Australian Government
Department of Climate Change, Energy, the Environment and Water

Australian & New Zealand
GUIDELINES FOR FRESH & MARINE WATER QUALITY

Response to public submissions on draft default guideline values for copper in freshwater

September 2026

Draft default guideline values (DGVs) for copper in freshwater were published on the Water Quality Guidelines website for a 3-month public consultation period. During this period, comments for the draft DGVs for copper in freshwater were received via public submission.

Responses to comments and any associated edits to the draft DGV technical brief are outlined in this report, de-identified for public record. In accordance with the formal post public comment DGVs approval process, the responses and revisions have been approved by the jurisdictional technical and policy oversight groups, and noted by the National Water Committee.

The default guideline values for copper in freshwater are now published as final. For additional information on the publication process, please refer to the pathway for toxicant default guideline value publication.

The Water Quality Guidelines Improvement Program thanks all submissions for their valuable contribution to the development of default guideline values for the protection of aquatic ecosystems.

Attachment A

Response to public submissions on draft default guideline values

Toxicant: Copper in freshwater

Technical comment	Response	Action taken
Approach to copper TMFs		
1. Based on Gadd (2021), the '2023 Draft Copper Guidelines' state: "As no BLM or MLR models for copper toxicity have been validated for Australian or New Zealand water quality conditions and species, an adjustment based on DOC concentration is used for the current DGVs. Of the modifying factors included in the BLMs and MLRs for copper, DOC is the most influential factor for determining copper toxicity, and it is the only factor that is consistent in all models and species." (p.6). No qualification is given for DOC being "the most influential factor" and there is no in-depth analysis of the supposed consistency by which DOC is said to modify copper toxicity	The technical brief acknowledges that other factors (pH, alkalinity, calcium) are important in modifying copper toxicity for some species. More information has been added to this section to describe the effect of these factors. Note that comparative to **acute** copper toxicity data (on which the BLM and its predecessors were developed), there are **fewer studies that examine the influence of pH, hardness, alkalinity and DOC on chronic toxicity**. The influence on chronic toxicity may not be the same as acute toxicity due to differences in the mechanism of action, and the ability of organisms to regulate internal copper concentrations in longer exposures. Therefore, the information provided is based on studies of chronic toxicity. Regardless, the available information suggests that the effect of pH, hardness and/or alkalinity on copper toxicity is unlikely to be a simple relationship across all water chemistry and across all species/trophic levels. The previously used hardness adjustment is no longer considered appropriate for all species and for a generic derivation. Accounting for these factors may require models more complex than a simple linear regression (such as the BLM, which includes both abiotic and biotic influences on copper bioavailability) or a suite of models, appropriate for different trophic levels. This is the approach that has been used internationally – using one or more BLMs. The BLMs include an abiotic component (speciation model) and a biotic component (coefficients that indicate binding to and competition for biotic ligands). DOC affects copper toxicity through an abiotic mechanism – complexation of copper. This influence is well-understood through measurements of copper using ion selective electrodes, and through speciation modelling. It is implemented in the BLM solely within the chemical speciation component of the model. By contrast, while pH influences copper speciation (an abiotic process) – with higher free copper concentrations at low pH – there are also biotic components represented in the BLMs (both acute and chronic versions). The H^+ ions compete with Cu^{2+} for binding sites on the biotic ligand, as represented through the log K_{HBL} values in the biotic component of the model. Similarly, the effect of hardness is primarily through competition of Ca^{2+}, Mg^{2+} and Na^+ for binding sites (log $K_{CaBL,}$ log K_{MgBL} log K_{NaBL}). The **BLM** model used in the **US EPA** criteria was developed from and assessed for **acute toxicity data** for 6 species (2 fish and 4 water fleas). This model is used in the US EPA criteria to adjust the acute toxicity values, and in accordance with the US process, the acute data are used to calculate the chronic criteria. The **EU** guideline value derivation process uses **chronic toxicity data for their BLM**. The acute BLM model was not adequate for predicting chronic toxicity, as demonstrated for *Daphnia magna* (De Schamphelaere et al. 2004). A different BLM version based on chronic *D. magna* data was developed (and validated) for invertebrates (one rotifer *Brachionus calyciflorus,* two molluscs *Lampilis siliquoidea* and *Hyridella depressa,* and an amphipod *Hyalella azteca*). The acute *D. magna* model (with different coefficients to the chronic model) was considered	Revisions made to Sections 3.2 and 3.3. New Section 3.4 and Appendix C added.

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Technical comment	Response	Action taken
	suitable for predicting bioavailability effects of chronic copper toxicity to fish, and used for all fish species. A third model based on algae is used for all algae and higher plants. In **Canada**, the **US EPA BLM was adapted** to predict chronic copper toxicity, and used across all fish and invertebrates. Furthermore, a plant BLM is also used in their derivation and is used for all plant and algal species. A review of these BLMs indicated key differences between the models – particularly with regard to the effect of hardness on copper toxicity. With the EU model, increased hardness results in lower toxicity estimates (i.e., no protective effect) whereas the Canadian model retains a protective effect of hardness (consistent with the acute model). The strengths and weaknesses of each model, and its applicability to Australian and New Zealand native species, would need to be evaluated before either model could be used for deriving ANZG guideline values. In the absence of that evaluation (and funding to do so), a more simplistic approach was sought to incorporate bioavailability. An alternative option of not incorporating toxicity modifying factors would result in overly conservative guideline values in many natural waters. Therefore, the DOC approach has been recommended as it is the only one of the three key TMFs (the others being pH and hardness) where the effect on toxicity modification is consistent across species, as this works through an abiotic mechanism. DOC reduces copper toxicity through formation of copper-organic matter complexes, and therefore it mitigates toxicity across all (biological) species. Further, the data available suggest its effect is stronger than the effect of pH, hardness and/or alkalinity. By contrast, though pH has an abiotic effect (on copper speciation), it also has biotic effects (through competition for binding sites and possibly other mechanisms for algae). <u>Changes to technical brief:</u> **This rationale for using a simple DOC regression was described in Gadd (2021) but is now repeated and expanded on in the technical brief.** Further explanation of the effects of TMFs has been added to section 3.2, including information about alkalinity. Figures demonstrating the effect of pH, alkalinity, hardness and DOC on copper toxicity for key species have now been included in a new appendix to the technical brief (Appendix C). Much of the text above has been added to the technical brief (section 3.3 Accounting for toxicity modifying factors) and the existing text largely removed. This was to more clearly describe the methods used internationally to account for TMFs. A new section has been added (section 3.4) which justifies why DOC is the only TMF considered and briefly outlines how these DGVs account for DOC. A reference has also been added to the text regarding DOC being "the most influential factor" (OECD 2017 – the findings of an international working group on metal risk assessment).	
2. In addition, largely absent is a discussion of the mechanisms of copper toxicity to aquatic biota.	The technical brief contained several paragraphs describing the mechanisms of copper toxicity (section 2.1), a level of information consistent with other technical briefs. This has been expanded on to address the submitter's comments, in light of the fact that the mechanisms of copper toxicity may need more explanation than other toxicants. <u>Changes to technical brief:</u>	Revisions made to Section 2.1.

