

Response to public submissions on draft default guideline values for zinc in marine water

September 2021

Draft default guideline values (DGVs) for zinc in marine water were published on the Water Quality Guidelines website for a 4-month public consultation period. During this period, comments for the draft DGVs for zinc in marine water 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. The responses and revisions have been approved by the original peer reviewers and the jurisdictional technical and policy oversight groups, and noted by the National Water Reform Committee.

The default guideline values for zinc in marine water 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.

Table 1. Public comments and technical brief revisions

Comment	Response	Action taken
Transparency We would first like to commend the DGV development team on their compilation of a comprehensive marine ecotoxicological database. It is apparent that the process used to assemble such a database was rigorous and that individual studies were reviewed for the appropriate technical information. However, given the comprehensive nature of the ecotoxicological database, there is one flaw that hampers the review process. The lack of citation or reference information for each line of data makes it exceedingly difficult to critically review data or studies not included in DGV derivation. As a consequence, it is difficult to cross- reference studies or data that have been included in derivation of guidelines for other jurisdictions. Additionally, it is difficult to independently evaluate if the majority of the ecotoxicological data should be excluded based on the selection criteria described in the technical brief. <u>We strongly recommend that each data line be cited</u> <u>appropriately, and that full reference information be made available</u> <u>with the data file.</u> Alternatively, a key to the appropriate document codes (i.e., "Paper ID" or "Reference ID number") could be provided. We acknowledge that references can be provided upon request, but it would be preferable to include the complete reference information as part of the data file associated with the technical brief.	Although reference details were provided for data that were used in the final derivation, it is acknowledged that it was not possible to locate the full reference details for all of the line items. This has now been rectified, and full reference details for every line item have been provided, cross-linked to the "Data source ID" number.	The Data entry spreadsheet has been updated to include a full list of source references in the "Source reference details" worksheet. The full citations are cross-linked to the Data source ID number, so that line items of toxicity data can be readily linked to the source reference.
 Inconsistency with recommendation from Warne et al. (2018) and concern with use of data from Reichelt-Brushett and Harrison (2005) The most sensitive species in the final species sensitivity distribution (SSD) is the coral <i>Acropora tenuis</i>, with a converted 	 Queries over the reliability and treatment of the Acropora tenuis toxicity value are noted, and dealt with below: As the value of 10 μg/L represented a LOEC, it does not represent any of the more preferred toxicity estimates of NEC, EC10, NOEC. 	The toxicity value for the coral Acropora tenuis has been removed from the derivation on the basis that it was not based on measured zinc concentrations. The technical

NOEC of 4 μ g/L. This species was not among the organisms included in the original "preferred" SSD, but it was included as supplemental data when the fit of the Burr III model to the original SSD was deemed to be poor. As such, this study was deemed to be of lower quality than the data from the original "preferred" SSD.

- The NOEC from Reichelt-Brushett and Harrison (2005) was reported as <10 µg/L, but it was decided that for conservatism, the LOEC of 10 µg/L would be converted to a NOEC by dividing by 2.5. As indicated directly in the text, this is contradictory to the recommendations of Warne et al. (2018). The specific recommendation of Warne et al. (2018) is: "When using ≥, >, ≤, and < values in calculating a GV, the actual value should be used (e.g., a value of >20 µg/L would, for the purposes of deriving a GV, be used as 20 µg/L)." Therefore, use of 10 µg/L for *A. tenuis* would be appropriate, and consistent with established methods.
- However, because of uncertainties in exposure conditions and ambiguity related to the measurement basis of zinc (i.e., measured vs. nominal concentrations reported in Reichelt-Brushett and Harrison (2005)), we believe the *A. tenuis* data from Reichelt-Brushett and Harrison (2005) should be excluded from the SSD. Specifically, most of the figures in Reichelt-Brushett and Harrison (2005) include (*) for data representing measured concentrations. The (*) is not included in the zinc figure for *A. tenuis*, introducing some ambiguity. Although it is stated in Reichelt-Brushett and Harrison (2005) that all metal concentrations in tests from 1996 were measured, the concentrations reported for zinc, appear to be nominal and the test appears to have been a range-finder toxicity test (i.e., widely spaced treatment levels). For this particular study, NOECs were considered preliminary, and it was indicated that additional study is necessary. This is an especially valid concern,

