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Australian & New Zealand

GUIDELINES FOR  
FRESH & MARINE  
WATER QUALITY

# Toxicant default guideline values for aquatic ecosystem protection

## Zinc in marine water

Technical brief

September 2021

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This publication is available at [waterquality.gov.au/anz-guidelines/guideline-values/default/water-quality-toxicants/toxicants](http://waterquality.gov.au/anz-guidelines/guideline-values/default/water-quality-toxicants/toxicants).

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### Acknowledgements

These default guideline values (DGVs) were derived by Dr Jennifer Gadd and Dr Chris Hickey, National Institute of Water and Atmospheric Research (NIWA), Auckland/Hamilton, New Zealand. This technical brief was internally reviewed by Dr Lisa Golding, Dr Graeme Batley and Dr Jenny Stauber from CSIRO Land and Water, Lucas Heights, NSW, Australia, and independently reviewed by two anonymous peer reviewers and by two contracted technical advisors, Dr Rick van Dam and Alicia Hogan. Valuable comments from the public consultation phase are also duly acknowledged. The DGVs were also reviewed and approved by jurisdictional technical and policy oversight groups and a National Water Reform Committee, prior to being published.

 New Zealand Government



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## Summary

The default guideline values (DGVs) and associated information in this technical brief should be used in accordance with the detailed guidance provided in the Australian and New Zealand Guidelines for Fresh and Marine Water Quality website ([www.waterquality.gov.au/anz-guidelines](http://www.waterquality.gov.au/anz-guidelines)).

Zinc is widely distributed in the Earth's crust and is an essential trace element for micro-organisms, plants and animals. The most common use is in galvanised products, including roofing and other building products. The major anthropogenic sources of zinc into marine environments include stormwater, particularly from tyre wear and runoff from galvanised iron roofs, metal processing and mining and discharges from municipal wastewater treatment plants (Malle 1992, IPCS 2001, Landner & Reuther 2004).

Since the 2000 revision of the marine zinc DGVs, new data have become available, including good quality Australasian species data.

Very high reliability DGVs for (dissolved; operationally defined as <0.45µm filtered fraction) zinc in marine water were derived from chronic (long-term) toxicity data for 16 species, comprising seven molluscs, two crustaceans, one annelid, one cnidarian, two macroalgae, one green microalga and two diatoms (Appendix B lists all chronic toxicity data used in the derivation). The DGVs for 99, 95, 90 and 80% species protection are 3.3 µg/L, 8.0 µg/L, 12 µg/L and 21 µg/L, respectively. The 95% species protection DGV may be under-protective for key sensitive species (e.g. bivalve molluscs, cnidarians). Although the 95% species protection DGV of 8.0 µg/L is still recommended for adoption in the assessment of slightly-to-moderately disturbed ecosystems, the 99% species protection DGV of 3.3 µg/L could be adopted if there are concerns about the protection of key sensitive species.

The Australian and New Zealand guidelines for fresh and marine water quality [website](#) (ANZG 2018) provides guidance for evaluating monitoring data against DGVs and recommends a decision scheme that includes consideration of the bioavailable fraction. The guidance for metals is provided in Appendix A, depicted as a decision tree.

# 1 Introduction

Zinc (Zn) (CAS number 7440-66-6) is a naturally occurring metallic element with an atomic number of 30. It is an abundant trace element, present in the Earth's crust at approximately 10–300 parts per million (Malle 1992), similar to chromium, copper and nickel (Landner & Reuther 2004). It is not naturally found as the native metal; instead, it is predominantly present in the form of sulfide minerals, particularly sphalerite (ZnFeS) (IPCS 2001). Carbonates and oxides of zinc occur less frequently (Stumm & Morgan 1996). There are large deposits of zinc minerals in Australia, Canada, the United States, Peru, China and Iran (IPCS 2001, Landner & Reuther 2004).

Zinc is now the fourth most commonly used metal (after iron, aluminium and copper) (IPCS 2001). The major application of zinc is in the galvanising of iron and steel, which accounts for nearly 50% of global zinc use (IPCS 2001). Pure zinc has low strength, so it is alloyed with other metals, such as copper to produce brass (the most widely used) or with aluminium, nickel, titanium or magnesium for various uses, such as casting and bearings (IPCS 2001, Landner & Reuther 2004). Zinc is also used as a reinforcing agent in rubber and as zinc oxide pigments for paint, while various zinc compounds are also used for dentistry, medicinal and household products (IPCS 2001, Landner & Reuther 2004). Sources of zinc in marine environments include stormwater, particularly from tyre wear in road runoff and runoff from galvanised iron roofs (Timperley et al. 2005, Kennedy & Sutherland 2008), metal processing and mining, and discharges from municipal wastewater treatment plants.

