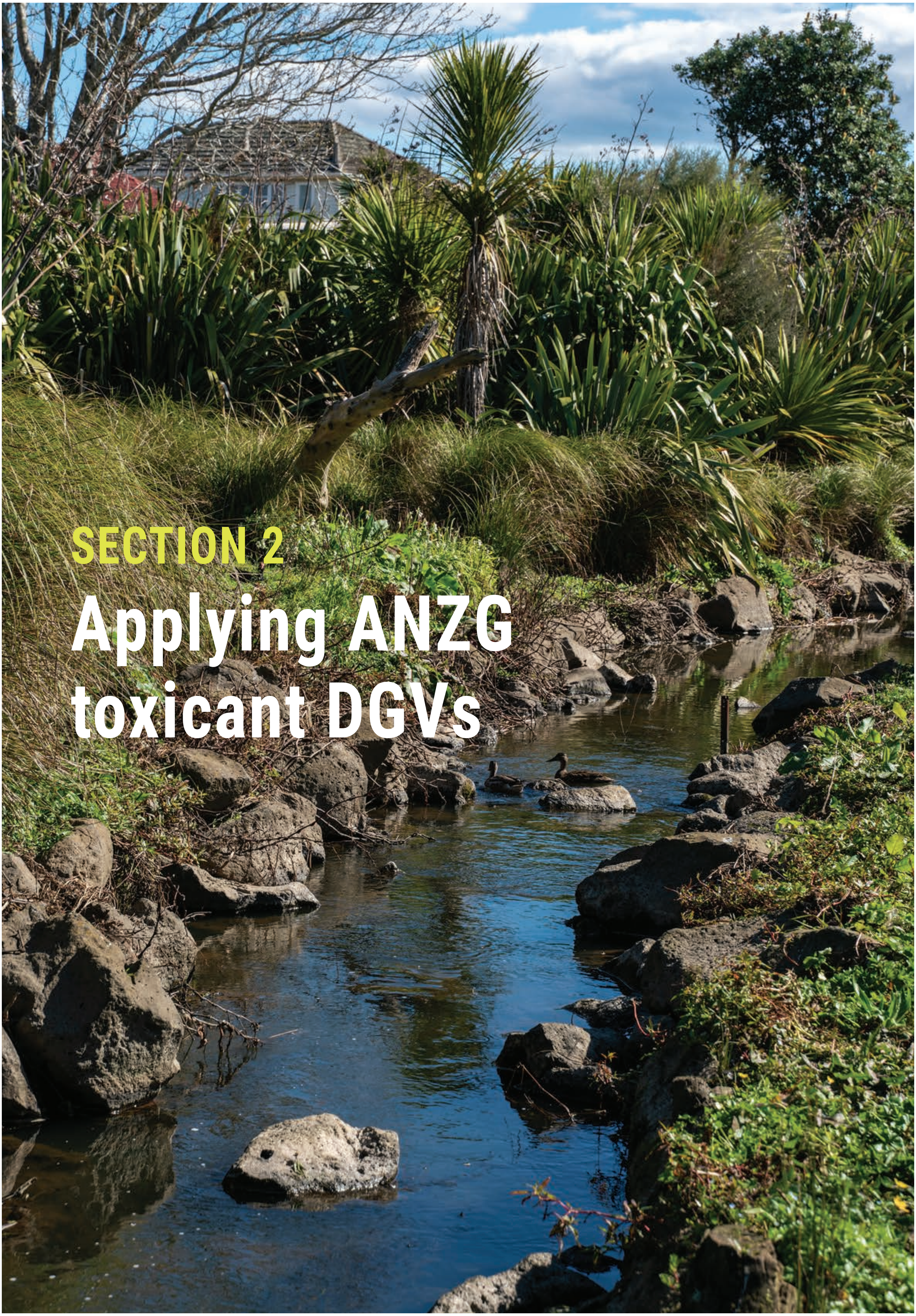
There may be cases where the detection limit is higher than the DGV. The DGV for copper for protection of 95% of species at DOC of 0.5 mg/L (0.47 µg/L) is slightly lower than the limit of detection recommended by NEMS for dissolved copper (0.5 µg/L). The DGV for protection of 99% of species (0.2 µg/L) is less than half that. Under high bioavailability conditions and with high levels of protection (i.e., 99%) it is also possible that some zinc DGVs would be below the NEMS recommended (minimum) method detection limit of 1 µg/L. In these cases, if dissolved copper and zinc are detected, the DGV can be assumed to have been exceeded. However, if dissolved copper or zinc are below detection it will be impossible to conclude whether a DGV has been exceeded or not. In such cases it will be impossible to conclude whether a DGV has been exceeded or not. This could be considered a special type of censored data and statistical methods to account for this are available[37]. In cases where there is a need to assess whether there have been changes over time in the exceedance of DGVs, a statistician should be consulted. These data should be included in any trend assessment as ignoring them could lead to incorrect conclusions about changes over time. When the NEMS recommended detection limits are followed, there should be few cases where detection limits are above DGVs.

[37] Helsel (2012). Statistics for censored environmental data using Minitab and R. New York, Wiley. Snelder, et al. (2021). Guidance for the analysis of temporal trends in environmental data. National Institute of Water and Atmospheric Research Ltd and Land Water People Ltd (LWP) *NIWA Client Report 2021017WN*. April 2021. National Institute of Water and Atmospheric Research Ltd,

[38] Whitehead, et al. (2022). Water quality state and trends in New Zealand rivers: analyses of national data ending in 2020. Ministry for the Environment *NIWA Client Report*. 2021296CH. February 2022.

SECTION 2

Applying ANZG toxicant DGVs



Section 2: Applying ANZG toxicant DGVs

2.1 Applicability of ANZG toxicant DGVs to receiving waters and discharges

KEY POINTS:

ANZG TOXICANT DEFAULT GUIDELINE VALUES

- **REPRESENT THE CURRENT BEST ESTIMATES OF CONCENTRATIONS THAT CAN BE USED TO ASSESS POTENTIAL FOR ADVERSE TOXIC EFFECTS ON AQUATIC LIFE**
- **ARE APPLICABLE TO FRESH WATER AND COASTAL WATER RECEIVING ENVIRONMENTS (BUT CAN BE USED IN OTHER CONTEXTS WITH CAVEATS, SEE TEXT)**
- **SHOULD BE USED WITH OTHER LINES OF EVIDENCE, USING A WEIGHT-OF-EVIDENCE APPROACH**

The ANZG DGVs provide for different levels of protection, appropriate to different levels of ecosystem condition, community or freshwater management objectives. The most commonly applied DGVs are those for protection of 95% of species, which is usually recommended for slightly to moderately disturbed (modified) systems.

The DGVs are intended to be applied to **receiving waters** for aquatic ecosystem protection. They are not designed for use as “end of pipe” compliance standards on contaminant discharges such as wastewater or stormwater[39].

The DGVs should be applied in receiving waters downstream of the point of discharge after “reasonable mixing” of the contaminants in the discharge with the receiving water. The term “reasonable mixing” originates from the Resource Management Act (RMA) 1991 and refers to the length of mixing (i.e., distance downstream) after which receiving water quality guidelines or standards are to apply. Reasonable mixing is typically determined by the relevant regional or unitary council on a case-by-case basis for discharges that are authorised by a resource consent. For discharges classified as permitted activities (i.e., not requiring a resource consent), a regional plan may define the length of the mixing zone over which reasonable mixing must occur. For more commentary and guidance on mixing zones and reasonable mixing, see the review by Cooke et al. (2010), including page 36 in relation to stormwater discharges.

In terms of the planning and policy use of ANZG guidelines, the DGVs can be used for: assessing environmental state under State of the Environment (SOE) reporting; within regional plans as receiving water standards; and for consenting of industrial, wastewater and stormwater discharges (for example, in assessments of environmental effects or as consent limits in the form of instream toxicant concentrations that should not be exceeded downstream of a discharge).

The framework for ANZG (2018) emphasises that DGVs should be used within a weight-of-evidence approach[40], including other lines of evidence to assess the effects of water quality on ecosystem receptors. These lines of evidence may include measurement of metals within stream bed sediment; assessing alterations in flow; in situ or laboratory-based toxicity tests; assessing bioaccumulation or

[39] DGVs can and have been used to calculate end-of-pipe compliance standards that allow for receiving water dilution (see Question 2.1).
[40] https://www.waterquality.gov.au/anz-guidelines/resources/key-concepts/weight-of-evidence

biomarkers of exposure or effect; assessing biotic assemblages or abundance of specific species (e.g., mayflies). An example of a biotic assemblage is the EPT taxa metric[41] (percentage of macroinvertebrate species in the orders Ephemeroptera (mayflies), Plecoptera (stoneflies) and Trichoptera (caddisflies)) which is considered a better indicator of toxic effects of metals than other invertebrate metrics. The ANZG (2018) website describes the weight-of-evidence approach in detail, including how to select and then acquire different lines of evidence, how to rate the quality of that evidence, how to evaluate each line of evidence, and combine the multiple lines of evidence in qualitative and quantitative assessments. The weight-of-evidence approach provides greater confidence in the conclusions of effects assessments — and therefore greater confidence any subsequent need for management decisions.

Question 2.1 Can I apply the ANZG DGVs to stormwater discharges?

The ANZG toxicant DGVs are **not** designed to be applied to end-of-pipe stormwater (or other) discharges. However, we note that there have been examples where the DGVs (or trigger values, based on ANZECC & ARMCANZ 2000) have been used as limits within resource consent conditions. Although that is not their intended purpose, if they are used in that way, **the DGVs would be conservative**, i.e., if they are not exceeded, there would be high confidence that the ecosystem was being protected. However, if the DGVs are exceeded, this does not mean that adverse effects are likely.

In some locations the DGVs have been applied to discharges after accounting for dilution in the receiving water after initial or reasonable mixing– for example if there is at least 10-fold dilution, then the DGV can be multiplied by 10 for comparison to the discharge[42]. Assessing dilution may not be easy for stormwater discharges where flow rates change rapidly and/or mixing in the receiving waters is variable. Furthermore, use in this context may be more complicated with bioavailability-based DGVs, as discharges may change pH, or concentrations of DOC or hardness in the receiving waters.

The DGVs are applicable to **receiving waters that receive stormwater discharges**, but may not be appropriate for assessing the potential effects of single, short pulses of stormwater that contain high toxicant concentrations (see sections 2.3 and 2.4).

[41] Iwasaki, et al. (2018). Quantifying differences in responses of aquatic insects to trace metal exposure in field studies and short-term stream mesocosm experiments. *Environmental Science & Technology 52(7)*: 4378-4384.

[42] See for example coastal discharge permit for Porirua Wastewater Treatment Plant https://www.wellingtonwater.co.nz/assets/WGN200229-Coastal-Discharge-Permit-Conditions-of-Consent-1408-CMA.pdf

2.2 Applicability of ANZG toxicant DGVs for different types of exposures

KEY POINTS:

- **ANZG DGVs are based on chronic exposure, which generally means several days to months**
- **This makes them suitable for state of the environment assessment**
- **The DGVs will be conservative (protective) if applied to copper and zinc data from samples that represent short-term (e.g. <3 days) exposures to higher concentrations**

All toxicant DGVs provided by ANZG (2018) are based on chronic (long-term) exposures, which are defined as “a period of time that is a substantial portion of the organism’s life span or an adverse effect on a sensitive early life stage.”[43] The guidance also states that “A substantial portion of an organism’s life span would typically be greater than 10%”[44]. Warne et al. (2018) also specify the duration of a toxicity test for different types of organisms (Table 2-1). These range from >24 hours for single-celled organisms (in practise this means a 48-hour test) to at least 21 days for fish and amphibians (usually meaning a 21–28-day test). Tests using early life stages including gametes or embryos have a shorter duration than those performed on other life stages (e.g., juveniles, adults) as these life stages typically last a short time but are very important in terms of an organism’s development. For many plants and animals with short generation times, a chronic exposure period can still represent a relatively short period of time (i.e., in the order of days rather than months).

[43] 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. August 2015 - updated October 2018. Canberra.

[44] Newman. (2010). Acute and chronic lethal effects to individuals. *In*: Fundamentals of Ecotoxicology, pp. 247–272. CRC Press, Boca Raton, Florida, USA.

Table 2-1: Classification of chronic toxicity tests for temperate species. Adapted from Warne et al. (2018).

Toxicity test	Life stage at test initiation	Relevant endpoints	Test duration
Fish and amphibians	Adults/juveniles	All[a]	≥21 days
	Embryos/larvae/eggs	All	≥7 days
Macroinvertebrates [b]	Adults/juveniles/larvae	All (except reproduction, larval development/metamorphosis/fertilisation)	≥14 days
	Adults/juveniles/larvae	Reproduction	≥14 days
	Embryos	Larval development/metamorphosis	≥48 hours
	Gametes	Embryo fertilisation	≥1 hour
Microinvertebrates [c]	Adults/juveniles/larvae	Reproduction	≥7 days
	Adults/juveniles/larvae	Lethality/immobilisation	≥7 days
	Embryos	Larval development	≥48 hours
	Gametes	Embryo fertilisation	≥1 hour
Macrophytes	Mature	All	≥7 days
Macroalgae	Mature	All	≥7 days
	Early life stages	Lethality	≥7 days
	Early life stages	Development	≥48 hours
	Early life stages	Fertilisation	≥1 hour
Microalgae	All	All	>24 hours
Microorganisms	All	All	>24 hours

a For chronic tests, 'All' encompasses all ecologically relevant endpoints measured in both single- and multi-generation tests.
b Macroinvertebrates include invertebrates where full-grown adults are ≥2 mm long (e.g., decapods, echinoderms, molluscs, annelids, corals, amphipods, larger cladocerans [*Daphnia magna*, *Daphnia carinata* and *Daphnia pulex*] and insect species where larvae are ≥2 mm long).
c Microinvertebrates are defined here as invertebrate species where full-grown adults are typically <2 mm long. (e.g., some cladocerans (*Ceriodaphnia dubia*, *Moina australiensis*), copepods, conchostracans, rotifer, acari, bryozoa and hydra.

The ANZG guidelines do not currently provide guidance on the duration or frequency that defines either short-term or long-term guideline values. This guidance may be provided in some countries; for example in the United States (US); they specify that a one-hour average concentration should not exceed the acute GV (called criteria in US EPA terminology) and a four-day average should not exceed the chronic GV, and that neither GV should be exceeded more than once every three years[45].

Based on the toxicity data used in their derivation, toxicant DGVs, including the draft copper and zinc DGVs will be generally applicable to water quality conditions that cover minimum periods of days (e.g., 2 days) to longer periods of weeks and months. Although some of the data included in a DGV derivation can be from studies of longer duration (e.g., 21 days) this does not mean that the DGVs are *only* applicable to these longer durations.

[45] Stephan, et al. (1985). Guidelines for deriving numerical national water quality criteria for the protection of aquatic organisms and their uses. Office of Research and Development, U.S. Environmental Protection Agency *EPA 600/53-84-099; PB85-227049*. Washington D.C.

In the absence of guidance from ANZG (2018), some indicative timeframes for applicability are provided in Table 2-2, where the chronic toxicant DGVs can be considered suitable to provide a reasonable estimation of toxicity risk.

Table 2-2: Indicative timeframes of relevance for applying ANZG toxicant DGVs.

Scenario	Example timeframe for discharge	Suitability for application of ANZG DGVs
Downstream of short-term spills	3 hours	Not suitable
Downstream of an intermittent but daily discharge	6-8 hours every day	Suitable
Downstream of continuous discharges for consent compliance	Continuous	Suitable
Downstream of stormwater discharges, data collected during storm events only	12-48 hours	Unclear, see text this section
Downstream of stormwater discharges with data collected during dry weather and storm events	Not applicable	Suitable
SOE data collected over the long-term	None	Suitable

The DGVs are *highly suitable* for assessing regional council SOE data which are typically based on water samples collected monthly and often during baseflow conditions[46]. Such data represent the conditions that organisms are exposed to most of the time.

The DGVs are *not* designed to be used for assessment of short (acute) exposure periods (e.g., from minutes and hours up to 2 days). When used in short-term assessments (in the absence of other guidelines) they will tend to be conservative. This means that if a DGV is not exceeded for a short duration discharge, there would be very high confidence that the system was being protected. However, if the DGV was exceeded, it would not be clear whether that would result in adverse effects or not. Short-term or acute GVs would be better suited for assessing short-term exposures, such as one-off events like a spill occurring for 6 hours, or an emergency discharge that lasts for up to 24 hours. The options for assessing short-term exposures are discussed in section 2.3.

In most locations and most years, stormwater discharges are *not* one-off acute events. Stormwater discharges occur multiple times per year, and often in relatively quick succession – there can be multiple rain events within a week. *Under these conditions, it is less clear whether chronic or acute guidelines would apply*. Options for assessing these intermittent discharges are discussed in section 2.4.