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Technical comment	Response	Action taken
	Some additional text and updated references have been added to the technical brief, along with a slight reorganising of the text to clarify acute vs chronic toxicity. Text added: "Intra-cellular copper can generate reactive oxygen species, which can then go on to damage DNA and proteins (Brix et al. 2022; Grosell & Wood 2002). Copper ions can also displace essential metal ions in biomolecules and bind to some proteins with high affinity, leading to their dysfunction (Grosell & Wood 2002). These molecular pathways, as well as the requirement to maintain the copper homeostasis, increase the energy demands and decrease the energy available for growth and reproduction (Brix et al. 2022; Meyer et al. 2007)." "Thus, chronic exposure to excess copper can, at a cellular and organ level, alter enzyme activity, blood chemistry and development of organs, and damage tissues, and at an individual level, lead to reduced growth, reproduction and survival." No new information was found for plant and algal toxicity and no new text has been added for this.	
3. Crucial, however, are those TMFs that influence copper speciation since the proposed mechanisms of copper toxicity across all taxa are based on the activity of the free cupric ion, Cu2+, and the copper hydroxide ion, CuOH+ (Allen & Hansen, 1996; USEPA, 2003). The toxicity of copper to aquatic biota is perhaps best articulated by Hyne et al. (2005) who note, "the toxicity of copper and zinc varies with water pH, alkalinity, and DOC concentration, and single figure guideline values would be misleading if they did not take these parameters into account" (p.1674). Hence, any approach that seeks to reduce the estimation of copper toxicity to a single TMF, such as DOC, is fundamentally flawed and potentially no better than the traditional hardness-only approach.	It should be noted that the testing by Hyne et al. (2005) was 48-hour survival tests – therefore an acute test – and the results would not be considered relevant for chronic toxicity guideline value derivation – both for species endpoints and response thresholds and as there can be differences in the mechanisms of toxicity. Notwithstanding that fact, the testing by Hyne et al. (2005) demonstrated an increase in copper EC50 values from 2.8 to 16 µg/L over a range of alkalinity of 30 to 125 mg $CaCO_3$/L for the single cladoceran species used for this evaluation. This is a factor of 5.7 increase across the range of alkalinities. By contrast, the EC50 increased from 1.6 to 73 µg/L over a range of DOC of <0.1 to 10 mg/L at pH 6.5, a factor of 45 increase. Note that alkalinities of 200 mg $CaCO_3$/L and over can also be found in Australian and New Zealand waters, so the range tested by Hyne et al. (2005) should be extended for a valid comparison. Assuming the same slope, the EC50 could be 26 µg/L at alkalinity 200 mg $CaCO_3$/L. This would represent a factor of 9 increase, still less than that shown for DOC. (Note that extrapolation to lower alkalinity values resulted in negative EC50 values). The authors agree that both pH and alkalinity influence copper speciation. It is also apparent that pH influences bioavailability through a biotic mechanism, as discussed above. Further, calcium and magnesium can also influence copper bioavailability, at least to some species. A more complex model, that considers multiple TMFs may indeed be the best approach to copper guideline value derivation. However, as stated earlier, in the absence of funding to evaluate the various available models, and to validate a model for Australian and New Zealand species, the pragmatic, single TMF approach has been considered preferable to the current guideline value (based on ANZECC/ARMCANZ 2000) with no adjustment for water chemistry. While BLM-based criteria have been developed in the United States for copper, these criteria have had minimal uptake due to the (actual and perceived) complexity of that approach. As at 2022, only 5 states had adopted the 2007 copper criteria and replaced the hardness-based criteria (US EPA 2022). This demonstrates that while sophisticated models may provide a better indication of toxicity and risk to aquatic organisms, it is also important to ensure that the guidelines are user-friendly.	No action required.