Zinc is a transition metal and exists commonly in the +2 oxidation state (Stumm & Morgan 1996). In saline water, approximately 45% of total zinc is present as the free cation ( $Zn^{2+}$ ), while complexes with chloride also dominate (Krauskopf 1956, Stumm & Morgan 1996). The solubility limit of zinc in saline water is approximately 9 000  $\mu\text{g/L}$  (CSIRO unpublished data). Adsorption of zinc to suspended particles, and the consequent sedimentation of these particles, is a major route of removal for zinc from the water column (Stumm & Morgan 1996). However, under chemically reducing conditions, for example, in anoxic sediments, zinc can desorb from particles and dissociate from iron and manganese inorganic complexes and organic complexes. Additionally, cations at a higher concentration, such as calcium, can exchange with zinc attached to organic ligands (Paalman et al. 1994, Stumm & Morgan 1996), which occurs with increasing salinity in estuarine water (Hatje et al. 2003).

Background concentrations of zinc in marine water are low and can be difficult to measure accurately, requiring use of ultra-trace techniques and special precautions to avoid sample contamination. In the North Pacific Ocean, zinc is found at 4–6  $\text{ng/L}$  (Bruland 1980). In the outer Otago Harbour, New Zealand, total zinc concentrations were 8–18  $\text{ng/L}$  (Hunter & Tyler 1987). Measurements off the coast of New South Wales, Australia, indicate total zinc is <22  $\text{ng/L}$  (Apte et al. 1998).

The ANZECC/ARMCANZ (2000) default guideline values (DGVs) for zinc in marine water for 99%, 95%, 90% and 80% species protection were 7  $\mu\text{g/L}$ , 15  $\mu\text{g/L}$ , 23  $\mu\text{g/L}$  and 43  $\mu\text{g/L}$ , respectively. These DGVs were considered high reliability, derived using the species sensitivity distribution (SSD) method and 75 toxicity values representing 24 species from six taxonomic groups (fish, crustaceans, echinoderms, molluscs, annelids and algae). All values were from chronic studies. Only three values were based on

no observed effect concentrations (NOECs). Most values were based on median effect/inhibition concentrations (EC50/IC50), median lethal concentrations (LC50), lowest observed effect concentrations (LOECs) or maximum acceptable toxicant concentrations (MATC), all of which were converted to NOEC equivalents by dividing by 5 for EC/LC50s and 2.5 for LOEC/MATCs. The lowest value was for a diatom, *Ceratoneis closterium* (formerly *Nitzschia closterium*), of 13 µg/L, converted from a 3-d IC50 (population growth rate) of 65 µg/L (Stauber & Florence 1990).

This technical brief provides revised Australian and New Zealand DGVs for dissolved zinc in marine water. These DGVs supersede the ANZECC/ARMCANZ (2000) DGVs and have drawn upon zinc risk assessments for the European Union (JRC-IHCP 2010) and revisions of zinc guidelines for the United Kingdom (Maycock et al. 2012). This revision incorporates data published since 2000, including chronic data for Australasian species. The revised DGV derivation process and the data used in the derivation are described in Section 4.

## 2 Aquatic toxicology

Zinc is an essential trace element for all trophic levels as it has a fundamental role in the structure and function of numerous proteins and in the maintenance of plasma membrane stability (IPCS 2001). Zinc is found in all tissues of mammals, fish and invertebrates (IPCS 2001). Deficiencies in zinc can lead to disorders, which are well-documented in humans and terrestrial animals and also observed in terrestrial plants. Deficiencies in zinc are relatively rare in aquatic organisms but may be observed in phytoplankton in the open ocean (IPCS 2001).

### 2.1 Mechanisms of toxicity

Most aquatic fauna can regulate internal zinc concentrations, either by excreting excess zinc (Rainbow & Luoma 2011) or by storing it in a detoxified form (Rainbow et al. 2015). However, when zinc intake exceeds an organism's detoxifying capacity, metabolically available zinc may accumulate and cause toxicity, primarily by disrupting the internal calcium balance (Hogstrand et al. 1995, Clifford & McGeer 2009, Tellis et al. 2014, Niyogi et al. 2016). In freshwater fish species, this can lead to hypocalcaemia and eventually mortality (Hogstrand et al. 1995). However, as calcium is at much higher concentrations in marine water, reduced calcium uptake is considered unlikely, and the mechanism of zinc toxicity to marine fish is not clear (Hogstrand 2012). Nonetheless, elevated concentrations can reduce growth and reproduction and increase mortality (Hogstrand 2012). In invertebrates, zinc appears to inhibit oxygen consumption rates and disrupt ammonia excretion (Cheung & Cheung 1995, Wu & Chen 2004), and elevated concentrations can lead to reduced growth rates and mortality (Li et al. 2016). In diatoms, zinc inhibits cell division, resulting in reduced growth rates (Stauber & Florence 1990). As there are various mechanisms of zinc toxicity to aquatic organisms, some of which are common to numerous taxa (e.g. calcium imbalance), zinc toxicity is highly unlikely to exhibit a bimodal or multimodal relationship.