[46] Note that where sampling has been on-going for long enough, samples may cover a range of flows close to the full distribution. Snelder and Kerr (2022). Relationships between flow and river water quality monitoring data and recommendations for assessing NPS-FM attribute states and trends. Prepared for Auckland Council by LWP, Land Water People. October 2022.

2.3 Options for assessing potential acute toxicity of copper and zinc

KEY POINTS:

- THERE ARE NO ANZG DGVS FOR ASSESSING TOXICITY TO SHORT-TERM EXPOSURES OF COPPER OR ZINC
- TOXICITY DATA FOR INDIVIDUAL NZ SPECIES CAN BE USED IN THE ABSENCE OF ACUTE GVS
- INTERNATIONAL LITERATURE AND NZ DATA SUGGEST THAT ACUTE TOXICITY GVS WOULD LIKELY BE NO MORE THAN 5 TO 10X HIGHER THAN THE CHRONIC GVS.
- RECENT ACUTE GVS FROM THE US AND CANADA CAN BE USED (WITH SOME CAVEATS; US GVS FOR ZN SHOULD NOT BE USED)
- THE RECOMMENDED APPROACH IS TO USE ACUTE TO CHRONIC RATIOS, NZ DATA AND OVERSEAS GVS TOGETHER TO PROVIDE MULTIPLE LINES OF EVIDENCE

Short duration exposures to copper and zinc (and other contaminants) are generally associated with lower toxicity (i.e., higher LC50 estimates, Figure 2-1) and the effects (such as mortality) may occur at concentrations an order of magnitude higher than chronic DGVs[47], depending on the length of that exposure.

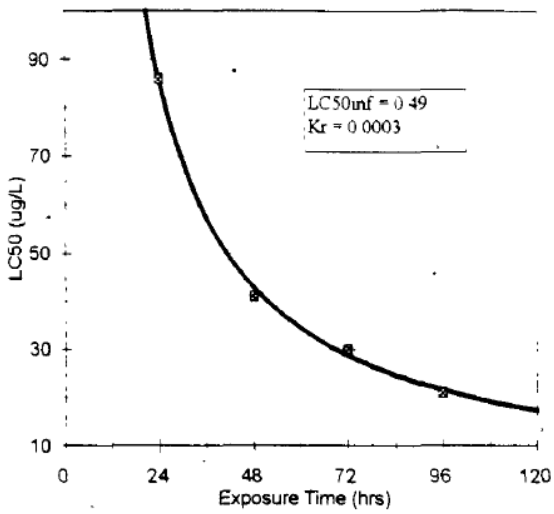


Figure 2-1: Copper toxicity versus exposure time for the freshwater amphipod *Gammarus pulex*[48]. Mortality/survival tests, conducted at hardness 100 mg $CaCO_3$/L.

There are currently no short-term or acute toxicity DGVs provided by ANZG (2018). However, the toxicant GV derivation method (Batley et al. 2018) provides some guidance on how to derive acute GVs; and acute GVs for chlorine in marine waters have been developed following this process[49]. In brief, acute GVs are derived from toxicity tests undertaken over short-term exposure durations (in

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[47] Stone, et al. (2021). The effects of pulse exposures of metal toxicants on different life stages of the tropical copepod Acartia sinjiensis. *Environmental Pollution 285*: 117212.

[48] US EPA (1995). Speed of action of metals acute toxicity to aquatic life. United States Environmental Protection Agency *EPA-822-R-95-002*. No time-response data available for amphipod response to zinc.

[49] Batley and Simpson. (2020). Short-Term Guideline Values for Chlorine in Marine Waters. *Environmental Toxicology and Chemistry 39(4)*: 754-764.

the order of hours, but up to 7 days for larger organisms and up to 21 days for adult and juvenile fish). These toxicity tests may be either lethal or sub-lethal (e.g., reproduction or growth). The toxicity estimates (i.e., EC10[50] values) recommended by ANZG (2018) to derive a short-term GV are the same type as those used to derive chronic toxicity DGVs[51].

This approach means that short-term GVs under ANZG (2018) are thresholds that indicate **protection** from adverse effects[52]. Therefore, if a short-term exposure concentration for a particular metal is below its corresponding short-term GV, no unacceptable effects would be expected.

Short-term toxicity GVs could be developed for copper and zinc in the future (see Appendix A for an overview of the steps that would be required). For both metals there is a clear understanding of the mechanisms of toxicity, there are sufficient toxicity data, and suitable models exist to adjust that toxicity data to account for toxicity modifying factors.

In the absence of ANZG acute toxicity GVs for copper and zinc, there are three options to assess potential toxicity associated with short duration discharges: compare with acute toxicity data for native NZ species, use estimated GVs based on acute to chronic ratios and use GVs from other jurisdictions. A suggested framework for this approach is provided in Figure 2-2. In the fourth step, the chronic DGVs are used to assess potential for toxicity. This framework could also be used in the opposite direction, to first screen sites with low risks of toxic effects. Each of the other three options can be used as a separate line of evidence in a weight-of-evidence approach to assess the potential toxicity risks. However, all three options, described in turn below, need careful consideration in their application.

[50] EC10 values are effect concentrations (ECs) estimated to produce a 10% change in the response being measured, or an effect in 10% of the test organisms.

[51] The only difference between the two DGVs is in the length of the toxicity tests used, e.g., 4 days for short-term/acute versus 21 days for long-term/chronic.

[52] This contrasts with the CCME approach, see section 2.3.3.

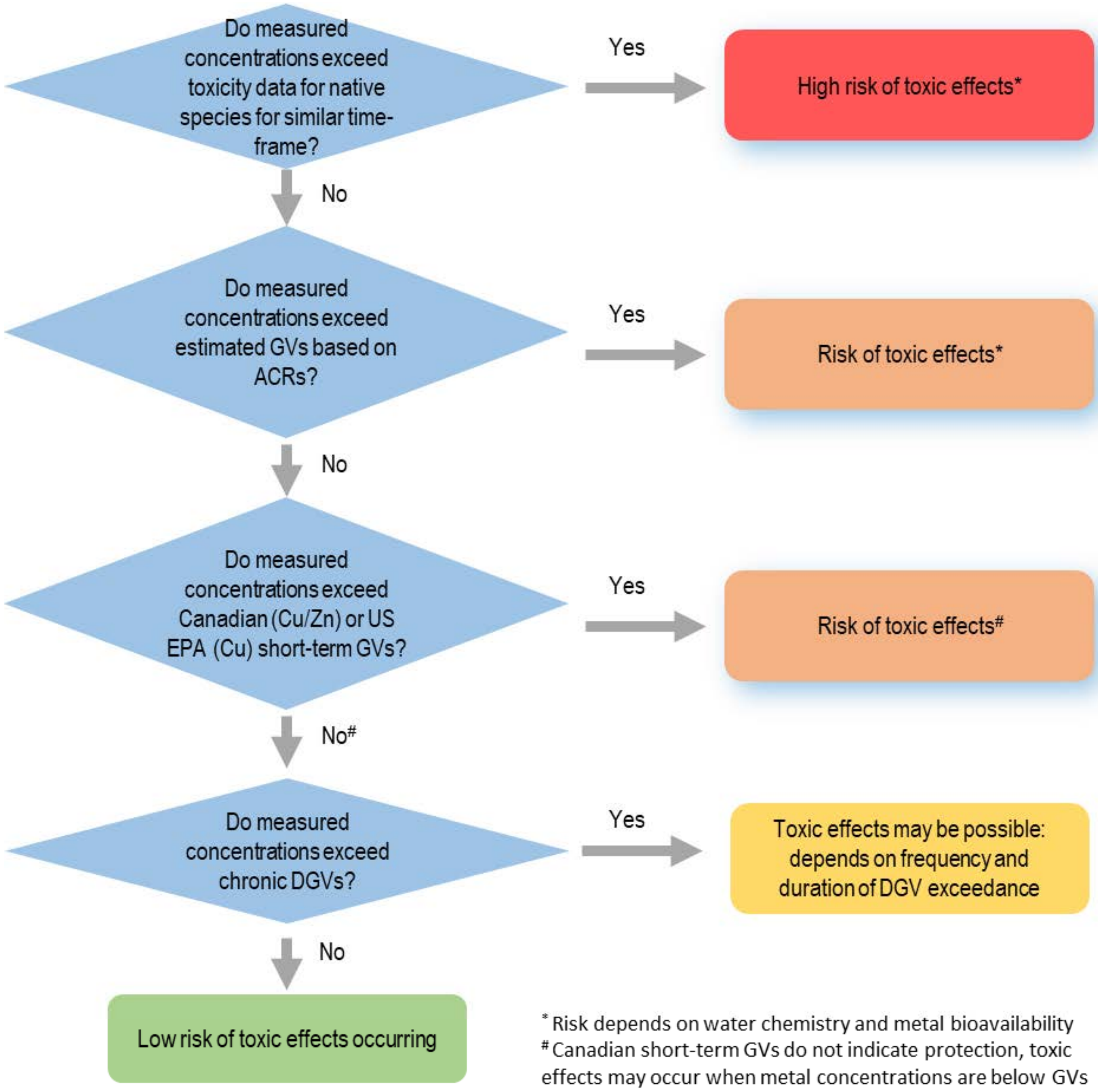

Figure 2-2: Flow chart for considering acute toxicity risks from short-duration discharges.

2.3.1 Comparison of monitoring data with acute toxicity data for native NZ species

Acute toxicity data are available for several native NZ freshwater fish and invertebrates that can be used to gain a preliminary indication of the potential for adverse effects from short-term discharges (Table 2-3, Figure 2-3). There is considerable range in the copper concentrations that can lead to adverse effects on survival – depending on both species and the duration of exposure. For example, the 24-hour copper LC50[53] for the freshwater mussel is 3.6 µg/L, compared to a 96-hour LC50 of 520

[53] LC50 values are lethal concentrations (LCs) that will result in death of 50% of the test organisms. LC50 values are a specific sort of EC50 (effect concentrations), where the effect is lethality.

µg/L for the common bully. There is less range in the toxicity data for zinc – with acute LC50 values roughly 200 to 500 µg/L, except the *Deleatidium* mayfly which is relatively insensitive at 9,000 µg/L[54].

Measured copper and zinc concentrations could be compared with these toxicity values for individual species within a weight-of-evidence assessment, following the process outlined by ANZG[55], and/or including the other methods outlined in sections 2.3.2 and 2.3.3. Measured concentrations above the toxicity values in Table 2-3 would indicate likely toxicity effects – though concentrations below these numbers would not necessarily indicate an ecosystem is adequately protected. This approach is not suitable for making conclusions about whether the ecosystem is being protected and is therefore not recommended for use in regulatory (e.g., consenting or planning) processes. This is because the comparison is against the 50% effect data (in many cases lethal effects) and the data set is relatively small. However, this comparison may be useful in a risk assessment process for highlighting when or where toxicity is more likely to occur.

Table 2-3: Dissolved copper and zinc toxicity data for survival of native NZ freshwater fish and macroinvertebrates.

Species	Timeframe (duration of toxicity test)	No effect concentration (NOEC), µg/L	Concentration that affects 50% organisms in test (EC50), µg/L	Reference
Copper				
Freshwater mussel (*Echyridella menziesii*)	24-hour	2.0	3.6	Clearwater et al. (2014)[56]
Pond snail (*Potamopyrgus antipodarum*)	96-hour	Not reported	17	Dorgelo et al. (1995)[57]
Water flea (*Daphnia thomsoni*)	48-hour	22	31	NIWA (unpublished)
Amphipod (*Paracalliope fluviatilis*)	96-hour	Not reported	70	Ouwerkerk (2017)[58]
Kōura (*Paranephrops planifrons*)	7-day	260	>300	Albert et al. (2021)[59]
Mayfly (*Deleatidium* sp.)	96-hour	Not reported	39	Hickey & Vickers (1992)[60]
Common bully (*Gobiomorphus cotidianus*)	96-hour	180	520	Hickey et al. (2000)[61]

[54] Hickey and Vickers. (1992). Comparison of the sensitivity to heavy metals and pentachlorophenol of the mayflies *Deleatidium* spp. and the cladoceran *Daphnia magna*. *New Zealand Journal of Marine and Freshwater Research 26*: 87-93. This study used field collected larvae 3-6 mm in body length, which may be less sensitive than first instar life stages, see Cadmus, et al. (2020). Size-dependent sensitivity of aquatic insects to metals. *Environmental Science & Technology 54(2)*: 955-964.

[55] https://www.waterquality.gov.au/anz-guidelines/resources/key-concepts/weight-of-evidence

[56] Clearwater, et al. (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)*: 213-226.

[57] Dorgelo, et al. (1995). Effects of diet and heavy metals on growth rate and fertility in the deposit-feeding snail *Potamopyrgus jenkinsi* (Smith) (Gastropoda: Hydrobiidae). *Hydrobiologia 316(3)*: 199-210.

[58] Ouwerkerk (2017). The effect of dissolved organic carbon (DOC) on the acute toxicity of copper and zinc for different freshwater species. Internship Report (AEW-70424). Hamilton, Wageningen University & Research and NIWA, Ecotoxicology group.

[59] Albert, et al. (2021). Toxicity of selected freshwater contaminants to juvenile kōura (*Paranephrops planifrons*). Prepared for Cultural Keystone Species Programme Partnerships. NIWA *NIWA Client report 2021138HN*. June 2021. Hamilton, NZ.

[60] Hickey and Vickers. (1992). Comparison of the sensitivity to heavy metals and pentachlorophenol of the mayflies *Deleatidium* spp. and the cladoceran *Daphnia magna*. *New Zealand Journal of Marine and Freshwater Research 26*: 87-93.

[61] Hickey, et al. (2000). New Zealand ecotoxicity data: Freshwater invertebrates and fish. Ecological risk assessment at contaminated sites. Manaaki Whenua Landcare Research, Lincoln, New Zealand.

Species	Timeframe (duration of toxicity test)	No effect concentration (NOEC), µg/L	Concentration that affects 50% organisms in test (EC50), µg/L	Reference
Common bully (*Gobiomorphus cotidianus*)	10-day	Not reported	125-1,000	Hickey et al. (2000)
Inanga (*Galaxias maculatus*)	96-hour	56	85	Hickey et al. (2000)
Alga (*Raphidocelis subcapitata* *)	4-hour	Not reported	140	Hickey et al. (1991)[62]
Zinc				
Freshwater mussel (*Echyridella menziesii*)	24-hour	258	368	Clearwater et al. (2014)
Pond snail (*Potamopyrgus antipodarum*)	96-hour	Not reported	530	Dorgelo et al. (1995)
Water flea (*Daphnia thomsoni*)	48-hour	100	220	NIWA (unpublished)
Amphipod (*Paracalliope fluviatilis*)	96-hour	Not reported	480	Ouwerkerk (2017)
Kōura (*Paranephrops planifrons*)	7-day	430	>430	Albert et al. (2021)
Mayfly (*Deleatidium* sp.)	96-hour	Not reported	9,000	Hickey & Vickers (1992)
Common bully (*Gobiomorphus cotidianus*)	10-day	Not reported	166-382	Ouwerkerk (2017)
Alga (*Raphidocelis subcapitata* *)	4-hour	Not reported	8,000	Hickey et al. (1991)[63]

Note: *In reference as previous name *Selenastrum capricornutum*.

[62] Hickey CW, Blaise C, Costan G 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: 383-403.

[63] Hickey CW, Blaise C, Costan G 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: 383-403.