However, values representing LOECs or EC50s can be used where there are insufficient preferred values to enable the derivation of the GVs or where the fit of the SSD model is poor and the inclusion of (converted) LOEC or EC50 data will improve the model fit. This was the case for the zinc marine DGVs, where an additional nine LOEC/EC50 values were added to the dataset of eight EC/LC10, EC20 and NOEC values.

• It is acknowledged that the decision to treat the value as a LOEC is contradictory to the guidance in Warne et al. (2018). However, the guidance in Warne et al. (2018) on how to treat $</\leq$ and $>/\geq$ values does not appropriately capture the specific details of, and differences between, $</\le$ and $>/\ge$ values, and will be corrected in the next update to the method. "<" values are typically reported where there is a statistically significant effect relative to the controls at the lowest concentration tested. As such, they do not represent NOECs and should not be automatically used as reported (noting that Burrlioz 2.0 does not have the ability to handle censored data, so rules on how to treat such data are required). It is more appropriate to judge "<" values on a case-by-case basis to determine whether they should be treated equivalent to a NOEC or a LOEC (i.e., whether or not a conversion factor should be applied to the value). This can be done by considering the measured effect size at this concentration. In the case of A. tenuis, the effect size was ~25%. As Warne et al. (2018) prefers the use of negligible effect (i.e., no effect or ≤10% effect) data for GV derivation, it is reasonable to conclude that a "<" value with an effect size of ~25% should be converted to a negligible effect (i.e., EC10/NOEC) equivalent. In doing so, it is reasonable to use the LOEC to NOEC/EC10 default conversion factor of 2.5. Such a conservative approach is consistent with the purpose of DGVs to help protect aquatic ecosystems.

brief text, SSD and DGVs have been updated accordingly. The revised DGVs are now slightly higher than when the coral value was included, as follows:

Protec- tion level	Original DGV (μg/L)	Revised DGV (μg/L)
99%	1.8	3.3
95%	5.2	8.0
90%	8.9	12
80%	16	21

A paragraph has been added in section 2.2 summarising toxicity data for corals and recommending further research. given that the NOECs for other corals described in Table 3 (of Reichelt-Brushett and Harrison (2005)) are at least 50-fold higher.

 Additionally, upon review of the database, and original publication, the Reichelt-Brushett and Harrison (2005) study does not report any physico-chemistry data, including pH, salinity, temperature, or dissolved oxygen. Exposures were performed in "sperm free seawater", but the source or details related to the exposure chemistry were not provided. Therefore, it is not possible to determine if the study satisfies the salinity criterion, without assumption. Based on the stated concerns, we recommend that this study be excluded from the DGV derivation, or that additional rationale be provided for its use.

• It is acknowledged that the test in question used widely-spaced concentrations. However, the recommendations provided in Warne et al. (2018) on how to deal with such data were appropriately followed. It is also acknowledged that Reichelt-Brushett and Harrison (2005) stated that the NOEC values for zinc and other metals "... are preliminary and further experiments should be done to verify these values." and also that, given the apparently variable responses of different coral species to zinc exposure, "...further experiments should be done to assess the variability in the effects of zinc on fertilization success." These are appropriate statements given the nature of the data; however, they do not necessarily render the data inappropriate for use in the DGV derivation. The zinc toxicity value for A. tenuis was extracted from the Australasian Ecotoxicity Database (Langdon et al. 2009), which quality assessed the data based on the scoring method developed by Hobbs et al. (2005), and which is similar to that used by Warne et al. (2018), where a score of >50% indicates the data are acceptable to use for DGV derivation (unless major flaws indicate otherwise). Langdon et al. (2009) reported a guality score of 71% for this test. To check this, the ANZG Technical Manager scored the test using the Warne et al. (2018) scoring method, which yielded a score of 60%. Whilst both of these scores are on the lower end of acceptability, the data are still deemed acceptable for use in derivation of DGVs. • The primary author was contacted for clarification on the measurement of zinc concentrations. The primary author confirmed that the zinc concentrations were in fact not measured. Notably, no data based on nominal concentrations were used for the DGVs derivation. Warne et al. (2018) states that "Normally, toxicity data calculated using nominal concentration data would not be used to derive GVs; however, professional judgement can be used to include such data provided a justification for their use is provided...". The A.