### 2.2 Acute toxicity

The acute toxicity of zinc in marine species ranges from 170 µg/L to up to the solubility limit based on 24-h to 96-h LC50 and EC50 values (USEPA 1987, 1996). Reviews suggest fish are less sensitive (JRC-

IHCP 2010) (24-h to 96-h LC50 values generally >10 000 µg/L) than crustaceans and molluscs (24-h to 96-h LC50 values generally 1 000–10 000 µg/L) (Janus 1993). Early life stages of invertebrates and fish are generally more sensitive than juveniles and adults (USEPA 1987). Testing on Australasian species suggests the same pattern, with crustaceans and molluscs (96-h LC50 values ~400–5 000 µg/L) more sensitive than annelids or fish (96-h LC50 values mainly >5 000 µg/L) (Markich et al. 2002, Langdon et al. 2009); however, differences may also be due to different life stages tested. Testing on New Zealand marine fish species using juvenile life stages suggests they may be more sensitive than North American species, with 96-h LC50 values of 1 830 µg/L for sole (*Peltorhamphus latrus*), 2 650 µg/L for kahawai (*Arripis trutta*) and 2 710 µg/L for flounder (*Rhombosolea plebia*) (Hall & Golding 1998). Early life stages of Australasian molluscs, crustaceans and echinoderms were much more sensitive than the adults (Markich et al. 2002, Langdon et al. 2009).

### 2.3 Chronic toxicity

Chronic toxicity occurs at lower concentrations than acute toxicity, with chronic LC50 values often around 10-fold lower than acute LC50 values (JRC-IHCP 2010). For example, for the marine shrimp *Callinassa australiensis*, the 14-d chronic LC50 value is 1 150 µg/L, compared to the 96-h acute LC50 of 10 200 µg/L (Ahsanullah et al. 1981). In a review of zinc toxicity to marine organisms, NOEC values from 3-d to 21-d tests ranged from 10 µg/L to >10 000 µg/L, with no clear differences between taxonomic groups (JRC-IHCP 2010). Only one study was found on the chronic effects of zinc on marine fish species. This study tested low concentrations of zinc to larvae of Atlantic herring (*Clupea harengus*) and reported developmental effects (jaw/branchial abnormalities) at concentrations of ≥50 µg/L and morphological effects at concentrations of ≥100 µg/L (Somasundaram et al. 1984). These concentrations are within the range reported for effects on other taxonomic groups (JRC-IHCP 2010, Maycock et al. 2012, Markich et al. 2002, Langdon et al. 2009).

Limited data on chronic toxicity of zinc to corals indicates large differences in sensitivity. Reichelt-Brushett & Harrison (2005) reported an approximate 25% reduction in fertilisation of *Acropora tenuis* at nominal zinc concentrations of 10 µg/L, making it amongst the most sensitive species reported in the literature. In contrast, Heyward (1988) reported an approximate 35% reduction in fertilisation of *Platygyra ryukyuensis* at 500 µg/L, while Reichelt-Brushett & Harrison (1999) reported no effects on *Goniastrea aspera* fertilisation at 500 µg/L. However, none of these coral data were based on measured zinc concentrations. Given the limited data and apparently wide range of sensitivity, further research on the toxicity of zinc to corals is required.

Some of the most sensitive marine species to zinc appear to be diatoms and green algae. For example, based on data reported by Fisher and Frod (1980) for two diatom species found in Australian coastal waters, Maycock et al. (2012) calculated EC10s of 1.4–70 µg/L for *Skeletonema costatum* and 2–47 µg/L for *Asterionella japonica*. The anemone *Aiptasia pulchella* has also been reported to be highly sensitive to zinc exposure, with a 28-d EC10 of 9 µg/L for reproduction and development (Howe et al. 2014).



### 3 Factors affecting toxicity

The dissolved form of zinc, particularly the free cation  $Zn^{2+}$ , is the most toxic form of zinc (Hogstrand 2012). Approximately 55% of total zinc is present in the dissolved form in saline water (Stumm & Morgan 1996) and 45% is attached to suspended particles. Adsorption of zinc to suspended particles and consequent sedimentation of these particles is a major removal route for zinc in water (Stumm & Morgan 1996). However, under chemically reducing conditions (e.g. in anoxic sediments), zinc can desorb from particles and dissociate from iron and manganese inorganic complexes and organic complexes. Additionally, cations present at higher concentrations can exchange with zinc, which occurs in estuarine water with increasing salinity (Paalman et al. 1994, Stumm & Morgan 1996, Hatje et al. 2003). This can lead to higher zinc concentrations in the mid-salinity zone of tidal creeks and estuaries compared to low-salinity and high-salinity zones (Ellwood et al. 2008).

The zinc free cation ( $Zn^{2+}$ ) concentration is approximately 80% of the dissolved concentration at the typical salinity, temperature and pH of seawater (35 ppt, temperature 25°C and pH 8.1) (Millero et al. 2009). This proportion of  $Zn^{2+}$  increases with decreasing pH to approximately 95% at pH 7.4 as hydroxide and carbonate complexes become insignificant (Millero et al. 2009). Increases in salinity result in lower concentrations of  $Zn^{2+}$  due to complexation with chloride (Stumm & Morgan 1996). These changes in zinc speciation with differing pH and salinity affect the toxicity to aquatic organisms. Typically, LC50 values increase (i.e. toxicity decreases) as salinity increases (Bryant et al. 1985, USEPA 1987, Niyogi et al. 2016). For example, mortality rates of sand prawn (*Callinassa kraussi*) larvae and eggs decreased as salinity increased from 20 ppt to 24 ppt, 30 ppt and 35 ppt, at a range of total zinc concentrations from 25 µg/L to 500 µg/L (Jackson et al. 2005). However, this trend is not consistent between species, with the reverse observed for some blue-green algae (Wilson & Freeburg 1980) and an inconsistent pattern with salinity observed for rotifers (Saunders 2012).