<table>
<tr><th>Technical comment</th><th>Response</th><th>Action taken</th></tr>
<tr><td></td><td><u>Changes to technical brief:</u>
No changes to technical brief related to this item.</td><td></td></tr>
<tr><td>Dissolved organic carbon</td><td></td><td></td></tr>
<tr><td>4. Much of the DOC measured in laboratory waters that has been passed through a purification/filtration system can be contaminated with non-humic DOC. Therefore, the potential contamination of laboratory water with non-humic DOC, meaning that toxicity data which relies on DOC measured in test water (and that did not have humics added) is more likely due to small particles of shed, or leached, plastic, is overlooked in the ‘2023 Draft Copper Guidelines’. Yet it brings into question the data the guidelines heavily rely on.</td><td>There are multiple sources of DOC in chronic toxicity tests, including:
- Dilution water from the purification system
- Faecal matter from the living organisms
- Detritus and debris (i.e., POM and DOM) from the food (which is a requirement in all chronic toxicity tests with fish and invertebrates)
- Exudates produced by plants or algae used as test organisms.
The specifications for Type 1 (ultra-pure) water are TOC ≤0.005 mg/L; and for Type 2 (pure) water ≤0.030 mg/L. However, it is acknowledged that resins can leach substantially higher concentrations, particularly in new (and inadequately flushed) systems, after storage, in aged systems or when UV light and membrane filters are not in place. It is therefore possible that in some cases a high proportion of the DOC measured in laboratory waters is leached from the plastic resins. It is unclear that this could be considered the most likely source of DOC in test waters though, given the additional possible sources.
In one particular case, the authors reported “unexpectedly high” DOC in their laboratory water, and attributed this to their nanopure water system with UV treatment removed (Clearwater et al. 2014; tests with the freshwater mussel Echyridella menziesii). We agree with the submitter that this DOC is unlikely to act like humic acid, and the toxicity test results therefore should not have been normalised to a DOC of 0.5 mg/L using the slope factor.
Two alternative approaches were considered for these data: no adjustment, firstly, assuming that the humic-like DOC in the water was negligible (i.e., <0.5 mg/L); and secondly removing these values from the toxicity dataset, due to the associated uncertainty with these results. Not adjusting these values or removing them from the SSD data set has the effect of very slightly increasing the calculated DGVs (Table D 1) at the 90% and 80% levels of protection (0.75 µg/L and 1.3 µg/L respectively) compared to the draft for public submission. The DGVs at other levels of protection are unchanged (marginal differences are removed when rounding to the recommended number of significant figures). The final decision was to remove these values (and therefore this species) from the derivation.
Table 1: Calculated GVs for dissolved copper in freshwater including and excluding E. menziesii.[a]
<table>
<tr><th rowspan="2">Option</th><th rowspan="2">No. species</th><th colspan="4">DGV for dissolved copper in freshwater (µg/L) a at specified level of species protection (%)</th></tr>
<tr><th>99</th><th>95</th><th>90</th><th>80</th></tr>
<tr><td>Draft for public submission [b]</td><td>59</td><td>0.2</td><td>0.47</td><td>0.73</td><td>1.3</td></tr>
</table>
</td><td>Toxicity value for Echyridella menziesii removed from the final dataset used to derive the DGVs.</td></tr>
</table>

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Technical comment	Response	Action taken
	Draft for public submission, DGVs calculated using ssdtools: 59, 0.15, 0.42, 0.67, 1.2 Not adjusting toxicity data for *E. menziesii*: 59, 0.17, 0.47, 0.74, 1.3 Remove toxicity data for *E. menziesii*: 58, 0.17, 0.47, 0.75, 1.3 a DGVs calculated using model averaging method in ssdtools package (Thorley et al. 2024). DGVs rounded to two significant figures. b DGVs were derived using the Burrlioz 2.0 software for data normalised to DOC of ≤0.5 mg/L. <u>Changes to technical brief:</u> Decision was to remove *E. menziesii* data from the derivation, given the uncertainty in the values. These data now included in Table 1 (data for Australasian species excluded from the derivation).	
5. Also critical is that the clear majority of DOC data the '2023 Draft Copper Guidelines' depend on is estimated, i.e., unmeasured, and typically assumed to be less than the analytical detection limit. The dataset that informs the ECCC BLM is based on 83 preferred endpoints (ECCC, 2021), yet a review of the dataset finds only 33% of connected DOC data is robust and, therefore, valid. The ANZECC methodology states, 'as a general rule, toxicity data published prior to 1980 should not be included' (Warne et al., 2018). Although the cut-off date is arbitrary, data should be assessed on merit alone; yet surely, the cut-off should apply to all data the '2023 Draft Copper Guidelines' depend on, not just the toxicity data that informs the species sensitivity distribution (SSD). The dependency on estimated DOC concentrations greatly weakens the '2023 Draft Copper Guidelines' SSD dataset	It is correct that a large proportion of the toxicity data used in the 2023 draft copper guidelines did not report DOC concentrations, and therefore these concentrations were assumed. DOC was reported for 202 of 396 originally included data points (51%) with the remaining values estimated by others based on the water source or assumed to be 0.5 mg/L. Estimates of DOC concentration in the water are used in all guideline value derivations internationally. For example, the US EPA BLM-based copper criteria (US EPA 2007) include a significant proportion of data where DOC was estimated based on information about the water source. In the EU copper risk assessment, 44 of 54 data points for invertebrates are based on assumed DOC. Estimating DOC concentrations does inevitably add a layer of uncertainty to the guideline value, particularly where the DOC is high (e.g. 5 mg/L or more). The effect of including toxicity data where the DOC concentration was estimated is demonstrated in sensitivity testing, completed as part of this response, and added as Appendix D in the technical brief. When all toxicity data with estimated DOC concentrations are excluded (and removing the data for *E. menziesii*, where there is uncertainty in the measured DOC), there are only data for 31 species. The dataset reflects more recent studies, mainly from after 2010, and only two studies before 2000, as DOC was rarely reported at that time. Based on those data, the SSD model fit remains reasonable suggesting that (from a statistical model fitting perspective) the DGVs could be based solely on data with measured DOC. The DGVs calculated from this SSD are provided in Appendix D and indicate little difference in the DGVs for high species protection as the there is little difference in the data and model fit at the tail of the distribution. Therefore, the inclusion of data with estimated DOC concentrations had a minimal effect on the calculated DGVs. On the other hand, a lower number of species used in the derivation has implications for providing information on the level of ecosystem protection provided for species/genus groups (i.e., the ecological risk assessment	Revisions made to Sections 4.1 and 4.2, and Appendix D. Final dataset, SSD and DGVs updated accordingly.