	 <i>tenuis</i> nominal value is, upon conversion to a negligible effect concentration, the lowest value in the dataset, by a small margin (just below the NOEC value of 5 µg/L for the scallop, <i>Mimachlamys</i> asperrima). Without conversion, it would be the 3rd lowest value in the dataset. To be consistent with the exclusion of all other data based on nominal concentrations, and noting the various other limitations of the <i>A. tenuis</i> experiment (noted above and in responder's comment) it is agreed that this value should be excluded from the dataset. It is noteworthy that the re-derived 95% species protection value of 8 µg/L is still lower than the original LOEC for <i>A. tenuis</i> of 10 µg/L. Text has been added to the technical brief recognising the <i>A. tenuis</i> value and also other values for corals (e.g., from Heyward 1988), and the need for more definitive zinc toxicity data for corals. Regarding the water physico-chemistry, the primary author confirmed that the chemistry was acceptable; however, the issue is redundant given the zinc concentrations in the test were not 	
Also note that insufficient chemistry data (i.e., lack of reported salinity) is also a potential issue for three additional species (<i>Ulva fasciata</i> , <i>Aiptasia pulchella</i> , and <i>Mytilus trossulus</i>). These three species were included in the preferred SSD (Appendix D) and the final SSD used to derive the DGV.	 It is noted that salinity is not reported for these three experiments. This was captured in the quality assessment. However, the data still passed the quality assessment and were used accordingly. There are often uncertainties in data that require some professional judgement. Some comments for each of these studies are provided below: Ulva fasciata – the tests were carried out in a 85:15 ratio of seawater to pore water. the paper stated that "Salinity of the porewater samples was adjusted, when necessary, to 30 ± 1 parts per thousand (ppt)". Given the porewater was salinity adjusted to 30 ppt, it is considered unlikely that the filtered seawater would have been below the salinity cut-off for marine water of 25 ppt. 	No action taken for DGVs technical brief.

	 Aiptasia pulchella – the paper stated that natural seawater was used for the tests. Other data supplied by one of the co-authors (Reichelt-Brushett) has shown that this collection site is always of appropriate salinity. Mytilus trossulus – Although not reporting salinity per se, this study did report Na and Cl concentrations in the test water (in mM units). When converted to mass units, the estimated salinity was ~30 ppt. This is well within the salinity cut-off for marine water of 25 ppt. Thus, it is appropriate for these three species to be retained in the zinc dataset used to derive the DGVs. 	
Decision scheme for evaluating monitoring data against DGVs As described in the Technical Brief, the marine zinc DGV is based on dissolved zinc. Given that, the first tier in the scheme presented in Appendix A must represent a screening evaluation, the second tier appears to represent the actual comparison of monitoring data to the DGV. However, it is not clear what is meant by "new guideline value" in the second and third tiers. The third tier of the scheme considers metal speciation. For a metal such as zinc, speciation modelling would likely be applicable. Therefore, it would be appropriate to define 'bioavailable' zinc. Would this apply to Zn2+, Zn2+ + ZnOH+, or all positively charged zinc species? Based on these comments, we recommended that some clarifying text be provided with regard to application of the decision scheme for comparison of monitoring data to the DGV.	The term "new" is an error and has been corrected. It is a relic from the 2000 Guidelines decision scheme for metals, where one would first correct a GV for hardness where applicable. However, this is not applicable for zinc in marine waters. As a user works through the decision scheme the original guideline value is retained and used. There is no new guideline value associated with the decision scheme for zinc in marine water. Regarding modelling of bioavailable zinc, this would refer to simple ionic complexes, although there needs to be recognition that there are colloidal forms and weak ionic complexes that can dissociate and cross biological membranes. Regarding measurement of bioavailable zinc, this involves a range of techniques designed to measure the 'labile' fraction of metals that has been shown to correlate with the fraction that is biologically available. Clarification of this has been added to the text of Appendix A.	Figure A 1 has been updated, and minor edits have been made to the text of Appendix A. Brief details around modelling and measurement of bioavailable zinc have been added to Appendix A.
Sensitive Species Inclusion Issue	Based on other public comments received, the toxicity value for the coral species, <i>Acropora tenuis</i> , has been removed from the dataset because it was identified as not being based on measured	No action taken for DGVs technical brief.