The toxicity of zinc in marine water is also, but to a lesser extent, influenced by temperature, with increasing toxicity observed at increasing temperature (USEPA 1987, 1996). This was shown in acute studies using an amphipod (*Corophium volutator*) and a mollusc (*Macoma balthica*); however, the effect was minor as LT50 values generally decreased by a factor of <2 for an increase in temperature from 5°C to 15°C (Bryant et al. 1985).

Organic complexes (such as with humic acids) are less important in saline water, as much of the ligand is bound to calcium and magnesium (Stumm & Morgan 1996). However, a small protective effect of DOC has been reported for the rotifer (*Brachionus plicatilis*) in 48-h zinc exposures, with an LC50 value of approximately 6 000 µg/L at DOC of 5 mg/L or 10 mg/L, compared to approximately 4 500 µg/L at DOC of 1.4 mg/L (Saunders 2012).

### 4 Default guideline value derivation

The DGVs were derived in accordance with the method described in Warne et al. (2018) and using Burrliz 2.0 software.

## 4.1 Toxicity data used in derivation

### 4.1.1 Collation of toxicity data

Toxicity data were collated from downloads of the ECOTOX database (USEPA 2016), the ANZECC/ARMCANZ (2000) water quality guidelines and compilations of Australasian toxicity data (Markich et al. 2002, Langdon et al. 2009). These were supplemented by searches using the journal abstracting service Web of Science for studies published during 2015-2016 and not included in the ECOTOX database, and internet searches for Australian and New Zealand toxicity data contained within grey literature, theses or unpublished reports.

The toxicity dataset was restricted to studies conducted over a chronic period (following details in Warne et al. (2018)). Data were only included for studies that measured the zinc concentrations either in the test solutions or in the stock solutions used to produce those, and that provided a clear concentration–response relationship. Although some studies reported concentrations as total zinc, all zinc in the test solutions was assumed to be dissolved, as the forms of zinc used in toxicity tests are readily soluble salts (provided the concentration used is below the solubility limit in saline water) and, in typical toxicity test media, there are few particulate phases to which zinc would adsorb. Therefore, the DGVs are derived as dissolved zinc concentrations.

Data were restricted to tests with salinity 25–36 ppt based on the guidance provided by Warne et al. (2018), although studies where the salinity at times exceeded 36 ppt were included where the mid-point of the range was approximately 35 ppt. Antarctic species and any other testing conducted at <1°C were not included in the derivation. Because there is some suggestion that DOC may affect the toxicity of zinc (see Section 3), the data were restricted to studies with DOC <2 mg/L. If a study did not report DOC, it was assumed to have low DOC (which would be found in typical test water), and the study was included in the derivation.

The data restrictions resulted in chronic toxicity data for several Australasian species not being included in the current derivation (see Appendix C), predominantly due to lack of measurement of zinc in the test media or stock solutions. The measurement of zinc in test solutions is especially important because zinc is commonly found in many products and on surfaces in general, and can easily contaminate test solutions such that measured concentrations may be higher than nominal concentrations. Some of these data were included in the derivation of a predicted no effect concentration (PNEC) for zinc in the United Kingdom (Maycock et al. 2012), as the protocol for this allows the use of nominal concentration data (Maycock et al. 2012). The most sensitive of the Australasian species were: the coral, *A. tenuis*, with a LOEC of 10 µg/L based on fertilisation after 5.5 h (Reichelt-Brushett & Harrison 2005); the Australian endemic purple sea urchin, *Heliocidaris erythrogramma*, with a NOEC of 13 µg/L based on larval development over 6 days (King 1999); the Australian blacklip abalone, *Haliotis rubra*, with an EC10 of 20 µg/L based on embryonic development over 2 days (Gorski & Nuggeoda 2006); and the microalga, *Chaetoceros compressum*, with an EC19 of 20 µg/L based on population growth rate over 3 days (Fisher & Froud 1984). Based on the dissolved zinc SSD, all of these species are protected by the DGVs for ≥95% species protection, although further assessment of the effect of zinc on *A. tenuis* or related coral species would enable more definitive knowledge of the sensitivity of this species and whether the DGVs are sufficiently protective.

All toxicity data were quality assessed to ensure their suitability for inclusion (Warne et al. 2018), with the exception of data that had already been quality assessed for the ANZECC/ARMCANZ (2000) guidelines or in the Australasian Ecotoxicology Database (Markich et al. 2002, Langdon et al. 2009).

#### 4.1.2 Use of the toxicity data

There were sufficient 'no or low effect' data (i.e. four EC/IC/LC10 values, one EC20 value and seven NOEC values) for eight species from six taxonomic groups (see Appendix B) to enable the derivation of a DGV using the species sensitivity distribution (SSD) method. However, the fit of the SSD model to the data was judged to be poor (see Appendix D). Therefore, the 12 chronic EC10/EC20/NOEC values for eight species were supplemented with eight (acceptable quality) chronic EC/LC50 values (converted to negligible effect concentration equivalents) for eight Australian and New Zealand species.