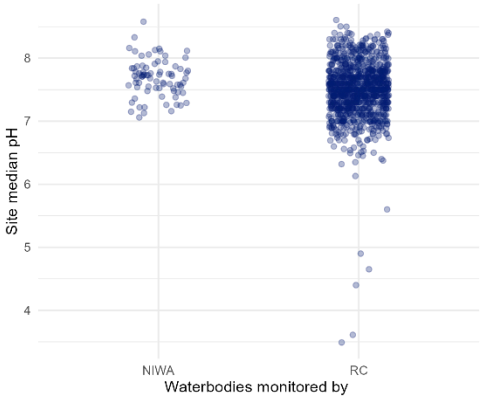
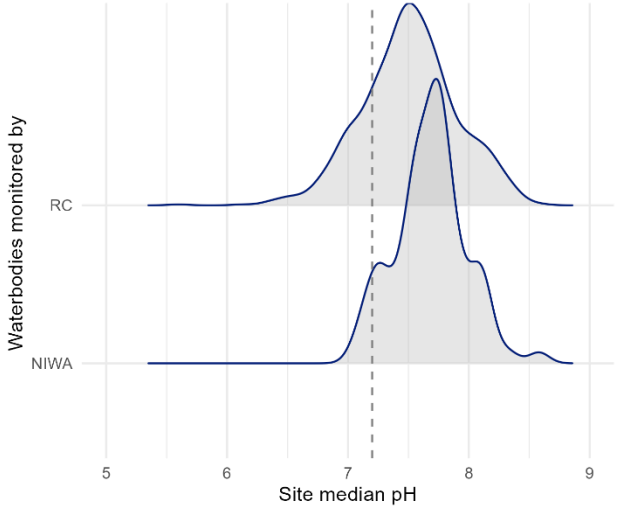
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Technical comment	Response	Action taken
because they result in unreliable normalisation of copper toxicity data. While some studies are robust, such as those of De Schamphelaere et al. (2006) and Trenfield et al. (2022), taking care to add humics to test water as well as measuring DOC, approximately 40% of data is associated with unreported DOC that is estimated mostly as 0.5 mg/L, although the detection limit-based estimates vary. The unreliability of DOC measurements, which underpin the '2023 Draft Copper Guidelines', is basis alone to recommend an extensive revision	component). (Note: A plot showing the sensitivity distribution of major groups has been added to Section 4.2). With the suggested option of excluding all estimated DOC from laboratory studies, there are no longer any insects, fungi or bacteria included in the derivation; the number of fish decreases from 15 to 4 and the number of crustaceans decreases from 11 to 4 (all water fleas, no amphipods or crayfish). To increase the number of species, toxicity data from tests where DOC was estimated were considered acceptable if the DOC was <2mg/L, and if no other data were available for that species. This reduced the uncertainty in normalising data with uncertain DOC concentrations, whilst retaining as many species as possible. <u>Changes to technical brief:</u> Sensitivity testing added to Appendix D including assessing the effect of excluding all data with estimated DOC. SSD plot using only data with reported DOC added to Appendix D, along with discussion of goodness of fit statistics and DGVs calculated from that data set. Further explanatory text added to the Appendix to describe which data/tests were excluded. Paragraph added to section 4.1 of technical brief to describe the inclusion and exclusion of data based on reporting of DOC. *Oncorhynchus kisutch* removed from Table 2 and Appendix A; changes to number of fish species, and SSD updated. Additionally, the genus grouped plot has been added to section 4.2.	
The DOC slope factor		
6. Two approaches were considered for the basis on which to select a DOC slope factor – one derived from Predicted No Effect Concentration (PNEC) data versus DOC (ECI; 2008), and the other derived from BLM-modelled water quality guideline values versus DOC (ECCC, 2021). Gadd (2021) favoured the latter and examined the effects of varying pH (range = 6.0–8.5), hardness (range = 30–330 mg/L as CaCO3), and DOC (range = 0.2–30 mg/L). Ultimately the most conservative (i.e., that which accounts for the least ameliorative effect on copper toxicity) slope factor (0.977) was selected, "based on	The method to derive a DOC adjustment has been significantly changed based on public submissions and subsequent peer technical review. The previous slope factor was based on BLM model outputs. The new adjustment is based on toxicity data from tests at different DOC concentrations. This method differs from the BLM approach used by US, EU and Canada, and is akin to the earlier method used by US EPA for deriving hardness slopes and to MLR methods that are being used in deriving other ANZG guideline values. The method based on toxicity data averages across many differing DOM types, instead of basing the DOC on a fixed proportion of humic acid. <u>Changes to technical brief:</u> A new appendix (Appendix D) has been added which outlines the calculation of the DOC adjustment. As mentioned above, this approach is also briefly outlined in section 3.4.	Revisions made to Section3.4. New Appendix D added.