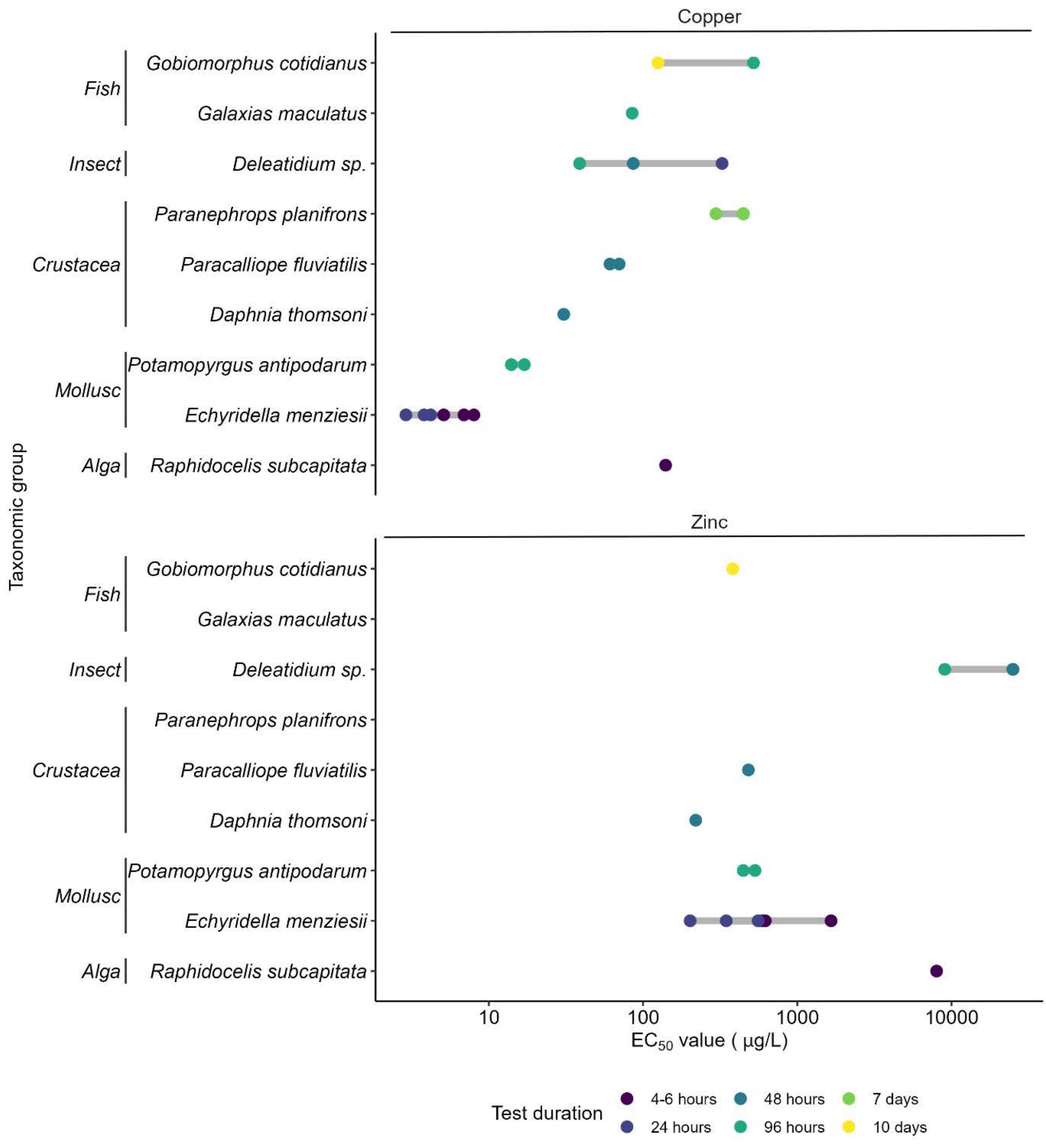

Figure 2-3: Copper and zinc acute toxicity data for aquatic species native to NZ. All data are EC50 values and relate to dissolved metal concentrations.

2.3.2 Acute to chronic ratios

Estimates of acute GVs could be based on acute to chronic ratios (ACRs) for copper and zinc. The ACR is the ratio between a toxicity value based on acute exposure (typically the median effect/lethal concentration, i.e., EC50/LC50) and a toxicity value based on chronic exposure (typically a negligible effect concentration, e.g. EC10, NOEC). For copper, ACRs are usually less than 10 , though ACRs greater than 100 have also been reported for some species that are not sensitive to copper (e.g., some freshwater snails). For zinc, ACRs summarised by US EPA (1996) ranged from <1 to 7, with one exception for a relatively sensitive fish (flagfish). Data for NZ native species suggest that both copper and zinc ACRs are in the order of 3-100 (shown in Figure 2 4 for copper; there were insufficient data for zinc).

These ACRs suggest that acute GVs would likely be less than 10-fold higher than the chronic GVs, and within the range of concentrations that have been measured in NZ urban streams[64]. In fact, this is demonstrated in the US EPA water quality criteria for copper[17], where the acute criterion is only 1.6-fold higher than the chronic criterion; and in the US EPA water quality criteria for zinc[18], where the acute and chronic criteria are the same value. Similarly, the Canadian short-term GVs for zinc[65] and copper[66] are only around 5- and 6-fold higher than their respective long-term GVs.

A geometric mean of the copper ACRs for NZ native species (shown in Figure 2-4) is 7.3[67]. Based on that, a copper acute GV would be no more than 3.4 µg/L at a DOC of ≤0.5 mg/L. There are insufficient data for NZ species for zinc to calculate an ACR, but based on international data, it may be in the range of 5x the chronic DGVs, equating to around 20 µg/L under high bioavailability conditions. These values are provided only as an indication of the magnitude of acute GVs. Although they could be used in assessing potential short-term toxicity as part of a larger weight-of-evidence approach, they should never be used as the only assessment for acute toxicity.

[64] Gadd, et al. (2019). Urban river and stream water quality state and trends 2008-2017. Envirolink *NIWA Client Report 2018328AK for Ministry for the Environment*. Revised October 2019. ; Margetts and Poudyal (2022). Christchurch City surface water quality annual report 2021. Prepared to meet the requirements of CRC214226. Christchurch City Council, *Christchurch City Council Report*. Christchurch City Council, Christchurch, New Zealand.

[65] 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. January 2018. Winnipeg, MB. https://ccme.ca/fr/res/2018-zinc-cwqg-scd-1580-en.pdf

[66] 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 *Water quality guideline series, WQG-03-1*. British Columbia, Canada. https://www2.gov.bc.ca/assets/gov/environment/air-land-water/water/waterquality/water-quality-guidelines/approved-wqgs/copper/bc_copper_wqg_aquatic_life_users_guide.pdf

[67] A geometric mean is used by US EPA for calculating an ACR for use in deriving guideline values.

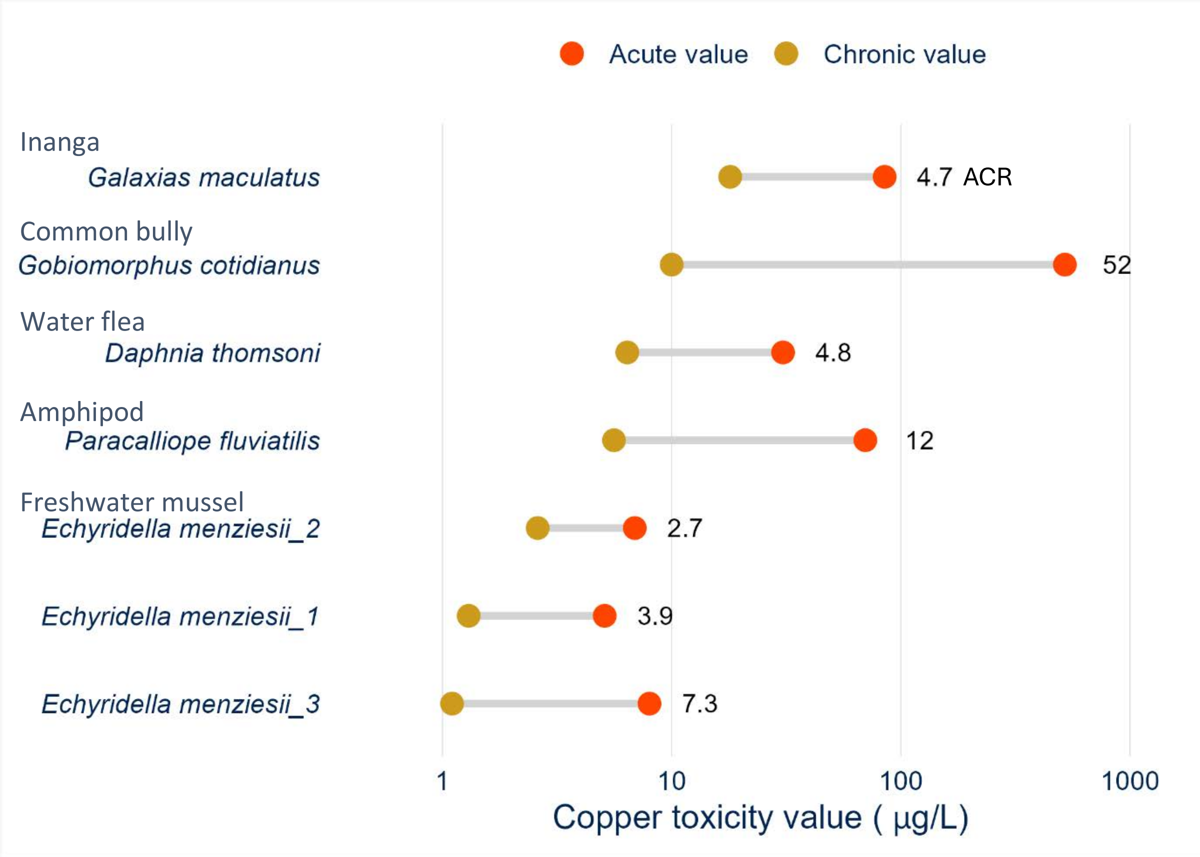

Figure 2-4: Comparison of copper acute and chronic toxicity data for aquatic species native to NZ. ACR = Acute to chronic ratio. Acute values are EC50 data and chronic values are EC10/NOEC data. Acute and chronic toxicity tests were undertaken under comparable conditions (hardness, DOC, pH).

2.3.3 Comparing monitoring data with guideline values from other jurisdictions

The US and Canada provide acute (and chronic) water quality GVs for copper and zinc (Table 2-4). There are no acute GVs currently in use in Europe for either of these metals.

The US EPA acute GVs (known as criterion maximum concentration or CMC) are for a “one-hour average not to be exceeded more than once every three years on average”[68]. These US GVs are based only on toxicity data for species that are resident in North America. This means data for species that are native to NZ and Australia, which may have particular ecological and/or cultural value here, are not included in deriving the US GV. In addition, algae and higher plants are not included in the US GV derivations (i.e., they are based on amphibians, fish and invertebrates only), though the effects on these taxa are considered qualitatively to consider their protection.

The US EPA zinc CMC was last updated in 1995[69], is based on adjustment for different water hardness and does not include any studies published after 1986. Since that time, there has been greater awareness of the effect that pH and DOC have in modifying zinc toxicity; and multiple studies have also subsequently been published. **We therefore do not recommend use of the zinc CMC to assess acute effects in NZ.** The US EPA CMC for copper was last updated in 2007[70], drawing on toxicity studies up until 2000, and uses an acute biotic ligand model (BLM) to address bioavailability issues. This approach is consistent with advances in understanding of bioavailability and toxicity.

The Canadian Council of Ministers of the Environment (CCME) provide short-term benchmark concentrations (their terminology for acute toxicity GVs) for some contaminants. These GVs use severe effects data (such as lethality) for defined short-term exposure periods. The exposure periods used by CCME generally align with those used by ANZG (2018), and some other aspects of the derivation are similar to the ANZG process. However, the CCME GVs are based on EC50 (or LC50) values (i.e., an indication of effects or lethality on 50% of organisms), which differs to the ANZG recommendation to use acute negligible effect values (e.g., EC10 values). This means they are less conservative. Although species resident in Canada are preferred by CCME for deriving GVs, non-resident species can also be included, and were included in developing the Zn GVs.

The CCME acute GV for zinc (dissolved) was derived in 2018[71], using a multiple linear regression approach and incorporated toxicity data up until 2012. The CCME has not derived an acute GV for copper. However, the state of British Columbia in Canada has an acute GV for copper[72], derived following the same general method as outlined by CCME for toxicant GVs, using a BLM and including data up to 2017. Similar to the US approach, the British Columbia GV is based on toxicity data only

[68] Note that although this text is included in the US EPA documents, it may not be regularly used in the US. In reality, sampling is rarely undertaken at a frequency that allows for calculation of a one-hour average. A. Ryan pers. comm.

[69] 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. EPA 820-B 96-001. September 1996. Washington D.C. https://nepis.epa.gov/Exe/ZyPURL.cgi?Dockey=20002924.TXT

[70] US EPA (2007). Aquatic life ambient freshwater quality criteria - copper. 2007 Revision. United States Environmental Protection Agency, Criteria and Standards Division. EPA-822-R-07-001. Washington D.C. https://www.epa.gov/sites/default/files/2019-02/documents/al-freshwater-copper-2007-revision.pdf

[71] 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. January 2018. Winnipeg, MB. https://ccme.ca/fr/res/2018-zinc-cwqg-scd-1580-en.pdf

[72] 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 *Water quality guideline series, WQG-03-1*. British Columbia, Canada. https://www2.gov.bc.ca/assets/gov/environment/air-land-water/water/waterquality/water-quality-guidelines/approved-wqgs/copper/bc_copper_wqg_aquatic_life_users_guide.pdf

for species found in British Columbia[73]. The CCME and British Columbia short-term benchmarks are based on EC50 values. As stated by CCME (2018), the benchmarks are designed to estimate severe effects and provide guidance on the *impacts* of transient situations, such as spill events and infrequent releases of contaminants. They *do not* indicate protection when metal concentrations are below the threshold – concentrations below the threshold may result in 50% mortality for the most sensitive species.

Table 2-4: Acute and/or short-term guideline values for dissolved copper and zinc from the US and Canada. Shaded rows indicate these could be used to assess the potential for acute effects from short-term exposures to dissolved copper and zinc as part of a weight-of-evidence approach.

Metal	Guideline value (µg/L)	Water chemistry	Notes	Year updated	Reference
Copper (dissolved)	1.8	Hardness of 30 mg/L; DOC of 0.5 mg/L	Criteria based on BLM	2007	US EPA (2007)[74]
	0.8	Hardness of 30 mg/L; DOC of 0.5 mg/L; pH 7.5	This concentration should not be exceeded at any time to meet the intended protection of the most sensitive species and life stage against severe effects. Short-term maximum WQGs are intended to assess risks associated with infrequent and transient exposure events such as spills	2019	British Columbia (2019)[75]
Zinc (dissolved)	43	Hardness of 30 mg/L	Criteria based on hardness only, does not include new data on sensitive species/early life stages	1995	US EPA (1996)[76]
	24	Hardness of 30 mg/L; DOC of 0.5 mg/L	These short-term benchmark concentrations do not provide guidance for protective levels of a substance in the aquatic environment, as they are levels that do not protect against adverse effects.	2018	CCME (2018)[77]

[73] This derivation followed the CCME protocol. Although data for non-resident species can be used, there were sufficient data for resident species to derive a copper GV.

[74] US EPA (2007). Aquatic life ambient freshwater quality criteria - copper. 2007 Revision. United States Environmental Protection Agency, Criteria and Standards Division. EPA-822-R-07-001. Washington D.C. https://www.epa.gov/sites/default/files/2019-02/documents/al-freshwater-copper-2007-revision.pdf

[75] 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 *Water quality guideline series, WQG-03-1*. British Columbia, Canada. https://www2.gov.bc.ca/assets/gov/environment/air-land-water/water/waterquality/water-quality-guidelines/approved-wqgs/copper/bc_copper_wqg_aquatic_life_users_guide.pdf

[76] 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. EPA 820-B 96-001. September 1996. Washington D.C. https://nepis.epa.gov/Exe/ZyPURL.cgi?Dockey=20002924.TXT

[77] 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. January 2018. Winnipeg, MB. https://ccme.ca/fr/res/2018-zinc-cwqg-scd-1580-en.pdf

2.4 Assessing potential copper and zinc toxicity related to intermittent discharges such as stormwater

KEY POINTS:

- **BOTH CHRONIC AND ACUTE EXPOSURES CAN OCCUR WITH STORMWATER DISCHARGES – THEREFORE BOTH CHRONIC AND ACUTE GVS ARE RELEVANT IN ASSESSING TOXIC EFFECTS**
- **ANZG DGVS ARE EXPECTED TO BE CONSERVATIVE WHEN APPLIED TO WATERS WITH INTERMITTENTLY HIGHER CONCENTRATIONS OF COPPER AND ZINC**

Stormwater discharges may be short-lived, generally less than 48 hours depending on rainfall duration and intensity, antecedent weather conditions, catchment size and other characteristics (e.g., topography). During these discharge periods, and particularly when there are multiple stormwater discharges in close proximity, copper and zinc concentrations in receiving waters (streams, rivers and estuaries) can increase by an order of magnitude for periods that may last only hours (e.g., Figure 2-5).

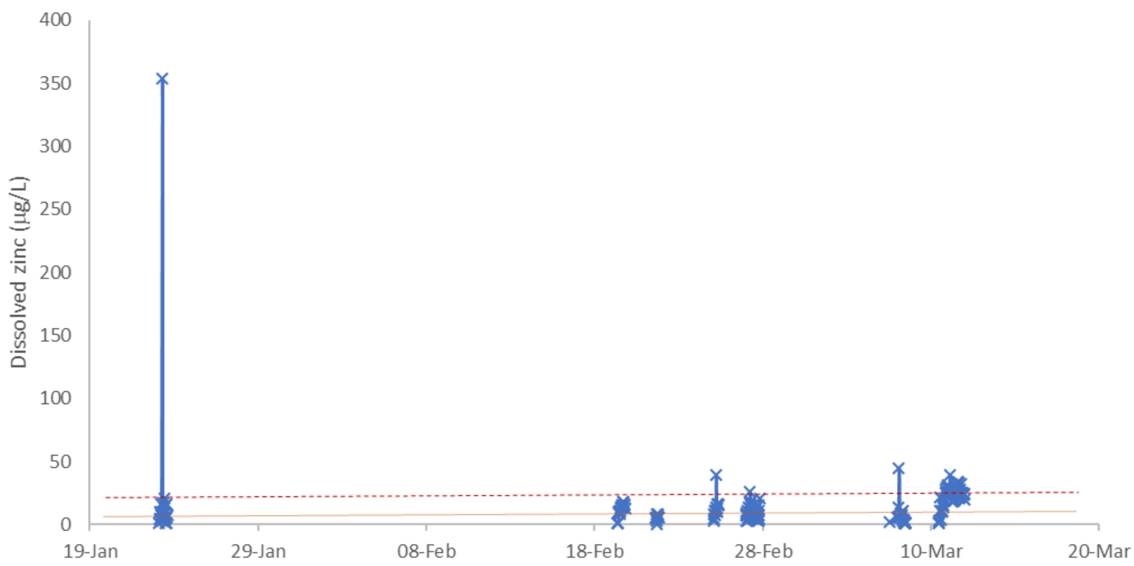

Figure 2-5: Dissolved zinc concentrations measured in an Auckland stream during different rainfall events. Orange line indicates acute GV (24 µg/L, from CCME (2018)) and orange indicates chronic draft DGV at index condition (4.1 µg/L). Zinc concentrations regularly exceed both acute and chronic GVs in this stream. Data collected 2004 from Auckland City Council study[78].