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We note that the proposed guidelines are lower than the existing guidelines in part due to the inclusion of more sensitive species in the analysis, including a species of coral - a taxonomic group which is well-known to be extremely sensitive to environmental perturbation. As most inshore waters in the north of New Zealand are largely absent of corals, we consider that the resulting levels of species protection may be overly conservative for many environments in this country. Further, we are concerned that more 'resilient' species may not be as regularly evaluated by researchers compared to more sensitive species i.e., a selection bias may exist whereby researchers don't consider that more resilient species require evaluation - bringing into question whether a 'percent species protection value' actually incorporates the full spectrum of species types and sensitivities. <i>Relief sought</i> We fully appreciate that the DVGs are intended to be applied with respect to local conditions. However, we ask that further guidance is given to regulators, to assist with the application of the proposed guidelines, particularly how they should be considered in the context of the local presence or absence of key species or phyla.	concentrations. Thus, the re-derived DGVs have increased from those in the draft version but are still about half of that of the corresponding ANZECC/ARMCANZ (2000) DGVs. It is noteworthy that the dataset used to derive the current draft DGVs is considered to be more reliable than the dataset used to derive the ANZECC/ARMCANZ (2000) DGVs, as summarised in section 4.1 of the draft technical brief. One of the assumptions of using the species sensitivity distribution approach is that the dataset represents a random sample of the species in the environment and, therefore, that it is representative of the range of sensitivities of species in the environment. The zinc chronic toxicity dataset used to derive the draft DGVs spans 3 orders of magnitude, and includes a small number of species that are either highly sensitive to zinc (e.g., toxicity values <10 μ g/L) or highly tolerant to zinc (e.g., toxicity values >1000 μ g/L), in similar proportions. ANZG (2018) provides guidance on the application of DGVs with respect to local conditions. Understandably, it is not feasible to anticipate and provide guidance for every site-specific issue (e.g., natural absence of particularly sensitive species at a location). Therefore, the Guidelines accommodate the use of best professional judgement to make decisions where the existing guidance does not cover a specific issue. Such judgement decisions need to be defensible and documented and discussed with local jurisdictions. This might include the need for site-	
the development of the DGV could be skewed toward more sensitive species.	discussed with local jurisdictions. This might include the need for site- specific studies to support any proposed modification of DGVs or development of site-specific guideline values.	
Salinity Gan	It is acknowledged that ANZG (2018) does not provide DGVs for	No action taken for DGVs technical
	estuarine waters. However, information on the reasons for this, and	brief.
	additional guidance on how to apply DGVs to such waters, was added to	
We note that the proposed guidelines are intended to apply for waters	the website in 2020, at the following links:	
with salinity of 25 parts per thousand or above, while the freshwater	······································	
guidelines apply to waters with salinity of <2 ppt. There are no default		