The resulting 20 toxicity values (see Appendix B) were consolidated to 16 single species values (Table 1) for use in the SSD by either calculating geometric means or selecting the toxicity value for the most sensitive endpoint, life stage and toxicity test duration for each species based on Warne et al. (2018). Details of the [data quality assessment](#) and the [data that passed the quality assessment](#) are provided as supporting information.

The 16 species represented in the dataset (Table 1) were from seven taxonomic groups: green algae (two species), brown algae, diatoms (two species), cnidarians, annelids, molluscs (seven species) and crustaceans (two species). There were no data for fish in the dataset as the only suitable chronic data, for the Atlantic herring, *C. harengus*, did not include measurement of zinc in the test medium or stock solutions. Warne et al. (2018) do not require that fish must be one of the four or more taxonomic groups represented in a dataset to be able to derive guideline values using the SSD approach. There were also no data for corals in the dataset as none of the published coral toxicity data were based on measured zinc concentrations.

The relatively even spread of taxa groups across the SSD confirmed the absence of a bimodal or multimodal toxicity relationship. This is supported by the fact that there are various mechanisms of zinc toxicity to aquatic organisms, some of which are common to numerous taxa (see Section 2.1).

The ANZECC/ARMCANZ (2000) DGVs for zinc in marine water were based on 24 species, seven more than the current derivation. The decrease in species used for the current derivation is due to: the new classifications for chronic toxicity tests, which require longer test durations than in the 2000 derivation (e.g. adult fish tests now require  $\geq 21$ -d (Warne et al. 2018) compared to  $\geq 7$ -d (ANZECC/ARMCANZ 2000)); the preference for using EC10/NOEC data rather than data converted from EC50s; and the preference for using data published after 1980.

The toxicity values in the dataset range 200-fold from lowest to highest. The lowest value was a NOEC of 5  $\mu\text{g/L}$  for the doughboy scallop *Mimachlamys asperrima* based on a 48-h larval development test (Krassoi et al. 1997). The least sensitive species was the Sydney rock oyster *Saccostrea glomerata*, with an estimated NOEC of 2 080  $\mu\text{g/L}$  converted from a 14-day LC50 for larval mortality of 10 400  $\mu\text{g/L}$ . Although this LC50 concentration is above the solubility limit of 9 000  $\mu\text{g/L}$ , it is acceptable to use toxicity values up to twice the solubility limit (Warne et al. 2018).

The salinity in the acceptable toxicity tests mostly ranged from 26 ppt to 35 ppt, with two studies reporting ranges that exceeded 36 ppt (for giant kelp *Macrocystis pyrifera* at 32–39 ppt (Anderson & Hunt 1988) and for Australian ghost shrimp *Callinassa australiensis* at 34–37.5 ppt). Based on the mid-point of the salinity ranges being  $\leq 36$  ppt, the toxicity values from both tests were included in the derivation. The temperature in the acceptable toxicity tests ranged from 11.5°C to 27°C. Nine data were from tests conducted at 25°C or higher and could be considered tropical tests.

**Table 1 Summary of single chronic toxicity values, all species used to derive default guideline values for zinc in marine water**

Taxonomic group (phylum)	Species	Life stage	Duration (d)	Toxicity measure (test endpoint)	Reported toxicity value (µg/L)	Final toxicity value (µg/L)
Diatom (Ochrophyta)	<i>Entomoneis punctulata</i>	Log phase	2	EC50 (Population growth rate)	765	153 <sup>a</sup>
	<i>Ceratoneis closterium</i>	Log phase	3	IC10 (Population growth rate)	84	84
Green alga (Chlorophyta)	<i>Dunaliella tertiolecta</i>	NR	3	EC50 (Mortality)	270	54 <sup>a</sup>
	<i>Ulva fasciata</i>	Zoospores	4	NOEC (Growth/Germination)	143	143
Brown alga (Ochrophyta)	<i>Macrocystis pyrifera</i>	Zoospores	16	NOEC (Reproduction)	1 070	1 070
Annelid (Annelida)	<i>Hydroides elegans</i>	Larvae	4	EC50 (Development)	119	24 <sup>a</sup>
Anemone (Cnidaria)	<i>Aiptasia pulchella</i>	Adult	28	EC10 (Reproduction)	9	9
Crustacean (Arthropoda)	<i>Allorchestes compressa</i>	Juveniles	28	LC10 (Mortality)	62	62
	<i>Callinassa australiensis</i>	Adult	14	EC50 (Immobilisation)	1 150	230 <sup>a</sup>
Mollusc (Mollusca)	<i>Crassostrea gigas</i>	Embryos	2	EC50 (Development)	119	24 <sup>a</sup>
	<i>Haliotis diversicolor</i>	NR	28	NOEC (Growth)	64	64
	<i>Mimachlamys asperima</i>	Larvae	2	NOEC (Development)	5	5
	<i>Mytilus edulis</i>	Eggs/Larvae	2	EC50 (Development)	175	35 <sup>a</sup>
	<i>Mytilus galloprovincialis</i>	Embryos	2	EC50 (Development)	182 <sup>b</sup>	36 <sup>a</sup>
	<i>Mytilus trossulus</i>	Embryos	2	EC20 (Development)	64	64
	<i>Saccostrea glomerata</i>	Larvae	14	LC50 (Mortality)	10 400	2 080 <sup>a</sup>

NR = not reported.