While aquatic organisms are typically able to endure exposure to higher metals concentrations for short periods, repeated exposure can result in toxic effects. Firstly, latent toxicity can occur, whereby, mortality can occur after the exposure ends[79]. Acute toxicity tests allow for this latent toxicity to occur – therefore acute GVs are relevant to exposures that are even shorter than the duration of an acute toxicity test (often 48-96 hours, 7-21 days for larger organisms and adult life

[78] Reed and Timperley (2004). Stream flow and stormflow water quality monitoring: Oakley Creek and Whau River. NIWA Client Report No. HAM2003-085.

[79] Diamond, et al. (2006). Implications of pulsed chemical exposures for aquatic life criteria and wastewater permit limits. *Environmental Science & Technology 40(16)*: 5132-5138; Gordon, et al. (2012). Review of toxicological effects caused by episodic stressor exposure. *Environmental Toxicology and Chemistry 31(5)*: 1169-1174.

stages). Acute GVs could provide a screening level assessment to indicate potential for toxicity related to stormwater discharges. In the absence of acute GVs specific to NZ, those from other jurisdictions, as estimated from ACRs, or toxicity data for individual species could be used following the suggested framework in Figure 2-2.

However, even when peak metal concentrations are below an acute GV (but above the chronic GV, see flow chart in Figure 2-2), adverse effects may occur, depending on the frequency of the stormwater discharges. Studies looking at the effects of copper and zinc from multiple short-term, pulsed exposures, show that harmful effects may occur even if concentrations are below acute GVs because of the repeated nature of the exposures. Recovery time between exposures is important, as this allows for organisms to eliminate the metals they accumulated during exposure. Different organisms will eliminate metals at different rates, and rates also differ for each metal – there is no single duration that would allow recovery for all metals and organisms, at least within the durations tested (typically 24 hours to 7 days or more).

With repeated exposures aquatic organisms do not have time to recover between pulses, and metals can accumulate to toxic concentrations.[80] Some studies have demonstrated that exposure arising from a few repeated pulses may cause harmful effects similar to those observed with continuous, longer-term exposure to metals at lower concentrations[81], though the effect of these pulses will depend on the metal.

The likelihood of adverse effects on aquatic life depends on the duration and frequency of the discharge events where the instream metal concentrations exceed chronic GVs. In urban streams that receive stormwater discharges, concentrations may exceed chronic GVs for only short durations during rainfall events. In some locations (e.g., Auckland, Wellington) these exceedances may be weekly; while in urban areas with drier climates, there may be long periods (up to months) between exceedances. There is currently no recommended method to account for the frequency and duration of GV exceedances within NZ. However, this issue has been discussed at length in the US in relation to stormwater and wastewater discharge permits; and guidance is provided for dynamic modelling approaches to assess exceedance of water quality standards [82]. That guidance may be useful in the NZ context as well.

In the interim, the flow chart in Figure 2-2 is suggested as a framework to assess possible toxicity from intermittent exposure to copper and zinc. The draft DGVs are expected to be conservative when applied to waters receiving intermittent stormwater discharges that only increase metal concentrations for relatively short time periods (e.g., hours to days). That is, if the DGVs **are not** exceeded, there would be high confidence that the ecosystem was being protected. If the DGVs **are** exceeded, this does not imply that an adverse effect *will* occur.

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[80] Bearr, et al. (2006). Effects of pulsed copper exposures on early life-stage *Pimephales promelas*. *Environmental Toxicology and Chemistry 25(5)*: 1376-1382; 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. Hoang, et al. (2007). Toxicity of Two Pulsed Metal Exposures to *Daphnia magna*: Relative Effects of Pulsed Duration-Concentration and Influence of Interpulse Period. *Arch. Environ. Contam. Toxicol. 53(4)*: 579-589.

[81] 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.

[82] Butcher, et al. (2003). Effluent Limits for Fluctuating Discharges: Volume 2: Alternate Frameworks for Water Quality Criteria. London, UK, IWA Publishing. ; Butcher and Diamond (2003). Effluent Limits for Fluctuating Discharges: Volume 1: Technical Guidance and Software. London, UK, Water Environment Foundation and IWA Publishing.

2.5 Estuarine and transitional waters

KEY POINTS:

- **THERE ARE NO GUIDELINE VALUES SPECIFIC TO ESTUARINE WATERS**
- **THE BEST APPROACH IS TO USE THE LOWEST (I.E. MOST CONSERVATIVE) OF THE FRESH WATER AND MARINE WATER DGVS**

The freshwater DGVs apply to waters with salinity <2 ppt; and the marine GVs apply to waters with salinity of 25-36 ppt (ANZG 2018). Estuaries typically have brackish, or transitional, waters that may fall between these two salinity ranges.

There are generally too few ecotoxicological data at intermediate salinities to be able to derive GVs specific to brackish ecosystems. Furthermore, estuarine systems are highly variable and dynamic, especially in relation to their physico-chemistry (e.g., salinity). It is therefore not possible to derive DGVs that would be appropriate for all estuarine waters all the time.

Different GVs could be used depending on the salinity or point in the tidal cycle at the time of water sample collection – with a freshwater GV used at low tide if salinity is <2 ppt and a marine GV used at high tide (>25 ppt). It is likely though that there will be many occasions (and/or sites) where salinity lies between these values. ANZG (2018) recommend "Where salinity of an estuarine water body changes frequently (i.e., with the tidal cycle), the lowest of the marine and freshwater DGVs for metals is recommended. [83]" An example using this approach is shown in Case Study 3.

The ANZG advice also states that the reliability of DGVs should be considered, as should differences in toxicity between fresh water and marine water. The copper and zinc DGVs for fresh water and marine water (whether based on ANZECC (2000) or the draft DGVs) are all considered to have very high reliability. It can be difficult to compare toxicity between fresh and marine waters due to the effect of water chemistry on toxicity and the different species found in each water type. Studies using fish that can tolerate fresh and marine waters [84] (including inanga / *Galaxias maculatus* [85]) indicate that toxicity is higher in fresh waters, possibly due to reduced bioavailability in saline waters. This suggests that the approach of taking the lowest (i.e. most conservative) DGV, is the best approach (after adjusting for water chemistry if needed).

[83] See here for details: https://www.waterquality.gov.au/anz-guidelines/guideline-values/default/water-quality-toxicants#guideline-values-for-other-water-types

[84] Bielmyer, et al. (2012). The effects of salinity on acute toxicity of zinc to two euryhaline species of fish, *Fundulus heteroclitus* and *Kryptolebias marmoratus*. *Integrative and Comparative Biology 52(6)*: 753-760; Bielmyer, et al. (2006). Physiological responses of hybrid striped bass to aqueous copper in freshwater and saltwater. *Archives of Environmental Contamination and Toxicology 50(4)*: 531-538. Loro and 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.

[85] Glover, et al. (2016). Salinity-dependent mechanisms of copper toxicity in the galaxiid fish, *Galaxias maculatus*. *Aquatic Toxicology 174*: 199-207.

Case Study 3: Application of DGVs in estuarine environments

Zinc concentrations are measured at Ōpāwaho/Heathcote River mouth site in Ihutai/Avon-Heathcote Estuary. The salinity at this site fluctuates from that of fresh water (<1 ppt) to 14 ppt, depending on the tide and river flow. In Table 2-5, freshwater DGVs are calculated (adjusting for water chemistry) and then the lowest of this and the marine DGV is selected for use, regardless of site's salinity.

Table 2-5: Example of process to select applicable zinc DGVs with changing salinity. Measured data should be compared with the DGVs shaded in dark green. Data sourced from SWQ Long Term, which is licensed under a Creative Commons Attribution 4.0 International licence by Environment Canterbury.

Site name	Salinity (ppt)	pH	DOC (mg/L)	Hardness (mg/L as $CaCO_3$)	Freshwater zinc GV (µg/L)	Marine zinc GV (µg/L)	Relevant zinc GV (µg/L)
Ōpāwaho/ Heathcote River at Ferrymead Bridge	3.3	8.1	7.7	85	15	8.0	8.0
	6.1	8.1	1.7	90	7.5	8.0	7.5
	13.1	8.2	1.4	95	6.8	8.0	6.8

2.6 Comparing copper and zinc monitoring data with the ANZG toxicant DGVs

KEY POINTS:

- **MANY TYPES OF DATA CAN BE COMPARED WITH THE DGVS, INCLUDING: SINGLE SAMPLES, SOE SAMPLES, WET WEATHER GRAB SAMPLES, EVENT-BASED AUTOSAMPLERS, HIGH FREQUENCY SENSORS, MODELS AT LOW OR HIGH FREQUENCY (E.G., ANNUAL DAILY AVERAGE MODEL; 15 MIN MODEL)**
- **THE IDEAL ASSESSMENT METHOD IS TO COMPARE EACH DATA POINT WITH THE DGVS AND CALCULATE SUMMARY STATISTICS OF EXCEEDANCE**
- **WHEN COMPARING ANY DATA SET, CONSIDER IF THE DATA REPRESENT THE FULL "POPULATION" OF EXPOSURES AT A SITE (E.G., SEASONAL AND FLOW VARIATION)**
- **GRAPHICAL METHODS (EG CONTROL CHARTS, CUMULATIVE DISTRIBUTIONS) CAN BE USEFUL FOR COMPARING DATA OVER TIME OR FREQUENCY OF EXCEEDANCE**

2.6.1 Sampling methods and data types

ANZG (2018) does not specify the types of monitoring data that should or could be compared with toxicant GVs. All data can be compared, including copper and zinc measurements from:

- single sampling events, including wet weather grab samples
- "SOE" monthly samples
- wet-weather samples collected using autosamplers
- high frequency *in situ* measurements (increasingly used for nitrate-N, though these do not yet exist for copper or zinc)
- *in situ* passive samplers such as DGTs[86]
- models operating at either low or high frequency (e.g., annual daily average model; 15 minute model predictions)

Irrespective of the data set used, it is important to consider if the data represent the full "population" / entire exposure period. Wet weather samples are unlikely to include metal concentrations in low or base flow conditions and so will be biased towards higher flows and metal concentrations. SOE monitoring results may be more representative of the usual stream conditions, provided data have been collected over a sufficient time period to capture a range of weather/flow conditions. Although statistically speaking, monthly SOE sampling (i.e., sampling undertaken once a month on a predetermined day and time), is a systematic form of sampling rather than random, many statisticians consider that it is equivalent to (or an acceptable substitute for[87]) random sampling. This means that if enough samples are collected, this form of sampling will be representative of the long-term "average" conditions in the waterbody[88].

[86] Diffusive gradient in thin film devices (DGTs), which accumulate metals (and other contaminants) during the period of *in situ* deployment. See Davison and Zhang. (1994). In situ speciation measurements of trace components in natural waters using thin-film gels. *Nature 367(6463)*: 546-548. And Gadd and Milne (2019). Monitoring water quality in urban streams and stormwater: guidance for New Zealand practitioners. Envirolink *NIWA Client Report*. 2019168AK. June 2019.

[87] McBride (2005). Using statistical methods for water quality management: issues, problems and solutions. Wiley Series In Statistics In Practice. New Jersey, John Wiley & Sons Inc.

[88] Snelder and Kerr (2022). Relationships between flow and river water quality monitoring data and recommendations for assessing NPS-FM attribute states and trends. Prepared for Auckland Council by LWP, Land Water People. October 2022.

Measurements at high flows and during rainfall events is also important in toxicological risk assessments. Any targeted event monitoring datasets can and should be analysed separately as being representative of event conditions. The results can also be plotted up in combination with data from sampling at baseflow as a time series of concentrations – ideally time-series of the flow hydrograph would be available for this.

A critical issue comes in calculating summary statistics for a site when targeted sampling has introduced bias into the data set [89]. There are three possible ways to deal with this:

- Do not calculate summary statistics – compare all data points with DGVs and calculate percentage exceedance (see section 1.3).
- Calculate separate summary statistics for different groups of data – stratifying by flow for example
- Consult a skilled data analyst or statistician to assist with the data analysis plan if you wish to combine the data sets (see https://www.waterquality.gov.au/anz-guidelines/monitoring/data-analysis).

2.6.2 Data analysis methods

ANZG (2018) recommends that an exceedance of a DGV is deemed to have occurred if the 95th percentile of the test distribution exceeds the GV"[90]. However, this guidance was written from the viewpoint of comparing monitoring data with a single DGV, rather than against a DGV that varies due to changing bioavailability. ANZG (2018) also states that 95% of values should fall below the GV - therefore the DGV is exceeded if more than 5% of values exceed the GV. The latter statement is more congruent with a DGV that changes over time – measured data can be compared with varying DGVs and the number of exceedances easily calculated. Comparing measured data with DGVs that change over time is discussed more in section 1.3 and 1.2.

We suggest that an appropriate method for comparing monitoring data against GVs is to compare each individual value, rather than to calculate a percentile value for comparison. This is particularly the case for small data sets – generally more than 40 samples[91] are required to calculate a 95th percentile value with high precision (such as 95% confidence).

Where a large data set exists, calculating a single statistic for comparison with a DGV does not maximise the value of the information contained within the data set. An alternative option, for samples collected regularly in time, at the same location, is to use a control chart (where individual measurements are plotted over time against GV that are either static or vary over time, Figure 2-6 top), or a cumulative sum (CUSUM) chart (Figure 2-6 bottom), where the cumulative sum of deviations from the GV are plotted over time, which tends to be more sensitive to smaller shifts[92].

[89] Kerr, et al. (2018). Monitoring heavy metal concentrations in turbid rivers: Can fixed frequency sampling regimes accurately determine criteria exceedance frequencies, distribution statistics and temporal trends? *Ecological Indicators 93*: 447-457.

[90] https://www.waterquality.gov.au/anz-guidelines/guideline-values/default/water-quality-toxicants#determining-if-a-toxicant-dgv-has-been-exceeded.

[91] Goudey. (2007). Do statistical inferences allowing three alternative decisions give better feedback for environmentally precautionary decision-making? *Journal of Environmental Management 85(2)*: 338-344.

[92] Mac Nally and Hart. (1997). Use of CUSUM Methods for Water-Quality Monitoring in Storages. *Environmental Science & Technology 31(7)*: 2114-2119.