Technical comment	Response	Action taken
a pH of 6.5 and a hardness of 11.6 mg/L". This "combination of very low hardness and low pH" was justified since this was "not unusual for Northern Territory waters in Australia and West Coast rivers in New Zealand" (Gadd, 2021). Such justification, at least in the New Zealand context, is poorly founded, and there are other flaws associated with the method of slope factor calculation, summaries of which are presented in Figure 4-3 and Table 4-3 of the '2023 Draft Copper Guidelines'.		
7. Figure 4-3 gives the impression that the logarithmic relationship between the Canadian Federal Water Quality Guidelines (FWQG), calculated from the ECCC BLM, and DOC is linear across the range of DOC concentrations, 0.2–30 mg/L. This is not the case. Figure 1 demonstrates this point by way of example. At pH 6.5 and a hardness of 30 mg/L (as CaCO3), an FWQG is incalculable by the ECCC BLM at DOC concentrations < 2.3 mg/L. FWQGs are similarly incalculable at pH 6.5 and a hardness of 100 mg/L (as CaCO3) at DOC concentrations < 1.3 mg/L, and at pH 6.5 and a hardness of 200 mg/L (as CaCO3) at DOC concentrations < 1.0 mg/etc. Central to the '2023 Draft Copper Guidelines' is the development of a toxicity data set in which copper effect concentrations are normalised using the derived slope factor (0.977). Yet, much of the toxicity data so normalised was gained under conditions that are outside the valid slope factor range. Simply put, such data cannot be normalised using a slope factor of 0.977.	It is correct that the FWQG are incalculable at combinations of low pH and low DOC, and at low pH, low hardness and moderate DOC. The slope factors calculated for any given pH and hardness excluded those values, and calculated the slope based only on higher DOC concentrations. As part of investigating these slope factors and responding to submissions and technical reviews, the slope factor approach has been completely changed and some of these concerns are no longer relevant. This response only covers issues that remain relevant. In the draft version, there were 81 data points (of 391) where such a slope factor was applied (tests in low pH and lower hardness waters). For nearly half of those datapoints the DOC was reportedly or assumed to be <0.5 mg/L and so no adjustment was made to the EC10 value. There were 48 data points where an adjustment was made on the basis of a slope factor with high uncertainty. To reduce the uncertainty associated with these slope factors, the following steps were implemented: - Toxicity data from tests with DOC > 10 mg/L have been excluded. This reduces uncertainty in the estimation of EC10 values at low DOC. This does not result in any reduction in species as there were additional data for the same species at DOC <10 mg/L. Toxicity data were not adjusted if there were available data at low DOC. The previous approach was to estimate toxicity values at low DOC and calculate a geometric mean. <u>Changes to technical brief:</u> Text describing the exclusion of data from tests with DOC > 10 mg/L has been added to section 4.1 (paragraph 6). Text describing the amended approach for slope factors has been added to section 4.2 (paragraph 4). *Prosopium williamsoni* has been removed from Table 2 (toxicity values used), Appendix A and the SSD plot. Text regarding number of fish species updated. Changes made to the EC10 values where required. <u>Changes to data entry spreadsheet:</u> The spreadsheet has been updated to exclude data where DOC > 10 mg/L; to exclude slope factors calculated from WQG <0.2 µg/L and to add the NOEC value for *D. thomsoni*.	Revisions made to Sections 4.1 and 4.2, and data quality assessment spreadsheet. Final dataset, SSD and DGVs updated accordingly.

Attachment A

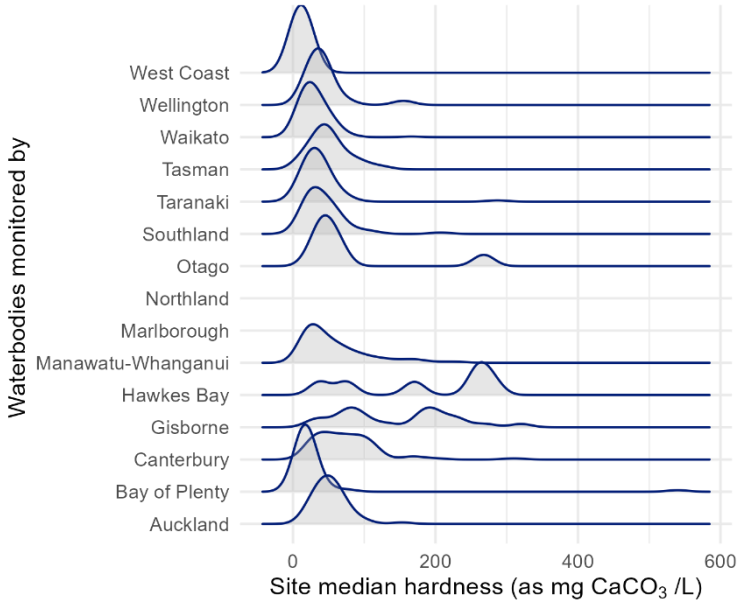
Technical comment	Response	Action taken
8. There are further flaws in the way in which the slope factor was derived. The selection of pH 6.5 as a key driver of slope factor selection has no basis, even under a conservative approach, and is also found contradictory within documentation that supports the '2023 Draft Copper Guidelines', where it is stated that "ranges of 7.2–8.2 have been reported previously for New Zealand (Batley et al. 2018)" (Gadd, 2021; p.29). In fact, the reported ranges are 10%-ile–90%-ile, and neither is the source of the data Batley et al., but Smith and Maasdam (1994). Regardless, the selection of pH 6.5 is extreme versus a recent calculation of a median pH of 7.7 across the New Zealand 77 National Rivers Water Quality Network (NRWQN) catchments (Julian et al., 2017). That low pH is not unusual for "West Coast rivers in New Zealand" is a poor representation of data found in the NRWQN, which contains pH data for four West Coast sites: Karamea at Gorge, Buller at Te Kuha, Grey at Waipuna, Grey at Dobson, Hokitika at Gorge, and Haast at Roaring Billy. Data extracted for the period January 1989 to February 2023 (https://hydrowebportal.niwa.co.nz) indicates a median pH of 7.57 across at sites – pH values of 7.00 or less were observed only 3.6% of the time, and pH values of 6.50 or less were observed only twice among the 1,620 data across 35 years; at Waipuna in June 2018 (pH = 6.46) and at Dobson in February 1997 (pH = 6.41). While a conservative approach to trigger value derivation, such as that which uses toxicity data at or below the threshold of	*Note: As the approach to determining the final DOC slope factor has changed, this comment is no longer relevant. However, a response to the comment has nevertheless been provided, for completeness.* The pH of 6.5 was not selected as a basis of slope factor. Rather, the most conservative slope factor was selected, and this happened to have a pH of 6.5. This was therefore selected as it was not outside the range of waters that could be present in Australia and New Zealand. By contrast, a slope factor based on a combination such as low pH and high hardness would not have been selected, as that type of water would very rarely (if ever) occur naturally. The NRWQN data set (as reported in Smith & Maasdam (1994)) was initially used in determining suitable values for NZ. That data set covers monitoring of 77 generally large rivers from around New Zealand, selected to represent a large area of the country (~40-50% total area; Smith & Maasdam (1994)). While this represents a useful data set, and hence was referred to in earlier documents, additional information for NZ rivers can now be found in the data collected by regional councils (see lawa.org.nz). Data are available from 2003 to 2022 from monthly monitoring. This source provides a more comprehensive data set for understanding water chemistry around New Zealand. This indicates differences between the data sets: the NRWQN is skewed to larger rivers (orders 3 to 8, median order 6) compared to the smaller streams often monitored by regional councils (median order 4, range 1 to 8;Figure 1). While the 10th and 90th percentile for pH in the NRWQN data set is 7.2 to 8.2 (based on the downloaded data from lawa); for sites monitored by regional councils the range is 6.9 to 8.1 (Figure 2; Figure 3). Further, there are a number of sites where the median pH is below 7.2, and even some sites where median pH is less than 6.5 (albeit very few). Around 17% of the monitored sites have a median pH <7.2; indicating a pH of 7.2 would not be conservative (Figure 3).  Figure 1: Stream order of the NRWQN monitored by NIWA (77 sites) compared to sites monitored by regional councils (RC, 1026 sites). Data points are jittered on the x- and y-axes to decrease overlap and show more values.	No revisions required as comment no longer relevant given new approach for determining the DOC slope factor.