guideline values for estuarine waters, as is applicable to the Glenbrook Steel Mill receiving environment. <i>Relief sought</i> We ask that further guidance is provided on the application of the proposed marine (and existing and future freshwater) guidelines to environments with salinities between 2 and 25 ppt - most estuarine waters.	https://www.waterquality.gov.au/anz-guidelines/guideline- values/default/water-quality-toxicants#guideline-values-for-other- water-types https://www.waterquality.gov.au/anz-guidelines/guideline- values/default/water-quality-toxicants/local-conditions#salinity-effects	
Limited Guidance for Assessing Bioavailability Issue We note that the proposed guidelines include a hierarchical approach for evaluating monitoring data against DGVs for metals, including consideration of the bioavailable fraction. However, the guidance regarding how to carry out an assessment of bioavailability or conduct Direct Toxicity Assessment (DTA) is limited and is a highly technical method that few experts are able to deliver in New Zealand. The Water Quality Guidelines website provides some guidance on assessing the bioavailable fraction, but we note that the referenced guidance on conducting DTA has not yet been published. Furthermore, we note that DTA is a technique which is normally used for assessing the toxicity of complex effluents whose characteristics do not vary significantly over time, such as industrial effluents. As such, we consider that the technique is of questionable relevance in situations such as roof runoff, where there may be many factors that affect the toxicity, above and beyond the nature of the product's coating. <i>Relief sought</i> We request that this guidance be developed and released with urgency so that it is usable within a reasonable timeframe of the proposed guidelines coming into effect, and ideally before they come into effect.	It is acknowledged that updated guidance on direct toxicity assessment (DTA) is currently not available on the ANZG (2018) website. Guidance on DTA that has been partially updated from ANZECC/ARMCANZ (2000) is currently proceeding through the approval process and will be uploaded to the website once it is approved. Interested parties can subscribe to website updates to receive notification of new content. Until updated guidance is available, the ANZECC/ARMCANZ (2000) DTA guidance (Section 8.3.6 of Volume 2) still stands, with a need to also consider relevant requirements for deriving guideline values as described in Warne et al. (2018).	No action taken for DGVs technical brief.

Uncertainty about Timeframes for Release of Further Guidelines Issue We understand that the remaining copper and zinc DGVs for fresh and marine waters may be due for release in the near future, but timeframes are uncertain. This creates considerable risk and uncertainty for consenting processes. Relief sought We request that more clarity be provided on expected timeframes for the release of these further guidelines.	Draft DGVs for copper in marine water are likely to be released for public comment in the second half of 2021. Draft DGVs for copper and zinc in freshwater are likely to be released for public comment in the second half of 2021 or in early 2022.	No action taken for DGVs technical brief.
 Specific comments The 2000 marine Zn guidelines reference 23 species, not 24 as indicated in Section 1 of the draft Technical Brief. 	 Responses The reference to 23 species in the 2000 Guidelines zinc in marine water information is incorrect (we can correct this). In fact, 24 species were used for the 2000 derivation. 	Corrections made to text where necessary.
 Section 4.1.1, recommended revision: "there are few particulate phases that zinc would adsorb to." This would replace "absorb". In Section 4.1.2, in reference to the first sentence: the associated data file indicates 3 EC10s, 1 EC20, 9 NOECs, and 3 NECs. Please review and confirm. 	 Correction in section 4.1.1. made. Thank you. This summary relates to the available data prior to reducing to one value per species. The numbers are correct if one checks the data in Appendix B. Reference to Appendix B has been added to the 	
 In section 4.1.2, in reference to the third sentence: there was 1 converted LOEC and 8 converted EC/LC50 values, based on the data file. Therefore, 8 of the original preferential values were used, plus 9 additional supplemental values, for a total of 17 single species values (i.e., Table 1). Please review and confirm. 	 relevant sentence. This text has been revised following the exclusion of the LOEC for <i>A</i>. <i>tenuis</i>. 12 chronic EC10/EC20/NOEC values for eight species were supplemented with eight chronic EC/LC50 values for eight species (not counting the 27 individual EC50s for <i>Mytilus galloprovincialis</i> that were used to calculate a geomean for this species as detailed in Appendix B. The text has been amended to reflect this. 	
• Table 2: "DGV for zinc in freshwater" should be "DGV for zinc in saltwater" or "Marine DGV for zinc".	Corrected. Thank you.	

References

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