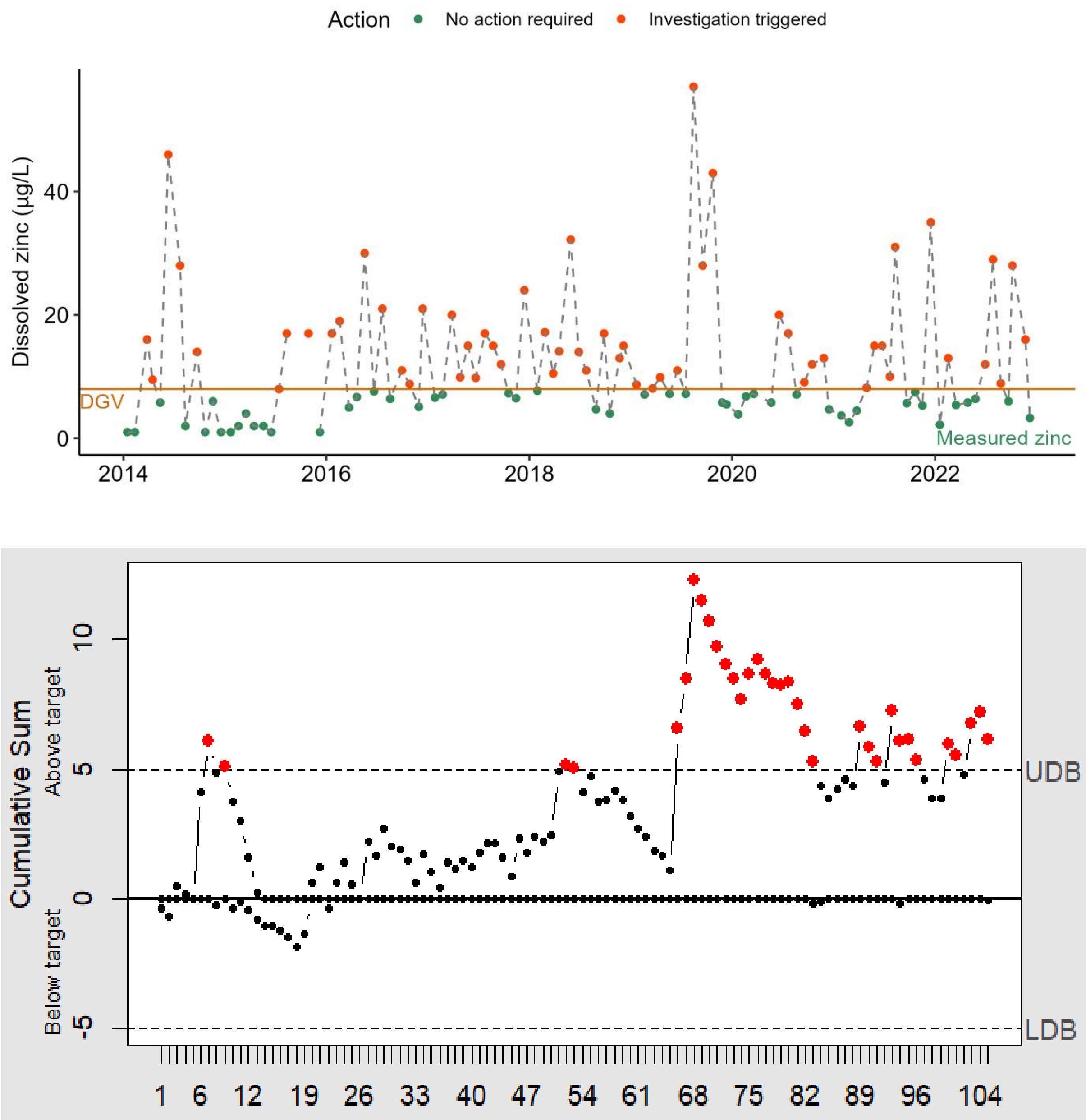
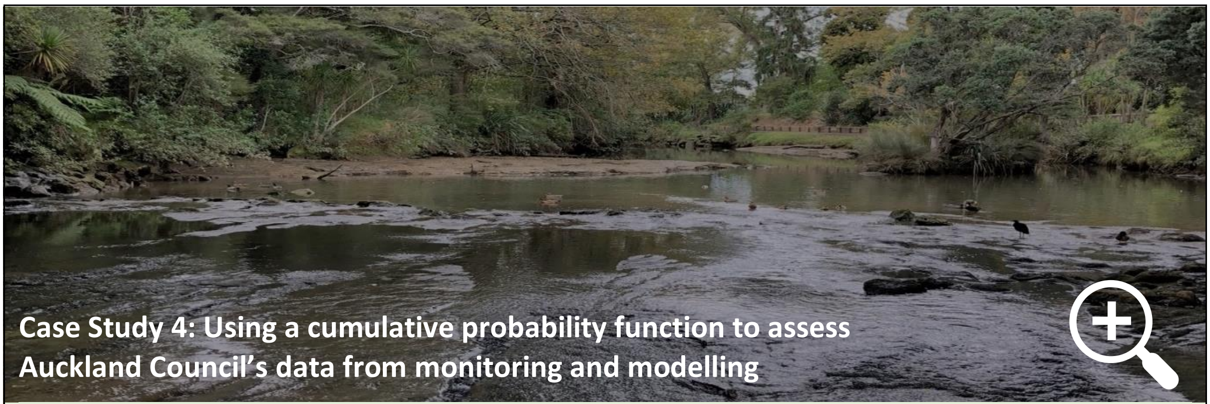


Figure 2-6: Control chart (top) and CUSUM chart (bottom) of monthly dissolved zinc concentrations for Ōpāwaho/Heathcote River at Ferrymead Bridge. DGV of 8 µg/L (for marine waters) used for both charts (orange line in top chart, target for CUSUM chart). In bottom panel the y-axis units indicate the cumulative sum variation from the target and the x-axis units represent the sample number (in order of time collected). UDB and LDB represent upper and lower decision boundaries respectively – the boundaries which indicate where the cumulative sum is out of range. Data supplied by Christchurch City Council. Investigations triggered by guideline value exceedance may include assessing other lines of evidence of adverse effects.

An alternative approach that may be appropriate for high frequency data is a quantitative or probabilistic risk assessment which uses all the exposure data and compares them either with a GV (acute GV or chronic DGV) or with a toxicity data set (Case Study 4). This method involves plotting the exposure data (i.e., measured data or modelled predictions) as a cumulative frequency and comparing that with a GV. This not only demonstrates the percentage of the samples/time that a GV is exceeded but can also illustrate the magnitude of exceedances.



Case Study 4: Using a cumulative probability function to assess Auckland Council's data from monitoring and modelling

Auckland Council have predicted dissolved zinc concentrations from their Fresh Water Management Tool (FWMT[93]). Data from the FWMT Baseline v1.0 (5 years predictions, 2013-2017, using 15-min predictions) are used this case study. Total zinc concentrations predicted by the FWMT were converted to dissolved zinc using the ratio of 0.688 [94].

Cumulative frequency curves are plotted for three sites (Figure 2-7): Oakley Creek (urban stream), Lucas Creek (urban stream) and Kaukapakapa River (rural river), and compared with the draft DGV at the index condition (4.1 µg/L) and the CCME acute GV (24 µg/L). This figure illustrates the proportion of samples that exceed GVs and can be used for screening sites for further investigation. Alternative lines could be used in this comparison, such as toxicity data (e.g., EC50s) for key native species.

Figure 2-7 indicates that dissolved zinc concentrations exceed the draft DGV in Kaukapakapa River around 4% of the time, but around 20% of the time in Lucas Creek and 40% of the time in Oakley Creek. Dissolved zinc concentrations almost never exceed the acute GV in Kaukapakapa River, but around 5% of the time in Lucas Creek and slightly more often in Oakley Creek.

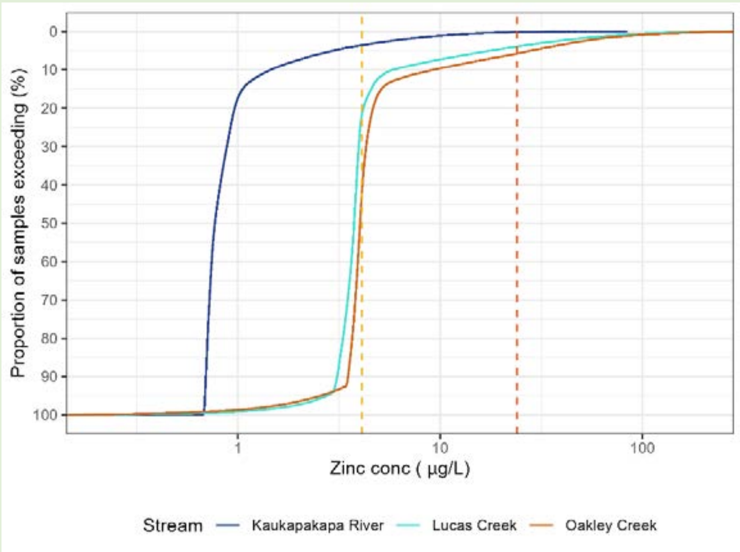


Figure 2-7: Comparison of modelled dissolved zinc concentrations with zinc guideline values. The orange dashed vertical line indicates acute GV (24 µg/L) and the yellow dashed line indicates the draft DGV at index condition (4.1 µg/L).

[93] Auckland Council (2021). Freshwater Management Tool: Baseline state assessment (rivers). Auckland Council Healthy Waters Department, Paradigm Environmental and Morphum Environmental Ltd. Auckland Council, Auckland.

[94] Auckland Council (2021). Freshwater Management Tool: Baseline state assessment (rivers). Auckland Council Healthy Waters Department, Paradigm Environmental and Morphum Environmental Ltd. Auckland Council, Auckland.

Another option suggested for assessing potential metal toxicity from intermittent exposure is to use a time-averaged concentration (TAC)[95]. This measurement is equivalent to the exposure organisms receive over the full time period of interest (Figure 2-8). The TAC method may be useful when comparing high frequency data, such as a daily or sub-daily time-series of modelled concentrations, with acute and chronic GVs. For example, in Figure 2-9, the predicted zinc concentrations regularly exceed both the acute and chronic GVs with concentrations reaching nearly 200 µg/L, though the duration of these exceedances is short and less than 1 hour in some cases (in which case the potential for adverse effects may be low, Figure 2-1).

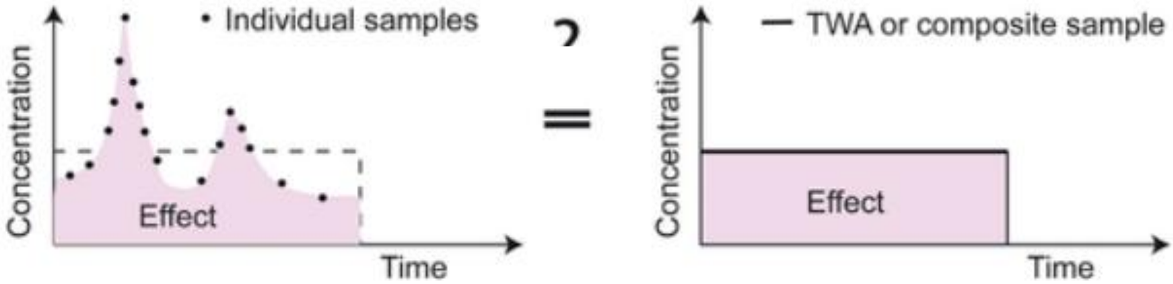


Figure 2-8: Illustration of the time-weighted average concentration method that can be used to assess toxicity of pulsed exposures. Adapted from Ashauer et al. (2020)[96].

The TAC approach has generally only been used (and tested) in a laboratory setting[97], usually averaging toxicant concentrations over 2 to 7 days. We are not aware of any studies that have tested the TAC approach for metals in anything other than laboratory settings. The method has been tested for pesticides in real-world settings[98] with this testing suggesting that a 14-day averaging period was suitable. However, the study authors also noted that this method may only apply for toxicants where toxicity effects occur rapidly (i.e., a fast mechanism of action), and where organisms recover rapidly: both must be faster than the time scale of fluctuations in toxicant concentrations. This may explain why for some metals and some aquatic species, the time-averaged approach can excessively over- or under-estimate the true toxicological effect[99], making this approach misleading.

The US EPA chronic toxicity criteria require that “a 4-day average concentration of the chemical does not exceed the criterion more than once every 3 years on average”[100]. No such guidance is provided by ANZG (2018) to indicate a suitable averaging period. Depending on the time period used, the TAC

[95] 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.

[96] Ashauer, et al. (2020). Effect modeling quantifies the difference between the toxicity of average pesticide concentrations and time-variable exposures from water quality monitoring. *Environmental Toxicology and Chemistry 39(11)*: 2158-2168.

[97] Angel, et al. (2010). Toxicity to *Melita plumulosa* from intermittent and continuous exposures to dissolved copper. *Environ Toxicol Chem 29(12)*: 2823-2830; Colvin, et al. (2021). Pulsed exposure toxicity testing: Baseline evaluations and considerations using copper and zinc with two marine species. *Chemosphere 277*: 130323.

[98] Ashauer, et al. (2020). Effect modeling quantifies the difference between the toxicity of average pesticide concentrations and time-variable exposures from water quality monitoring. *Environmental Toxicology and Chemistry 39(11)*: 2158-2168.

[99] Hoang, et al. (2007). Toxicity of Two Pulsed Metal Exposures to *Daphnia magna*: Relative Effects of Pulsed Duration-Concentration and Influence of Interpulse Period. *Arch. Environ. Contam. Toxicol. 53(4)*: 579-589; Bearr, et al. (2006). Effects of pulsed copper exposures on early life-stage *Pimephales promelas*. *Environmental Toxicology and Chemistry 25(5)*: 1376-1382.

[100] Stephan, et al. (1985). Guidelines for deriving numerical national water quality criteria for the protection of aquatic organisms and their uses. Office of Research and Development, U.S. Environmental Protection Agency *EPA 600/53-84-099; PB85-227049*. Washington D.C.

for the Auckland data set shown in Figure 2-9 ranges from 8.3 to 14 µg/L. The average metal concentration decreases where the averaging period includes long periods of baseflow, and increases where it includes multiple rainfall events. Thus, the length of the averaging period used to calculate this TAC is extremely important. A four-day averaging period, based on the US EPA chronic toxicity criteria, suggests that the chronic DGV would be exceeded for relatively long periods, when compared to the concentrations with no averaging (Figure 2-10). This method could be a useful way to assess the potential effects of intermittent discharges; however we suggest that further consideration of this approach is needed, including differences in the uptake and release of metals by aquatic organisms, before suitable averaging periods can be recommended.

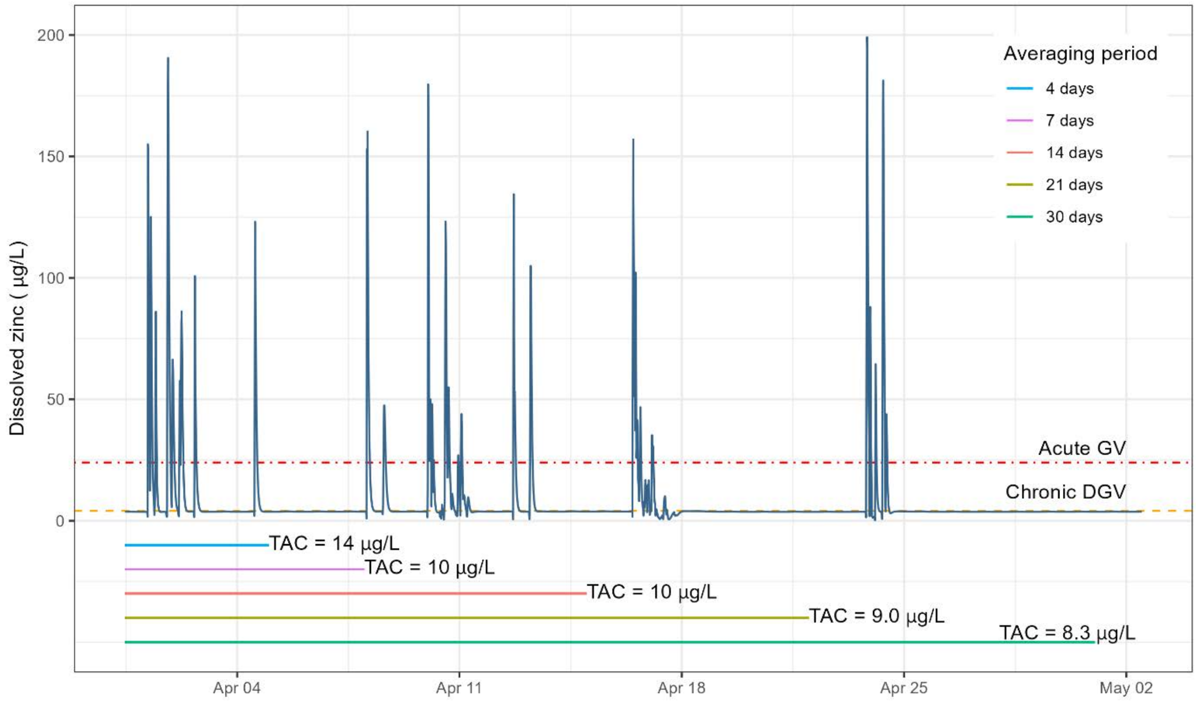


Figure 2-9: Comparison of time-averaged metal concentrations calculated over different durations, demonstrated with modelled data for Lucas Creek in Auckland (Apr-May 2016). In this example, the TAC decreases as the duration increases; however that result is specific to this set of data. Different patterns of storm events can indicate increasing TAC with duration up to 30 days. Modelled estimates of dissolved zinc concentrations (blue line), supplied by Auckland Council [101]. Data are predictions from FWMT Baseline v1.0 (15-min predictions, total zinc concentrations converted to dissolved zinc using the ratio of 0.688). An acute GV of 24 µg/L (red dot-dash, from CCME (2018)) and a chronic DGV at index condition of 4.1 µg/L (orange dash) also shown on the figure.

[101] Auckland Council (2021). Freshwater Management Tool: Baseline state assessment (rivers). Auckland Council Healthy Waters Department, Paradigm Environmental and Morphum Environmental Ltd. Auckland Council, Auckland.