Technical comment	Response	Action taken
effects, is warranted; unwarranted is the application of multiple layers of conservatism. The selection of pH 6.5, in the New Zealand setting, as a basis for the slope factor is an example of an unnecessarily conservative approach. It is considered a pH of 7.7 (refer Julian et al., 2017) is realistic in the New Zealand setting and that a pH of 7.2 is conservative, noting that the 10%-ile pH for West Coast sites in the NRWQN is 7.20, i.e., the same as reported by Smith and Maasdam (1994) across all New Zealand. A close analysis of recent hardness concentrations across the NRWQN has not been conducted but it is considered unlikely the 1989–2023 statistics differ greatly from that previously reported, viz., median = 26 mg/L (as CaCO3) and 10%-ile - 90%-ile percentile = 16-56 mg/L (as CaCO3) (Smith & Maasdam; 1994; Batley, et al., 2018). Therefore, like pH, an overly conservative hardness concentration, in the New Zealand setting, forms part of the basis for the DOC slope factor selection.	 Figure 2: Median pH at each site in the NRWQN monitored by NIWA (77 sites) compared to sites monitored by regional councils (RC, 1026 sites).  Figure 3: Distribution of the site median pH in the NRWQN monitored by NIWA compared to sites monitored by regional councils (RC). Dashed line is at pH 7.2, the pH value suggested by submitter as	

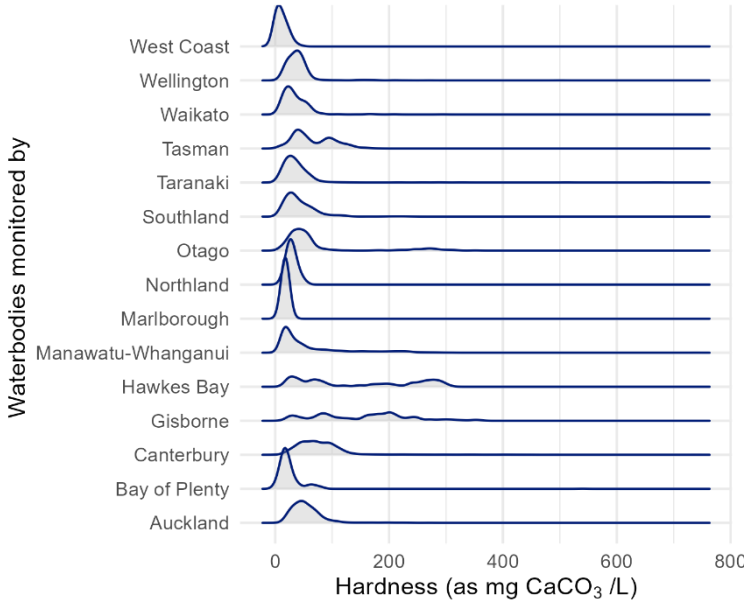
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	conservative. Note scale here cropped to pH 5 to 9 which removes some sites with low pH (including some sites affected by volcanic or geothermal activity). Based on the regional council data set, pH values of 7.00 or less occur in 16.5% of samples (excluding three sites on the Whangaehu River, and the Waiotapu Stream). Similarly, pH values less than 6.51 have occurred over 3000 times (2.6% samples). This is a much higher proportion than those reported by the submitter for the NRWQN data set (3.6%, twice), which likely reflects the broader range of rivers and streams monitored by councils, and possibly greater fluctuations in pH that can be observed in smaller streams. Unfortunately, LAWA does not collect or report water hardness data; and there have been no further analyses of hardness for the NRWQN. However, a number of Councils throughout NZ have been collecting these data, sometimes in relation to use of hardness-related metal guideline values. A database has recently been compiled which contains 17,852 values from 729 sites across 13 regions of New Zealand (Gadd et al. 2026). This demonstrates the generally low hardness waters of the rivers and streams in NZ (Figure 4 and Figure 5). The median hardness (across all data) is 44 mg $CaCO_3$/L (10-90th percentiles 16.7-107 mg $CaCO_3$/L); somewhat harder than the NRWQN dataset. Based on site medians, the overall median is 36 mg $CaCO_3$/L (10th-90th percentiles 16-100 mg $CaCO_3$/L); this is higher than the 11.6 mg $CaCO_3$/L used for the slope factor (although perhaps surprisingly the median value of the monitored streams and lakes is less than 11.6 mg $CaCO_3$/L at 4% sites).	

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	 Figure 4: Distribution of the site median hardness as measured at all sites by regional councils.	