**a** Values were chronic LC/EC50 values that were converted to chronic NOEC/EC10 values by dividing by 5 (Warne et al. 2018).

**b** Value represents a geometric mean of 27 EC50 values (see Appendix B for details).

## 4.2 Species sensitivity distribution

The cumulative frequency (species sensitivity) distribution (SSD) of the 16 marine zinc chronic toxicity data reported in Table 1 is shown in Figure 1. The SSD was plotted using the BurrIioz 2.0 software. The model provided a good fit to the data (Figure 1).

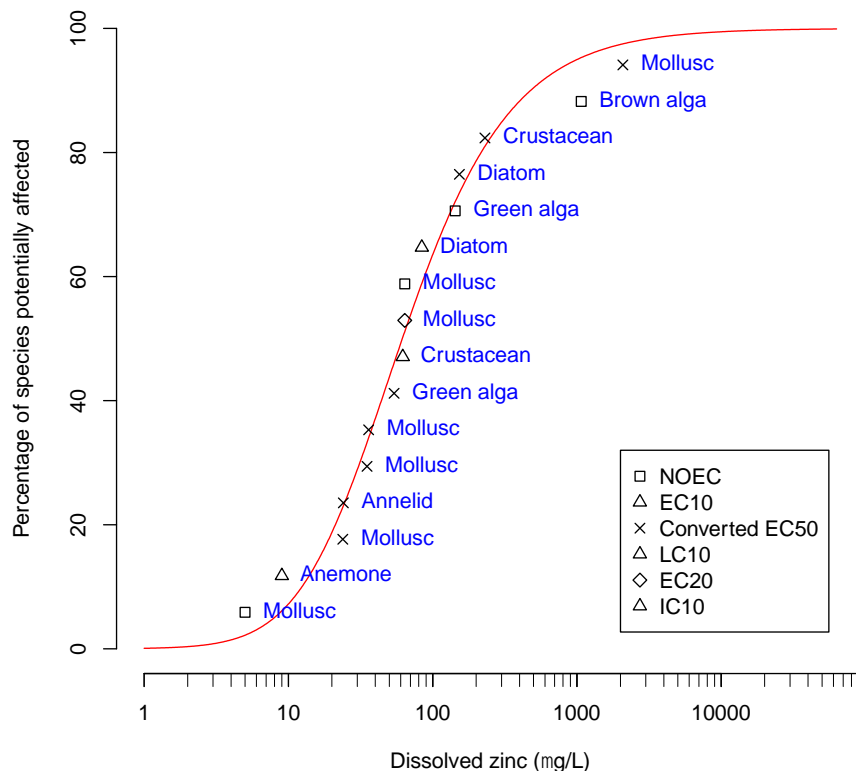


Figure 1 Species sensitivity distribution, zinc in marine water

## 4.3 Default guideline values

It is important that the DGVs (Table 2) and associated information in this technical brief are used in accordance with the detailed guidance provided in the Australian and New Zealand Guidelines for Fresh and Marine Water Quality [website](#) (ANZG 2018).

The DGVs for 99, 95, 90 and 80% species protection are shown in Table 2. The DGVs apply to dissolved zinc in marine water with salinity of 25–36‰ and pH of 6.5–8.0. For marine water outside this range, site-specific factors affecting toxicity should be considered, including modelling of metal speciation (see Appendix A).

The 95% species protection DGV is higher than or very close to the toxicity values for the two most sensitive species (see Table 1 and Figure 1), which is slightly more than would be expected for a dataset of 16 values (i.e. typically, this DGV might be expected to be higher than toxicity data for no more than one species). This suggests that the 95% species protection DGV may not be sufficiently protective of the specified percentage of species. For most slightly-to-moderately disturbed

ecosystems, the 95% species protection value is still likely to be applicable. However, if there are concerns that the DGV may not offer sufficient protection for key sensitive species (e.g. bivalve molluscs, cnidarians) in the water body of interest, an increased level of conservatism in the application of the DGVs may be warranted; for example, the 99% species protection DGV of 3.3 µg/L could be applied to a slightly-to-moderately disturbed ecosystem.

**Table 2 Toxicant default guideline values, zinc in marine water, very high reliability**

Level of species protection (%)	DGV for zinc in marine water (µg/L) <sup>a</sup>
99	3.3
95	8.0 <sup>b</sup>
90	12
80	21

**a** The DGVs apply to water with salinity 25–36 ppt and pH 6.5–8.0.

**b** DGV may not be sufficiently protective of the specified percentage of species (see text for details).

#### 4.4 Reliability classification

The zinc in marine water DGVs have a very high reliability classification (Warne et al. 2018) based on the outcomes for the following three criteria:

- Sample size—16 (preferred)
- Type of toxicity data—chronic EC10-20, NOEC and converted chronic EC50/LC50/LOEC
- SSD model fit—good (Inverse Weibull model).