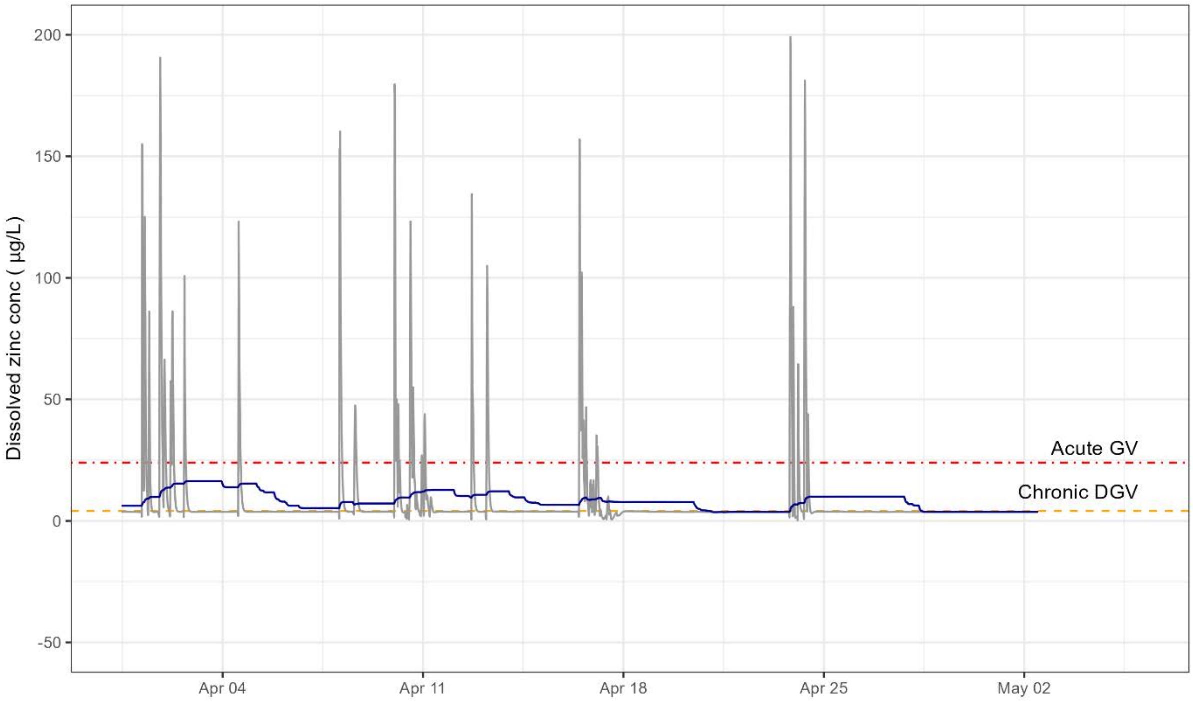
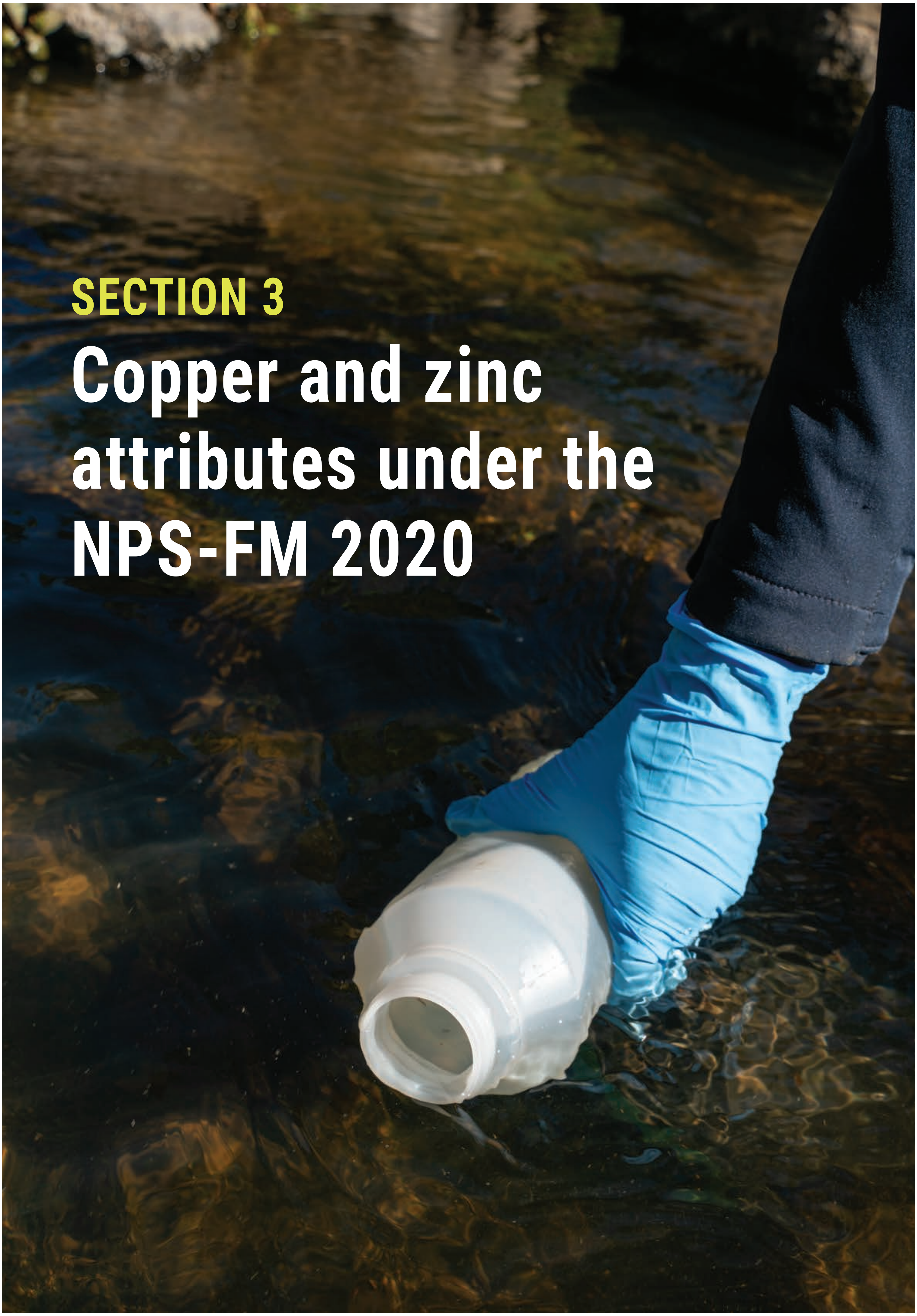


Figure 2-10: Comparison of 15-min modelled metal concentrations (grey) for Lucas Creek with 4-day time-averaged concentrations (blue). Modelled estimates of dissolved zinc concentrations (blue line) for period Apr-May 2016, supplied by Auckland Council [102]. Data are predictions from FWMT Baseline v1.0 (15-min predictions, total zinc concentrations converted to dissolved zinc using the ratio of 0.688). An acute GV of 24 µg/L from CCME (2018) and a chronic DGV of 4.1 µg/L (index condition) also shown on the figure.

[102] Auckland Council (2021). Freshwater Management Tool: Baseline state assessment (rivers). Auckland Council Healthy Waters Department, Paradigm Environmental and Morphum Environmental Ltd. Auckland Council, Auckland.

SECTION 3

Copper and zinc attributes under the NPS-FM 2020



Section 3: Copper and zinc attributes under the NPS-FM

The National Objectives Framework (NOF) of the NPS-FM 2020 (as amended February 2023) includes a series of attributes (in Appendix 2A and 2B) that regional councils must use to assess the extent to which certain freshwater values (e.g., aquatic ecosystem health, human health for recreation) are provided for in a river or lake. Although copper and zinc are not included in the NOF, the NPS-FM provides flexibility for councils and communities to identify additional attributes that they consider are important in providing for a particular freshwater value. Copper and zinc may be important attributes for ecosystem health in some locations. For example, copper and zinc are relevant in urban streams where elevated concentrations of metals arise as a result of inputs from municipal and industrial stormwater discharges, and may be relevant in locations affected by mining or agricultural uses of metals. In this section, we outline how a council might include dissolved copper and dissolved zinc as region-specific attributes in their regional plan, using the draft DGVs presented in section 1.1.

Table 3-1 outlines an approach developed in 2019 for attribute tables for copper and zinc for Auckland [103] (and subsequently used by some other NZ councils). The attribute tables used a two-number (median and maximum) approach to provide protection from chronic toxicity of copper and zinc based on annual median and maximum concentrations for bands A to B, and from acute toxicity based on the maximum concentrations in band C. Although that attribute table specified a maximum, this was replaced with a 95th percentile when used by Auckland Council[104] and Greater Wellington Regional Council[105].

The attribute thresholds in those tables were based on the copper and zinc DGVs available at that time – which were those derived under ANZECC & ARMCANZ (2000).

Table 3-1: Thresholds based on different protection levels (PL) as used for dissolved copper and zinc attribute tables developed for Auckland Council by Gadd et al. (2019).

Attribute band and description	**Numeric Attribute State**	
	Annual Median	**Annual Maximum**
A 99% species protection level: No observed effect on any species tested	< 99% PL DGV	< 95% PL DGV
B 95% species protection level: Starts impacting occasionally on the 5% most sensitive species	< 95% PL DGV	< 90% PL DGV
C 80% species protection level: Starts impacting regularly on the 20% most sensitive species (reduced survival of most sensitive species)	< 80% PL DGV	< Short-term GV
D Starts approaching acute impact level (ie risk of death) for sensitive species	> 80% PL DGV	> Short-term GV

[103] 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 Council Technical Report 2019*. Auckland.

[104] Auckland Council (2021). Freshwater Management Tool: Baseline state assessment (rivers). Auckland Council Healthy Waters Department, Paradigm Environmental and Morphum Environmental Ltd. Auckland Council, Auckland.

[105] Te Awarua-o-Porirua Whaitua Committee (2019). Te Awarua-o-Porirua Whaitua Implementation Programme. Greater Wellington Regional Council. April 2019. Wellington.

3.1 Recommended new copper and zinc attribute tables

KEY POINTS:

- **RECOMMENDED COPPER AND ZINC ATTRIBUTE TABLES ARE BASED ON UPDATED DRAFT DGVS (SECTION 1) AND INTERNATIONAL SHORT-TERM GVS (SECTION 2.3)**
- **"BIOAVAILABLE" COPPER AND ZINC CONCENTRATIONS SHOULD BE COMPARED WITH THE VALUES IN THESE TABLES**
- **THE SHORT-TERM GVS SHOULD BE REPLACED WITH NZ GVS IF THEY BECOME AVAILABLE**
- **THE RECOMMENDATIONS FOR DATA REQUIREMENTS AND TIME-FRAME ARE INTERIM AND THESE SHOULD BE REVIEWED AND REFINED AFTER THE TABLES HAVE BEEN USED BY DIFFERENT COUNCILS**

Recommended copper and zinc attribute tables are presented as Table 3-2 and Table 3-3, respectively. These attribute tables are considered suitable for both rivers and lakes, as the DGVs they are based on were derived using both lotic and lentic species. The attribute tables specify a time period for grading assessments (3 years) and requirements for the number of samples (at least 30 samples). An example of the use of these attributes is shown in Case Study 5.

These tables adopt the two-number system, using median and 95th percentiles as set out in Table 3-1. While comparing a median to the draft DGVs is not consistent with the recommendations of ANZG (2018) (a conservative approach using the 95th percentile is recommended), because the grading under the NPS-FM may trigger management actions, it is preferable to base that grading on metal concentrations that are observed most of the time (i.e., the median) rather than only rarely (e.g., 5% of the time). This also reduces the likelihood of state switching[106].

The attribute tables refer to "bioavailable" concentrations so measured dissolved copper and zinc concentrations should be converted to estimated bioavailable concentrations before comparison. The numeric attribute states for bioavailable copper are based on the draft DGVs at DOC concentration of 0.5 mg/L. This represents conditions with high bioavailability and is therefore (intentionally) conservative. The numeric attribute states for bioavailable zinc are based on the draft DGVs at the index condition of pH 7.5, hardness 30 mg/L and DOC of 0.5 mg/L. This index condition similarly represents conservative conditions that assume high bioavailability. It is important to note that this index condition is not the same as a tier 1 DGV as described in section 1.1. Because that tier 1 DGV for zinc has not yet been determined, and there is a pressing need for zinc attribute tables in NZ, we have pragmatically recommended the index condition for the attribute tables. Use of the index condition in the attribute table does not mean that this should be used as a tier 1 DGV more generally for water quality management.

Ideally the short-term GVs used in the attribute tables would be derived following the ANZG (2018) framework and using species native to NZ. In the absence of these NZ GVs, short-term GVs from other jurisdictions are used. For copper, the US EPA (2007) short-term GV is used for the C/D attribute band thresholds against which a (measured) 95th percentile value is compared (Table 3-2). As outlined in section 2.3.3, this copper GV was derived in 2007 based on toxicity data up to the year 2000 and using a biotic ligand model (BLM) to address bioavailability issues, consistent with advancements in understanding of bioavailability and toxicity. The zinc attribute table requires a

106 McBride (2016). National Objectives Framework: Statistical considerations for design and assessment. Ministry for the Environment. Wellington, NZ.

(measured) 95th percentile to be compared against a C/D attribute band threshold that is based on the CCME (2018) short-term GV[107]. Although the CCME (2018) short-term (i.e., acute) GVs are not thresholds for protection like the US EPA GVs, as noted in section 2.3.3, the CCME (2018) GV for zinc is based on very recent toxicity data, incorporates hardness, DOC and pH as factors that affect bioavailability, and uses a derivation process that is more consistent with the ANZG process recommended to derive short-term GVs. If short-term GVs are derived for NZ, these should replace the US EPA (2007) and CCME (2018) (acute) GVs for copper and zinc, respectively.

[107] 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. January 2018. Winnipeg, MB. https://ccme.ca/fr/res/2018-zinc-cwqg-scd-1580-en.pdf

Table 3-2: Recommended copper attribute table for use by NZ regional councils.

Value (and component)	**Ecosystem health (Water quality)**	
Freshwater body type	Rivers and lakes	
Attribute and unit	Bioavailable copper (µg Cu/L)	
Attribute band and description	Numeric Attribute State*	
Narrative attribute state	**Median**	**95th percentile #**
A Unlikely to be toxic effects even on the 5% most sensitive species	≤ 0.2†	≤ 0.47†
B Potential toxic effects on 5% most sensitive of species, unlikely to be toxic effects on more than 10% of species.	>0.2 and ≤ 0.47†	>0.47 and ≤ 0.73†
Bottom line	0.47†	0.73†
C Potential toxic effects on many sensitive species (20% species). Acute toxicity possible for the most sensitive species (5% species).	>0.47 and ≤ 1.3†	>0.73 and ≤ 1.8‡
D Potential toxic effects on multiple species, including acute toxicity	> 1.3†	> 1.8‡
Assessment of numeric attribute states should be made after adjustment for bioavailability using this equation: $Bioavailable\ copper = Dissolved\ copper \div \left(\frac{DOC}{0.5}\right)^{0.977}$ Where copper is in µg/L and DOC is dissolved organic carbon, in mg/L		
Based on a monthly monitoring regime where sites are visited on a regular basis regardless of weather and flow/water level conditions. Record length for grading a site based at least 30 samples collected over a 3-year period.		
The **grading classification** using median and 95th percentile attribute thresholds should be made based on monitoring data collected over 3 years. Attribute band must be determined by satisfying both numeric attribute states (i.e., both columns in any one row) or, if that is not possible, according to the worst numeric attribute state. * Best practice for ecological risk assessment is to annually assess classification against 95th percentile using the preceding 12-months' data. Exceedance of an attribute threshold would be considered an **"orange" warning level** for adverse ecological effects and provide an indicative classification and a trigger for investigation. # 95th percentile to be calculated using the Hazen method[108].		
†Numeric attribute state based on draft DGVs at DOC ≤0.5 mg/L. ‡Numeric attribute state based on US EPA CMC at DOC 0.5 mg/L, hardness 30 mg/L, pH 7.5.		

[108] https://environment.govt.nz/publications/bathewatch-user-guide/hazen-percentile-calculator/

Table 3-3: Recommended zinc attribute table for use by NZ regional councils.