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	 Figure 5: Distribution of the hardness as measured at all sites by regional councils. Regardless of the relevance of using a slope factor for a pH of 6.5, further analysis of that slope factor indicates that it was based on values where the Canadian WQG could not be calculated. Therefore, that slope factor should not have been used for the adjustment of DGVs for waters with DOC > 0.5 mg/L. The next lowest slope factor (where WQGs were predicted at all DOC concentrations) was 1.00. This was for a pH 7.0 and hardness 31 mg/L, a combination that occurs in some waters in both NZ and Australia. <u>Changes to technical brief:</u> The slope factor used for the adjustment of DGVs has been changed and the comment is no longer relevant. Consequently, no changes made associated with this issue.	
Copper speciation		
9. The combined effects of pH and alkalinity in copper BLM models are profound since they strongly influence copper speciation. At pH	Agree that pH and alkalinity influence copper speciation and along with hardness will be important in assessing bioavailability in waters with low DOC. DOC is more than 0.5 mg/L in roughly 97% of data for streams in NZ (pooling multiple measurements across all sites). Around 96% of sites with data had a median DOC greater than	Revisions made to Section 4.4. Also refer to

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6.5, which was selected for the slope factor derivation in the '2023 Draft Copper Guidelines', alkalinity in water is dominated by dissolved carbon dioxide, whereas at pH 7.7, i.e., the median for New Zealand rivers and streams, alkalinity is dominated by bicarbonate. The effect of pH and alkalinity on copper speciation and, ultimately, toxicity cannot simply be ignored. While the '2023 Draft Copper Guidelines' assert without evidence that DOC is "the most influential factor" in determining copper toxicity, it is trivial to demonstrate that pH and alkalinity are more important than DOC, particularly when DOC concentrations are low – and protecting species at low DOC concentrations is a key premise of '2023 Draft Copper Guidelines'. For example, in the absence of DOC: • At slightly depressed pH and zero alkalinity (6.5 and 0 mg/L, as CaCO3, respectively) total copper provides 80.7% mg/L free Cu2+, with most of the balance being Cu(OH)2. • At slightly depressed pH and low to moderate alkalinity (6.5 and 27 mg/L, as CaCO3, respectively) total copper provides 59.2% mg/L free Cu2+, with most of the balance split between Cu(OH)2, CuCO3, and CuHCO3+. • At neutral pH and low to moderate alkalinity (7.0 and 27 mg/L, as CaCO3, respectively) total copper provides 24.2% mg/L free Cu2+, the most dominant other species being Cu(OH)2 (47.2%) and CuCO3, (22.1%). • At slightly elevated pH and low to moderate alkalinity (7.7 and 27 mg/L, as CaCO3, respectively) total copper provides 1.8%	0.5 mg/L (Gadd et al. 2026). Australian rivers and streams generally have higher DOC concentrations than in NZ (Gadd et al. 2026). Therefore, while pH, alkalinity and hardness may be very important for bioavailability in some locations, for the majority, DOC will be the more important driver of copper speciation and therefore bioavailability. The DGVs, with the DOC regression, are not designed to provide an accurate estimation of risk for every feasible situation. DGVs are for generic application in the absence of more relevant guidelines (including site-specific guidelines). In locations with low DOC but higher alkalinity or hardness, the DGVs may provide a conservative measure of risks from copper toxicity. This is conservatism is consistent with a tiered risk assessment process – indicating where effects are possible. Exceedance of the DGVs does not imply that effects will occur. The ANZG guidelines specifically recommend using DGVs as one line of evidence. Further, the implementation guidance for metals suggests that additional methods can be used to further investigate speciation and bioavailability – such as speciation measurements or modelling (covered in Appendix B). Regarding the submitters comments on speciation: Trenfield et al. (2022) reported an IC10 for the water flea of 1 µg/L, and estimated the bioavailable fraction to be 0.03 µg/L (3% bioavailable), based on WHAM. The normalisation of that data from DOC of 2 mg/L to 0.5 mg/L resulted in an IC10 value of 0.3 µg/L. That assumes 30% of the measured copper is bioavailable at DOC 0.5 mg/L; as stated by the submitter, a three-fold increase in bioavailability at the lower DOC. This increase in bioavailability is broadly consistent with predictions using the Windward BLM where the "free Cu" concentration increases 5-fold when DOC reduces from 2 mg/L to 0.5 mg/L (at pH 6.6 and Ca 0.2 mg/L). Further, tests with the publicly-accessible BLM-based tool biomet (https://bio-met.net/) indicate that 30% of the copper is bioavailable at DOC of 2 mg/L (pH 6.6, Ca 0.2 mg/L); whereas 100% is bioavailable at DOC 0.5 mg/L (same pH and Ca). This is a three-fold change, as per the normalisation used for the draft ANZG copper derivation. <u>Changes to technical brief:</u> As outlined under point 1, information has been added to the technical brief regarding the effect of alkalinity on copper toxicity. No changes have been made to the normalisation of the data from Trenfield et al. (2022), or other data, as the DOC-only approach remains the method for DGV calculation. Text has been added to section 4.4 following the guideline values table to clarify that other models can be used where appropriate.	response to comment 5.