However, it is important to recognise that eight of the 16 final toxicity values in the dataset were based on converted chronic EC/LC50s, which introduces an additional degree of uncertainty into the DGVs that is not reflected in the very high reliability classification. Despite this uncertainty, the current DGVs are considered a marked improvement on the ANZECC/ARMCANZ (2000) values.

# Glossary

Term	Definition
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.
ARMCANZ	Agricultural and Resource Management Council of Australia and New Zealand.
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 or an adverse effect on a sensitive early life stage.
default guideline value (DGV)	A guideline value recommended for generic application in the absence of a more specific guideline value (e.g. a site-specific guideline value) in the Australian and New Zealand Guidelines for Fresh and Marine Water Quality. Formerly known as 'trigger values'.
DOC	Dissolved organic carbon.
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.
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.
endpoint	The specific response of an organism that is measured in a toxicity test (e.g. mortality, growth, a particular biomarker).
guideline value	A measurable quantity (e.g. concentration) or condition of an indicator for a specific community value below which (or above which, in the case of stressors such as pH, dissolved oxygen and many biodiversity responses) there is considered to be a low risk of unacceptable effects occurring to that community value. Guideline values 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.)
IC50	The concentration of a substance in water or sediment that is estimated to produce a 50% inhibition of the response being measured in test organisms, relative to the control response, under specified conditions.
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.
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.
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.
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.
LT50 (median lethal time)	The time required for a specific concentration of a substance in water or sediment to be lethal to 50% of a group of test organisms, relative to the control response, under specified conditions.
maximum acceptable toxicant concentration (MATC)	The geometric mean of the lowest exposure concentration that causes a statistically significant adverse effect (LOEC) and the highest exposure concentration where no statistically significant effect is observed (NOEC).



Toxicant default guideline values for aquatic ecosystem protection: Zinc in marine water

<b>Term</b>	<b>Definition</b>
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.
PNEC	Predicted no effect concentration.
ppt	Parts per thousand (‰). A measure of salinity.
site-specific guideline value	A guideline value that is relevant to the specific location or conditions that are the focus of a given assessment or issue.
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 (chemical)	Most commonly used for metals, chemical species are different forms of a particular chemical that may include different oxidation states, isotopes, complexes with organic ligands (in the case of metals) or with particulate matter.
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.
toxicity	The inherent potential or capacity of a material to cause adverse effects in a living organism.
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.

## Appendix A: Recommended actions to assess bioavailable fraction of zinc

A decision tree for evaluating monitoring data against default guideline values (DGVs) or site-specific guideline values for zinc in marine water, which includes consideration of the bioavailable fraction, is shown in Figure A 1. The outcomes of the process shown here for water chemistry assessment should be used with other lines of evidence, for example, biodiversity assessment or direct toxicity assessment, in a weight of evidence approach to assessing overall water quality.

With respect to the modelling of bioavailable zinc, it would be necessary to consider simple ionic complexes; however, it is also known that there are colloidal forms and weak ionic complexes that can dissociate and cross biological membranes. Approaches such as the biotic ligand model might be a reasonable modelling option for some metals, but to date no such model is available for zinc in marine waters. Alternatively, speciation modelling is also an option, for example, the Windermere Humic Aqueous Model (WHAM7), which includes a solution speciation model as well as sub-models for ion binding to humic and fulvic acids, clay and oxides of iron, aluminium, manganese and silica (UK CEH 2021). The measurement of bioavailable zinc involves the use of 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 (see Batley et al. 2004). Currently, the use of Chelex columns and diffusive gradients in thin films (DGT) are the most widely used approaches.

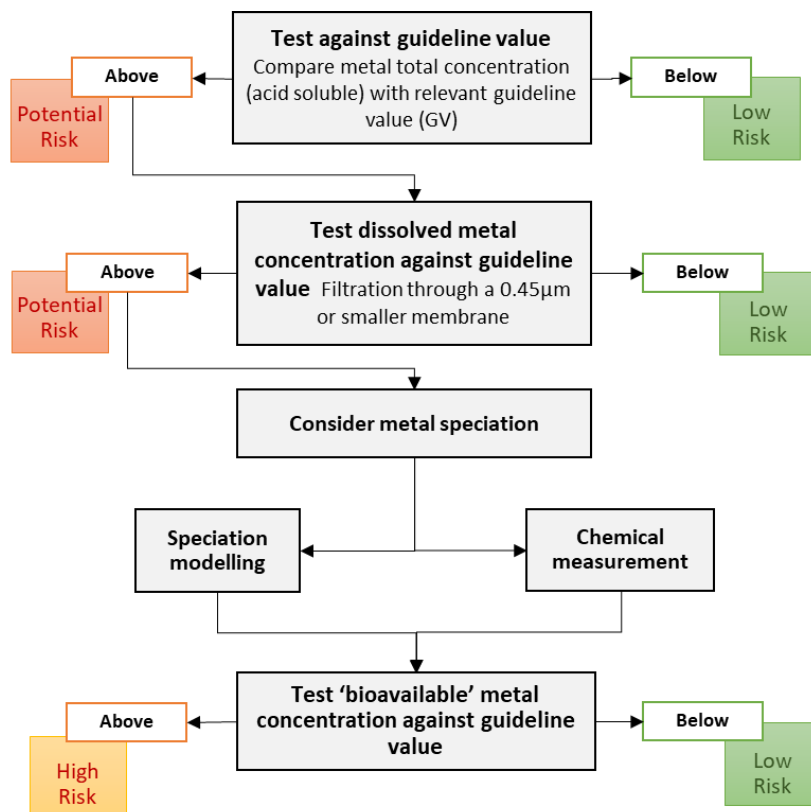


Figure A 1 Actions to assess bioavailable fraction of zinc in marine water

## Appendix B: Toxicity data that passed the screening and quality assessment and were used to derive the default guideline values