Value (and component)	**Ecosystem health (Water quality)**	
Freshwater body type	Rivers and lakes	
Attribute and unit	Bioavailable zinc (µg Zn/L)	
Attribute band and description	Numeric Attribute State *	
Narrative attribute state	**Median**	**95th percentile#**
A Unlikely to be toxic effects even on the 5% most sensitive species	≤1.5 †	≤4.1 †
B Potential toxic effects on 5% most sensitive of species, unlikely to be toxic effects on more than 10% of species.	>1.5 and ≤4.1†	>4.1 and ≤6.8 †
Bottom line	4.1†	6.8†
C Potential toxic effects on many sensitive species (20% species). Acute toxicity possible for the most sensitive species (5% species).	>4.1 and ≤12 †	>6.8 and ≤24 ‡
D Potential toxic effects on multiple species, including acute toxicity	>12 †	>24 ‡
Compliance with numeric attribute states should be undertaken after adjustment for bioavailability.		
Based on a monthly monitoring regime where sites are visited on a regular basis regardless of weather and flow/water level conditions. Record length for grading a site based at least 30 samples collected over a 3-year period.		
The **grading classification** using median and 95th percentile attribute thresholds should be made based on monitoring data collected over 3 years. Attribute band must be determined by satisfying both numeric attribute states (i.e., both columns in any one row) or, if that is not possible, according to the worst numeric attribute state. * Best practice for ecological risk assessment is to assess classification against 95th percentile on an **annual basis**. Exceedance of an attribute threshold in any 12-month period would be considered an **“orange” warning level** for adverse ecological effects and provide an indicative classification and a trigger for investigation. # 95th percentile to be calculated using the Hazen method[109].		
†Numeric attribute state is based on pH 7.5, hardness 30 mg/L, DOC 0.5 mg/L. ‡CCME short-term guideline value at hardness 30 mg/L, DOC 0.5 mg/L.		

[109] https://environment.govt.nz/publications/bathewatch-user-guide/hazen-percentile-calculator/

Question 3.1 How are these different to previous draft tables for copper and zinc?

Table 3-2 and Table 3-3 are updated from previously published attribute tables[110], by:

- specifying a time period for grading assessments and requirements for the number of samples,
- updating the numeric attribute state thresholds from the ANZECC & ARMCANZ (2000) DGVs to the updated draft DGVs as presented in Table 1-1,
- using "bioavailable" copper and zinc concentrations, rather than dissolved, to account for factors that influence metal bioavailability, and
- replacing the US EPA (1995) acute GV[111] for zinc with the CCME (2018) short-term GV[112] for the C/D thresholds that are compared with a 95th percentile.
-

3.2 Timeframe for grading sites with this attribute

The attribute tables recommend the use of data collected over a 3-year period to grade rivers and lakes in terms of copper and zinc. The three-year period was selected as a balance between a shorter time frame (for example, one year) that is more suitable for toxicology assessments, and a longer time frame (for example 5 years) that captures a range of flow and environmental conditions. This is an interim recommendation and should be revisited after application of the attribute tables in multiple regions. For example, although 5 years of sampling has been demonstrated to broadly represent the flow regime in Auckland streams[113], this may not be the case in other regions, especially those with drier climates.

Ideally the time frame for grading sites for **toxicity** attributes should be relatively short to provide protection – annual grading has been recommended for attributes related to toxicity[114]. This ensures that any exceedances of GVs are limited, both in time and number (e.g., 1 value out of 12 for 1 year of monthly monitoring). Conversely, with a five-year time frame, the 95th percentile thresholds could be continuously exceeded for 3-4 months in a row without changing the grading, but potentially resulting in adverse effects. Where that threshold is the band C/D threshold, adverse toxic effects that are more than minor would be expected. Further, concentrations could exceed the median B/C threshold for just under 2.5 years (implying potential adverse effects on up to 20% of species), and still get a B grading.

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[110] 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 Council Technical Report 2019*. Auckland.

[111] 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. EPA 820-B 96-001. September 1996. Washington D.C. https://nepis.epa.gov/Exe/ZyPURL.cgi?Dockey=20002924.TXT

[112] 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. January 2018. Winnipeg, MB. https://ccme.ca/fr/res/2018-zinc-cwqg-scd-1580-en.pdf

[113] Snelder and Kerr (2022). Relationships between flow and river water quality monitoring data and recommendations for assessing NPS-FM attribute states and trends. Prepared for Auckland Council by LWP, Land Water People. October 2022.

[114] Hickey (2014). Derivation of indicative ammoniacal nitrogen guidelines for the National Objectives Framework. NIWA *NIWA Memorandum MFE13504*.

On the other hand, assessments using only one year of data (e.g., sampling monthly) are unlikely to provide satisfactory precision for an estimate of the median or 95th percentile and could also lead to risks of false state switching (where the attribute state changes over time due to uncertainty associated with the small sample size, rather than a real change in the waterbody[115]). Furthermore, higher metal concentrations typically occur during higher stream flows and these "high flow" events are short-lived, particularly in urban environments where the hydrology is affected by rapid transport over impervious surfaces and through piped networks. When sampling is undertaken monthly, a five-year period is likely to include more samples at high flows (or flows above median) than would be included in a single year of sampling. Assessments over a single year are also more influenced by climate variability (e.g., a particularly wet or dry year) than assessments over a longer period.

We recommend that the 95th percentile is assessed annually, not for formal attribute grading purposes but to provide an indication of the likelihood for adverse effects. This is consistent with the recommendations by ANZG (2018), which recommends comparing 95th percentiles of monitoring data with DGVs to assess potential for ecological harm, and that even a single observation greater than the DGV indicates exceedance of that DGV[116]. Any changes in grades during these annual assessments can be tracked over time and this would facilitate management intervention more rapidly than when grading using a three-year period or during the five-yearly reporting.

3.3 Data requirements for assessing attribute state

Data requirements (below) for assessing copper and zinc as attributes are considered interim. The recommendations are provided to guide initial use of the attribute tables for grading sites, however they should be revised when the tables have been applied in two to three regions and when more data become available for assessing their applicability across the country.

The attribute tables recommend at least 30 samples collected over the 3-year period. McBride (2005) suggests at least 30 samples is good for providing certainty around a median and will also provide greater certainty of the 95th percentile value (as compared to 12 measurements used in the annual assessments).

Stream metal concentrations are typically highly right skewed (mean greater than median, few very high points) and the 95th percentile value will differ depending on the method used for calculation. Consistent with other NOF attributes, the Hazen method should be used to calculate percentiles for copper and zinc attributes as it provides a "middle-of-the-road" estimate.

The text "*where sites are visited on a routine basis regardless of weather and flow/water level conditions*" is included because samples should be collected under a range of flow (or in the case of lakes, water level) conditions. It is assumed that the copper and zinc attribute states should apply across the full flow range of any waterbody, and therefore monitoring should also represent this flow range.

In urban settings, metal concentrations are frequently higher during higher stream flows - that is, those associated with rain events that wash contaminants into streams. A data set based on only low flows would likely under-estimate the higher concentrations that freshwater organisms are at times

[115] McBride (2016). National Objectives Framework: Statistical considerations for design and assessment. Ministry for the Environment. Wellington, NZ.

[116] https://www.waterquality.gov.au/anz-guidelines/guideline-values/default/water-quality-toxicants#determining-if-a-toxicant-dgv-has-been-exceeded

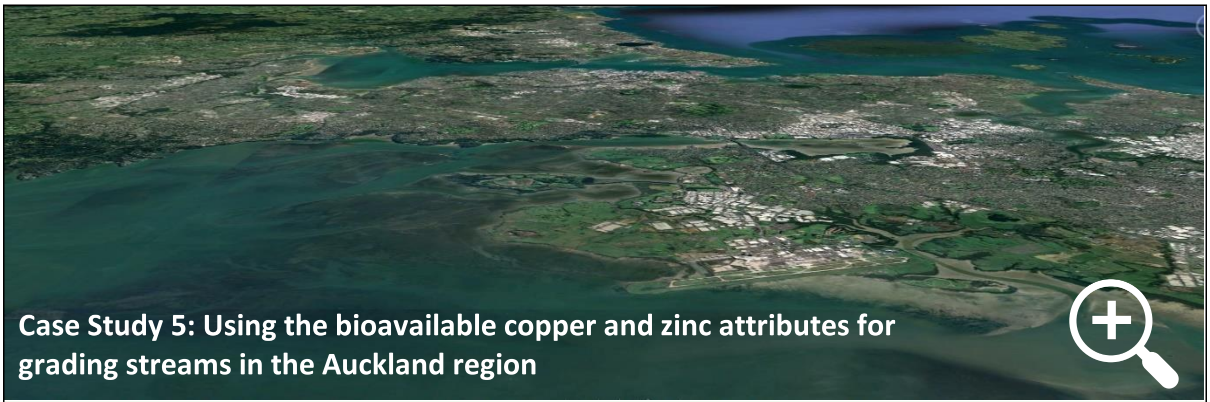
exposed to. On the other hand, a data set based solely on storm event sampling only would not indicate the conditions organisms are exposed to most of the time. This is important as most of the band thresholds in the copper and zinc attribute tables are derived from chronic DGVs.

It could be argued that higher flow events (i.e., those above median flow, occurring after several mm of rainfall) represent only short-term exposures to higher metal concentrations, and that these should not be included when comparing to the attribute table. However, toxicity can occur with repeated exposures to higher concentrations. The band C/D threshold is based on short-term GVs to address these short-term exposure events (i.e., the C/D band threshold represents an acute toxicity threshold).

3.4 Estimating bioavailable copper and zinc concentrations

The attribute states are defined as “bioavailable”, and DOC (for both copper and zinc), pH and hardness (zinc only) monitoring data will be required to estimate bioavailable concentrations. Users should adjust measured data to “bioavailable” copper and zinc using look-up tables/R scripts (see Appendix A) before comparing these values with those in the attribute tables. This is analogous to the approach used for ammonia (toxicity) in Table 5 of the NOF, whereby ammonia is adjusted based on pH.

Dissolved copper and zinc concentrations could be compared with the respective attribute table without adjusting for bioavailability, but this would result in a poorer grading than a comparison based on “bioavailable” concentrations (see Case Study 5).



Case Study 5: Using the bioavailable copper and zinc attributes for grading streams in the Auckland region

This case study box illustrates the use of the attribute tables for the Auckland Region. Auckland Council have measured DOC, pH and hardness in their SOE programme since around 2017 (depending on the site) and sought to grade streams based on copper and zinc concentrations measured in that period. This involved three steps:

1. The measured TMF values were used to calculate "bioavailable" copper and zinc in each sample at each site. For copper, the equation in the attribute table was used. For zinc, a calculation was required using R code[117].
2. The "bioavailable" concentrations were summarised, with median and 95th percentiles calculated over a three-year period (in this case, 2019-2021).
3. The summary statistics were compared against the attribute tables to identify the grading band.

Figure 3-1 shows the grading results for 33 stream sites using bioavailable copper and zinc concentrations.

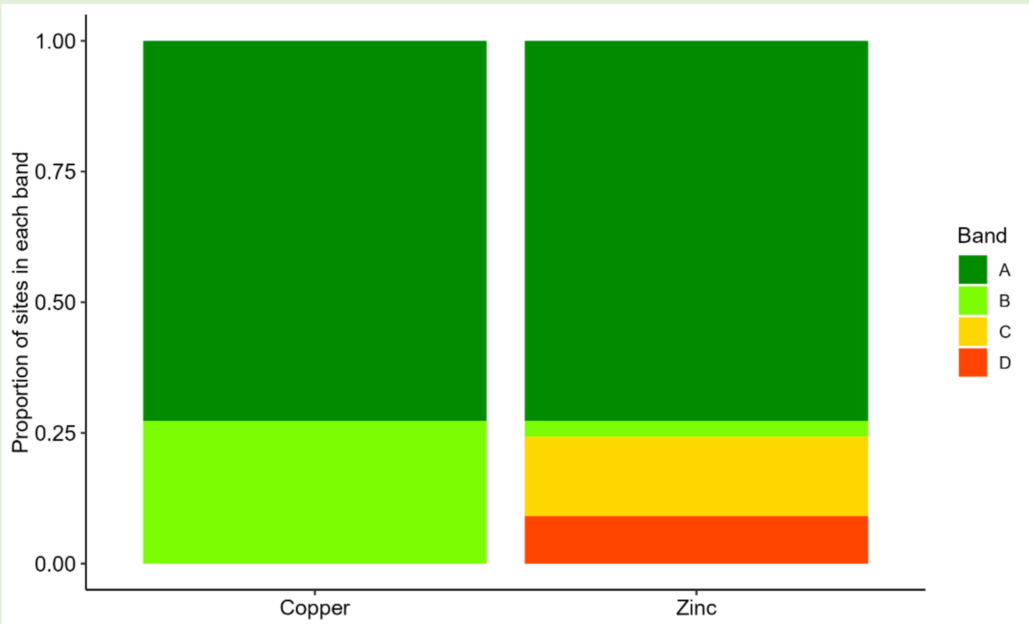


Figure 3-1: Attribute bands for copper and zinc based on a comparison of bioavailable concentrations with attribute table values (adjusting each sample for bioavailability).

[117] To be made available via Envirolink website.

Figure 3-2 presents the attribute grading results without adjusting copper and zinc concentrations for bioavailability. This approach is overly conservative, resulting in many more sites with poorer grades, especially for copper.

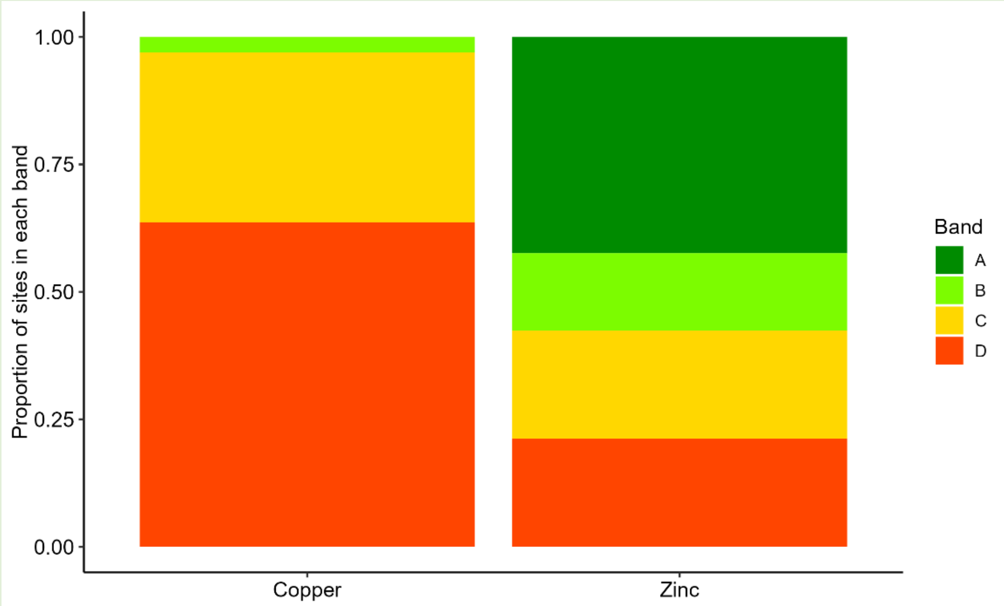


Figure 3-2: Attribute bands for copper and zinc based on comparing dissolved concentrations (not adjusted for bioavailability) to attribute table values.

3.5 Suitable types of data for attribute state assessments

The NPS-FM (2020) implies that regional councils monitor attributes through sampling and measurement, however copper and zinc concentrations from model predictions can also be compared with the attribute tables.

Comparison of modelled copper and zinc concentrations will likely be complicated by the lack of corresponding TMF data (see also section 1.7). The way that any comparison is undertaken would depend on the purpose of modelling. Purposes may include:

- Identifying locations where water quality has degraded over time or is expected to degrade in the future.
- Identifying locations of higher risk where further investigations will occur (which may include sampling and measurement of TMFs).
- Identifying locations of higher risk where remediation will be required.

Screening level assessments (with no adjustment for bioavailability) may be suitable to identify degradation over time, but are not recommended for identifying where remediation is required – screening would not provide enough certainty around the locations with high and low risk.

Question 3.2 What is the "burden of proof" applied in the attribute tables?

In discussing statistical considerations for design and assessment of attributes under the NOF McBride (2016)[118] recommends deciding on the burden-of-proof. This is related to the sampling error and the risks of misclassification errors, i.e., the probability of wrongly concluding an attribute threshold has been exceeded when in fact it has not (false positive, Type I error); and the probability of incorrectly concluding an attribute threshold has NOT been exceeded, when in fact it has (false negative, Type II error).

McBride (2016) describes three options to account for sampling error (below) which are then considered in relation to the copper and zinc attribute tables:

- Take a permissive approach, assuming that a NOF attribute threshold *has not* been exceeded unless convinced otherwise;
- Take a precautionary approach, by assuming that a NOF attribute threshold *has* been exceeded unless convinced otherwise; and
- Take the data at face-value with no prior assumption, and use the Hazen method to calculate percentiles.

McBride (2016) recommends the face-value approach (option 3) when the band thresholds used in an attribute table are based on a precautionary approach. The ANZG (2018) DGVs for toxicants are intended to be conservative and protective, being based on data that relates to negligible toxicity. That means that the dissolved copper and dissolved zinc attribute band thresholds are based on a precautionary approach; adopting such an approach is consistent with recent NPS-FM implementation guidance [119]. Therefore, the face-value approach seems the most appropriate approach to burden-of-proof. On that basis, the Hazen method should be used to calculate sample percentiles.