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mg/L free Cu2+, the most dominant other species being Cu(OH)2 (88.7%) and CuCO3, (8.3%). The rigorous work of Trenfield et al. (2022) is an example of how copper speciation informs copper toxicity in practice and further highlights the deficiencies of the '2023 Draft Copper Guidelines'. Among the several species studied, the authors determined the IC10 for the highly copper sensitive water flea Moinodaphnia macleayi was 0.0010 mg/L at pH 6.6, 26.5°C, DOC 2.0 mg/L (apportioned as fulvic acid and humic acid), and alkalinity 2.0 mg/L (CaCO3); the WHAM7 chemical speciation model (Lofts & Tipping, 2011; Tipping et al., 2011; UKCEH, 2021) was used to estimate the bioavailable copper fraction (i.e., Cu2+ + CuOH+) as 0.00003 mg/L. The '2023 Draft Copper Guidelines' normalises the *Moinodaphnia macleayi* IC10 to 0.0003 mg/L, which infers the bioavailable fraction increases more than three-fold at pH 6.5, 20.0°C, DOC 0.5, but this is not the case. Additionally, if the WHAM7 model is modified to typical New Zealand pH and alkalinity conditions, the bioavailable copper fraction is reduced by more than 50%, which indicates there should be a commensurate increase in the IC10. These examples of the marked changes in copper speciation with increasing pH and alkalinity highlight a significant gap in '2023 Draft Copper Guidelines'. While it is acknowledged that the toxicity of copper to aquatic biota is complex, it is considered the DOC-only approach used in the '2023 Draft Copper Guidelines' grossly over-simplifies the development of DGVs, rendering them essentially meaningless		
Copper toxicity data		
10. Notable is the high degree of DOC estimation, due to it either not being	As acknowledged above, the copper DGV does rely on a high degree of estimation for DOC (60%).	

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measured at all or being undetectable, which greatly weakens the data, particularly since the effect of DOC is singled out as the critical factor influencing copper toxicity and is used to normalise data. This echoes the concern of USEPA (2007), that "if DOC measurements for the surface water cannot be obtained from a reliable source, then the toxicity test should not be included in … BLM normalization".	This is not unusual for copper guideline values internationally. The US EPA copper GVs, based on the BLM, are also based on estimated DOC, as are the EU guideline values and the Canadian. In all cases, authors of those documents used information about the water source to estimate the DOC, and those estimates have been used for the ANZG derivation. The effect of the estimated DOC has been reduced where possible by assuming a DOC of 0.5 mg/L for laboratory waters and NOT adjusting the toxicity values. It is possible that the DOC in laboratory waters could be much less (e.g., 0.1 mg/L). However, as the toxicity values are not adjusted when DOC concentrations are 0.5 mg/L or less, there is no difference between assuming 0.1 mg/L and 0.5 mg/L. Assumptions of more DOC (e.g., 1 mg/L in tap water) would result in EC10 values being adjusted downwards. Errors in these estimates could affect the calculated DGVs. The effect of including and excluding these values was assessed in a sensitivity test (see response to item 9); and indicated that DGVs would be lower when only data from tests with measured DOC were included. <u>Changes to technical brief:</u> As outlined in section 9, Appendix D added to the DGV technical brief, which outlines the effect of including and excluding data with estimated DOC.	
11. An example of the poor application of a DOC estimate on copper toxicity data is found for the freshwater shrimp *Gammarus pulex* for which the reported NOEC is 0.011 mg/L (Maund et al., 1992). The copper concentration is normalised to 0.0054 mg/L based on a DOC concentration of 1.0 mg/L, yet DOC is not even reported by the authors. This also evidences that toxicity data provided in the '2023 Draft Copper Guidelines' may not have been visited first-hand, rather that secondary sources have been used.	Secondary sources have been used to collate toxicity data and additional physico-chemical data. These secondary sources include the US EPA criteria, Canadian GVs and the EU risk assessment report for copper (supported by the European Copper Institute). In some cases, these documents include data that was not available in the original papers as they have sought further information from authors. In the example of *Gammarus pulex*, the DOC is not based on further communication; it was estimated for the EU risk assessment report based on rules used by Santore et al. (2002) for tests in tap water, and is consistent with the US EPA approach. This value, and others based on further communication or rules, were adopted for the ANZG copper derivation to increase the amount of data available and the number of species. <u>Changes to the technical brief:</u> Data for this species retained, based on rules outlined in response to point 7. Estimated DOC concentrations now indicated in Table A.1.	
12. The relevance of using all copper toxicity data to derive DGVs across all regions of Australia and New Zealand also requires reflection, particularly since many of the species that prove to be the major drivers of the final DGVs are those from tropical freshwaters of low ionic strength. Elsewhere it has been	There are six species included that are based on tests in very low hardness waters (2-3 mg/L) with slightly acidic pH (6.3 to 6.8). The reported EC10 concentrations from these tests range from 1 to 9.5 µg/L. Such reported EC10	Final dataset, SSD and DGVs updated.

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noted that "the unique high sensitivity" of such species, "likely due to the very low ionic strength of the waters", results in an overly conservative toxicity assessment versus under more typical water quality conditions (ANZG, 2023b). And, while it is important to protect sensitive species, a site-specific approach, such as that followed by Trenfield et al. (2022), to setting guidelines values is recommended for highly atypical environments.	values are low, but not outside the range of those reported for other species in test waters (e.g., Australian freshwater mussels 0.7-1.3 µg/L; *A. transmontanus*, EC10 values 1.1 to 3.9). Although the pH and hardness in the test waters were low, as the model used was only based on DOC, these values were not excluded. If a full BLM or MLR method was used for these copper DGVs, it is likely that these values would have been out of range of the models and therefore excluded. Because the DOC in the test waters was around 2 mg/L (depending on species) the DOC adjustment results in estimated EC10 values of 0.3 to 3.5 at a DOC of 0.5 mg/L. Three of these are ranked in the five most sensitive species, with estimated EC10 values less than 0.7 µg/L. The effect of using a DOC adjustment only for these copper DGVs means that the EC10 value is only adjusted downwards. If a BLM or MLR approach that also considers pH and hardness were used, the EC10 values could increase when adjusting from the low pH and hardness of the tests to an index condition. Based on that, it was agreed that these values could be removed from the SSD. In fact, tests in waters with very high hardness were excluded from the derivation as the effect of hardness on the toxicity values was not accounted for with the DOC-only approach. Removing tests in waters with very low hardness could be considered consistent with that reasoning. <u>Changes to the technical brief:</u> Toxicity data have been removed from the derivation based on the low hardness. These data are now included in Table 1 (data for Australasian species excluded from the derivation).	

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