3.6 Attribute type

Attributes in the NOF and those set by regional councils can be either limit-setting attributes (as set out in Appendix 2A of the NPS-FM 2020) or action-planning attributes (as set out in Appendix 2B of the NPS-FM 2020). For limit-setting attributes, councils must limit resource use to achieve target attribute states (but can include non-regulatory measures as well). For action-planning attributes, councils must produce an action plan to achieve target attribute states (but can limit resource use as well). For copper and zinc, a limit on resource use might include restrictions related to the use of high metal-yielding building materials (such as copper or zinc roofing), restricting the loads of copper and zinc in consented discharges, or a land use control (such as the control or extent of an activity). In contrast, an action plan may focus on the methods that would reduce copper and zinc concentrations in the receiving environment, for example by requiring additional stormwater treatment, reductions in transport usage, educational and incentive programmes etc.

It is up to individual councils to decide whether dissolved copper and zinc should be established as limit-setting attributes or action-planning attributes. That decision may relate to the information

[118] McBride (2016). National Objectives Framework: Statistical considerations for design and assessment. Ministry for the Environment. Wellington, NZ.

[119] Ministry for the Environment (2023). Guidance on the National Objectives Framework of the National Policy Statement for Freshwater Management. Ministry for the Environment. Wellington.

available for their region, including the ability to quantify copper and zinc inputs to fresh water. Regardless, the body of evidence for the two tables (Table 3-2 and Table 3-3) is similar to those for ammonia (toxicity) and nitrate (toxicity) which are compulsory limit-setting attributes in the NOF.

Broad principles for developing NOF attributes were provided with implementation guidance for the 2014 version of the NPS-FM (MfE 2014)[120]. These principles are set out in Table 3-4, along with an assessment for dissolved copper and dissolved zinc.

Table 3-4: Assessment of dissolved copper and zinc information against the broad principles for developing NOF attributes as outlined by MfE (2014).

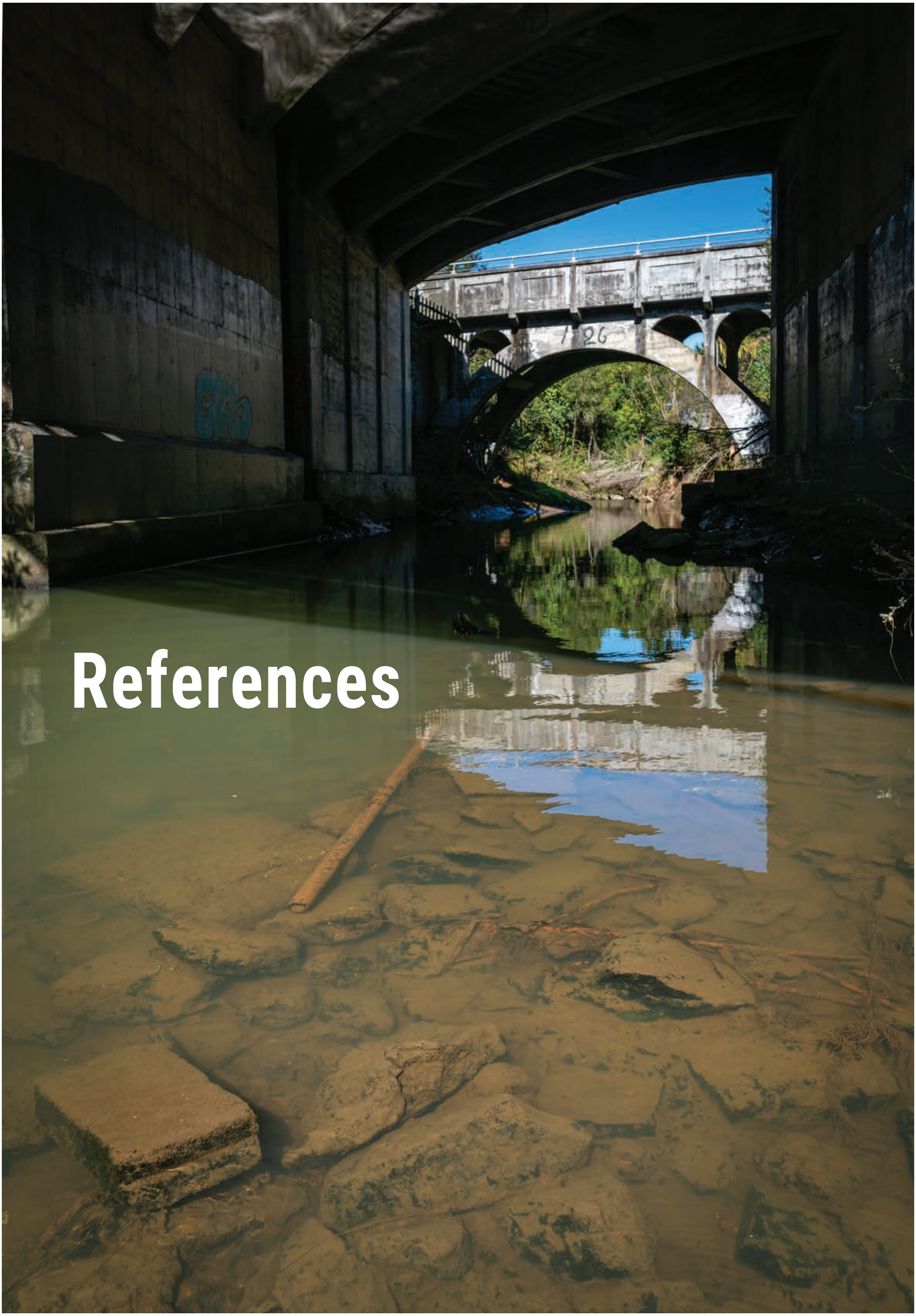
NOF attribute requirements	Assessment for dissolved copper and zinc
1 Link to the National value	
Is the attribute required to support the value? Does the attribute represent the value?	Yes, metal attributes are accepted as important aspects of ecosystem health, particularly within urban environments
2 Measurement and band thresholds	
Are there established protocols for measurement of the attribute?	Yes there are and these are set out in the NEMS Discrete Water Quality (Part 2 Rivers)
Do experts agree on the summary statistic and associated time period?	Yes, as per an expert panel workshop[121]
Do experts agree on thresholds for the numerical bands and associated band descriptors?	Yes, these were agreed in a previous project (see Gadd et al. 2019[122]) and updated in this report
3 Relationship to limits and management	
Do we know what to do to manage this attribute?	Yes, this is widely understood.
Do we understand the drivers associated with the attribute?	Yes, the main driver is urbanisation however, relationships with land use and rainfall/stream flow are complex.
Do quantitative relationships link the attribute state to resource use limits and/or management interventions?	Yes, this is broadly understood.

[120] MfE 2014b. *National Policy Statement for Freshwater Management 2014: Draft Implementation Guide*. ME 1162, Ministry for the Environment, Wellington.

[121] Workshop held 15 June 2023, attended by Drs Jennifer Gadd, Chris Hickey, Coral Grant, and Juliet Milne.

[122] 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 Council Technical Report 2019*. Auckland.

NOF attribute requirements	Assessment for dissolved copper and zinc
4 Evaluation of current state of the attribute on a national scale	
What do we know about the current state of the attribute at a national scale?	There is a good understanding of Cu and Zn at the national scale for urban streams. Less is known about Cu and Zn associated with other land uses.
Is there data of sufficient quality, quantity and representativeness to assess the current state of the attribute on a national scale?	Cu and Zn are typically only regularly measured in larger urban areas. There is limited data for much of the country. These attributes are not being proposed for nationwide implementation but can be adopted by individual councils where considered relevant.
5 Implications of including the attribute in the NOF	
Do we understand/can we estimate the extent (spatial), magnitude, and location of failures to meet the proposed bottom line for the attribute on a national scale?	It is likely that many urban streams would fail the recommended bottom line for zinc.
Do we understand the implications for socio-economic impacts?	Not assessed (out of scope for this guidance) but may be significant



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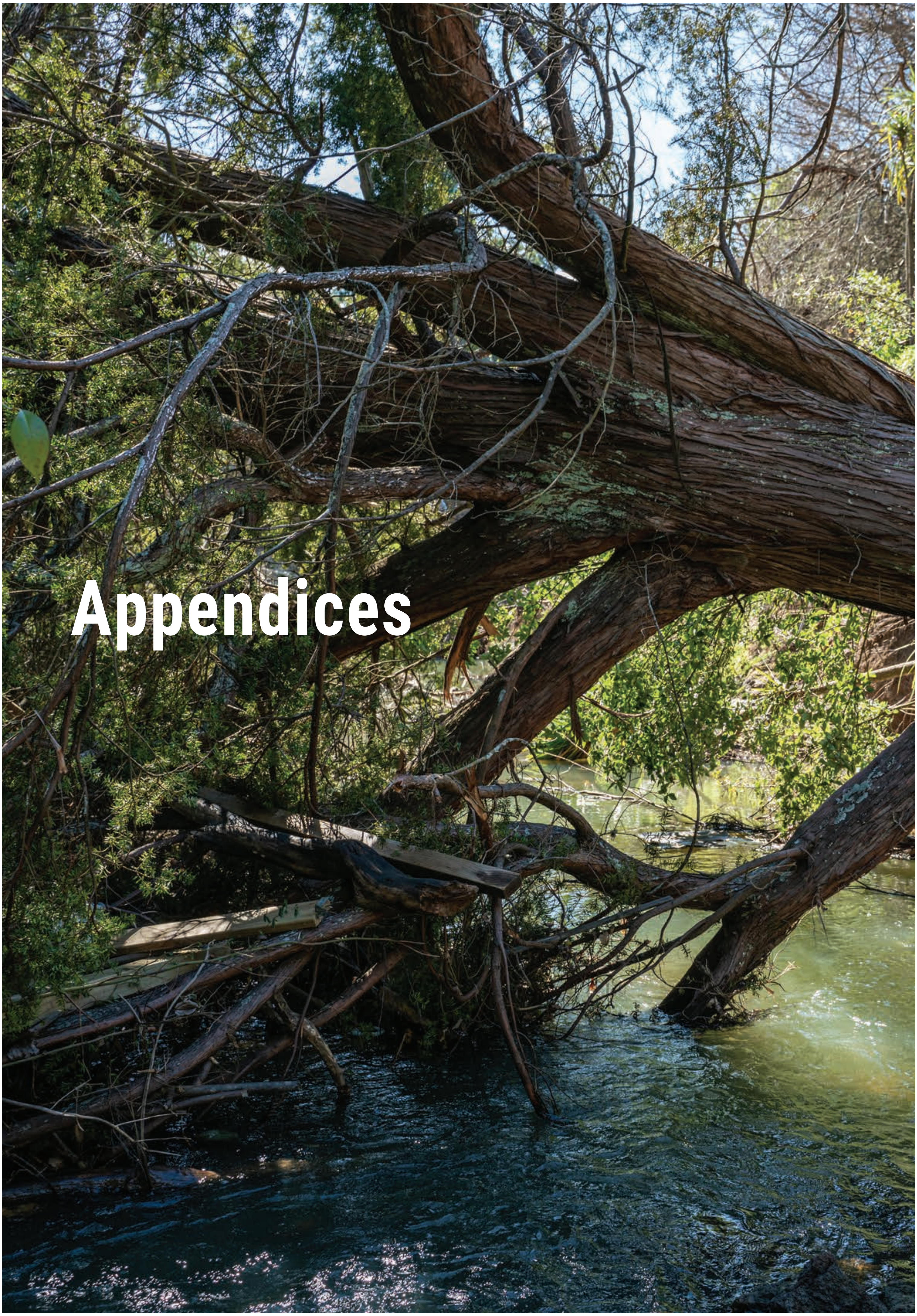
Appendices



Appendix A: Links to the draft DGVs

The draft DGVs as submitted to ANZG can be accessed from:

https://www.waterquality.gov.au/anz-guidelines/guideline-values/default/water-quality-toxicants/toxicants/draft-copper-fresh-2023

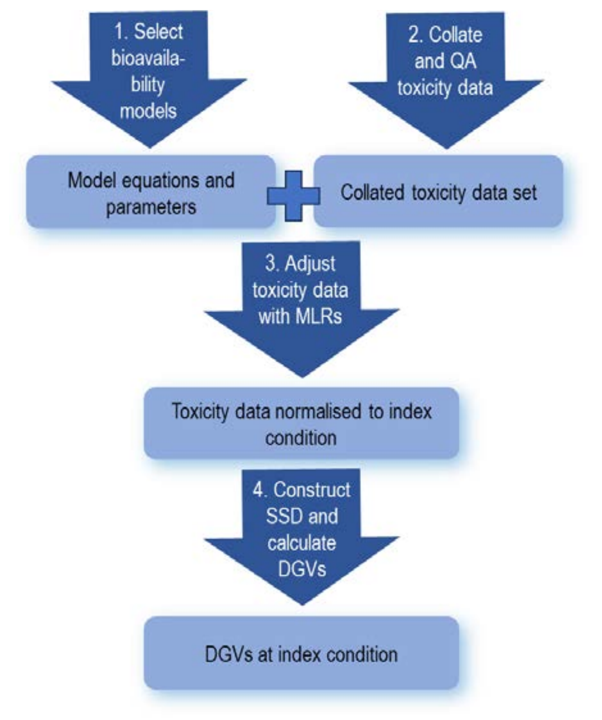
https://niwa.co.nz/static/web/NIWA_download/Zinc_fresh_DGV_draft.pdf

The code to adjust zinc water quality guideline values can be accessed from a public github repository:

https://github.com/niwa/CuZn_DGV_adjusters/tree/main

Appendix B: Overview of derivation process for dissolved copper and zinc DGVs

The derivation methods for the dissolved copper and zinc DGVs are briefly described in the technical briefs submitted to ANZG, outlined in Figure B.1 and summarised in Table B.1.



1. Model selection and rationale described in Gadd (2021; 2023). For copper: simple linear regression with DOC. For zinc: multiple linear regressions with DOC, pH and hardness. Species and trophic-level models used (fish/amphibians, invertebrates, and 2 algal models).

2. Follows process in Warne et al. (2018), only using data where copper or zinc, pH and hardness were measured in the toxicity test solutions

3. Analogous to ANZECC & ARMCANZ DGVs where toxicity data were normalised to a hardness of 30 mg $CaCO_3$/L. For copper, simple conversion using linear regression equation. For zinc, four different equations and sets of model parameters

4. SSDs fitted with a Burr model using Burrlioz, and the DGVs calculated from various percentiles to provide different levels of protection

Figure B.1 Steps required to derive bioavailability-based DGVs for copper and zinc (freshwater).

When normalising the toxicity data for deriving the copper DGVs, a simple equation based on DOC was used, analogous to normalising to a standard hardness in the ANZECC & ARMCANZ (2000) DGVs. A similar equation (Equation 1) can be applied to the DGVs to calculate bioavailability-adjusted DGVs at any concentration of DOC.

However, zinc uses four different models with different parameter sets to normalise the toxicity data prior to derivation of the DGV. Because of this, there is no simple single equation to calculate bioavailability-adjusted DGVs for zinc. The different equations and parameter sets (slopes) for fish, invertebrates and algae mean that the relative positions of organisms in the species sensitivity distribution (SSD, the ranking of species according to their sensitivity) can change with different chemical conditions. Each toxicity data point (each representing a different species) must be adjusted based on the selected water chemistry (DOC, pH and hardness) of interest (step 3). The SSD then has to be re-fitted and DGVs calculated from the modelled SSD (step 4). This requires a set of algorithms, currently coded in R, and an R-shiny tool is expected to be developed to assist users.

Table B.1 Aspects related to bioavailability-adjustment for copper and zinc freshwater DGVs.

	Copper	**Zinc**
TMFs included in DGV derivation	DOC only	DOC, pH and hardness
Type of bioavailability model used	1 linear equation model	4 multiple linear equation models (species-specific or for different trophic levels)
Method for adjustment of DGVs	Requires equation only	Requires recalculation of DGV

Appendix C: Steps to develop acute water quality guideline values

Acute (or short-term) water quality guideline values for copper and zinc in freshwater could be developed for use in NZ. This would likely require the following steps:

Step 1: Review models used to account for differing bioavailability of copper and zinc in toxicity test waters and in natural waters. These models may include biotic ligand models (BLMs) or multiple linear equations (MLRs), either existing or to be developed. Determine which model would be best for deriving acute GVs, considering factors such as suitability for protection of native species and ease of use. This selection process is likely best undertaken through an expert panel process. Ideally test models by assessing toxicity to native species in test waters with different chemistry (e.g., pH, hardness and DOC).

Step 2: Collate acute toxicity data for copper and zinc, including the data for toxicity modifying factors such as pH, hardness and DOC. Quality assess the toxicity data following the process outlined in Warne et al. (2018) (Note that the collation step has been completed to some extent through data collation for the chronic DGVs but these data have not been quality assured).

Step 3: Adjust collated toxicity data to a standard water chemistry (i.e., index condition) and derive acute GVs.

Step 4: If necessary, develop tools to support calculation of acute GVs for different water chemistry. This step would not be necessary where the same equation is applied to all trophic levels (such as the equation for copper freshwater DGVs).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