**Table B 1 Summary, chronic toxicity data that passed screening and quality assessment, zinc in marine water**

Taxonomic group (phylum/division)	Species	Life stage	Exposure duration (d)	Toxicity measure (test endpoint)	Salinity (ppt)	Temperature (°C)	Concentration (µg/L)	Reference
Diatom (Ochrophyta)	<i>Entomoneis punctulata</i>	Log phase growth	2	EC50 (Population)	34	21	765	Franklin et al. (2001)
–	–	–	–	–	–	–	<b>153<sup>b</sup></b>	<b>VALUE USED IN SSD</b>
Diatom (Ochrophyta)	<i>Ceratoneis closterium</i>	Exponential phase	3	IC10 (Population)	34	27	84	Johnson et al. (2007)
–	–	–	–	–	–	–	<b>84</b>	<b>VALUE USED IN SSD</b>
Green alga (Chlorophyta)	<i>Dunalliella tertiolecta</i>	NR	3	EC50 (Growth)	26	20	270	Hall and Golding (1998)
–	–	–	–	–	–	–	<b>54<sup>b</sup></b>	<b>VALUE USED IN SSD</b>
Green alga (Chlorophyta)	<i>Ulva fasciata</i>	Zoospores	4	NOEC (Growth)	NR	20	143	Hooten and Carr (1998)
		Zoospores	4	NOEC (Reproduction)	NR	20	143	Hooten and Carr (1998)
		Zoospores	4	NOEC (Population)	NR	20	143	Hooten and Carr (1998)
–	–	–	–	–	–	–	<b>143</b>	<b>VALUE USED IN SSD</b>

Toxicant default guideline values for aquatic ecosystem protection: Zinc in marine water

Taxonomic group (phylum/division)	Species	Life stage	Exposure duration (d)	Toxicity measure (test endpoint)	Salinity (ppt)	Temperature (°C)	Concentration (µg/L)	Reference
Brown alga (Ochrophyta)	<i>Macrocystis pyrifera</i>	Zoospores	2	NOEC (Reproduction)	34–36	11.5–17.0	2 683 <sup>c</sup>	Anderson and Hunt (1988)
		Zoospores	16	NOEC (Reproduction)	32–39	11.5–17.0	1 070	Anderson and Hunt (1988)
–	–	–	–	–	–	–	<b>1 070</b>	<b>VALUE USED IN SSD</b>
Annelid (Annelida)	<i>Hydroides elegans</i>	Larvae	4	EC50 (Development)	34	28	119	Gopalakrishnan et al. (2008)
–	–	–	–	–	–	–	<b>24 <sup>b</sup></b>	<b>VALUE USED IN SSD <sup>b</sup></b>
Anemone (Cnidaria)	<i>Aiptasia pulchella</i>	Adult	28	EC10 (Reproduction)	NR	25	17	Howe et al. (2014)
		Adult	28	EC10 (Reproduction & Development)	NR	25	9	Howe et al. (2014)
–	–	–	–	–	–	–	<b>9</b>	<b>VALUE USED IN SSD</b>
Crustacean (Arthropoda)	<i>Allorchestes compressa</i>	Juveniles	28	LC10 (Mortality)	31	19	61.5 <sup>d</sup>	Ahsanullah and Williams (1991), Maycock et. al (2012)
–	–	–	–	–	–	–	<b>62</b>	<b>VALUE USED IN SSD</b>
Crustacean (Arthropoda)	<i>Callinassa australiensis</i>	Adult	14	EC50 (Immobilisation)	34–38	18–20	1 150	Ahsanullah et al. (1981)
–	–	–	–	–	–	–	<b>230 <sup>b</sup></b>	<b>VALUE USED IN SSD</b>
Mollusc (Mollusca)	<i>Crassostrea gigas</i>	Eggs/Larvae	2	EC50 (Development)	34	20	119	Martin et al. (1981)
–	–	–	–	–	–	–	<b>24 <sup>b</sup></b>	<b>VALUE USED IN SSD</b>
Mollusc (Mollusca)	<i>Haliotis diversicolor</i>	NR	28	NOEC (Growth)	35	25	64	Tsai et al. (2004)
–	–	–	–	–	–	–	<b>64</b>	<b>VALUE USED IN SSD</b>

Toxicant default guideline values for aquatic ecosystem protection: Zinc in marine water

Taxonomic group (phylum/division)	Species	Life stage	Exposure duration (d)	Toxicity measure (test endpoint)	Salinity (ppt)	Temperature (°C)	Concentration (µg/L)	Reference
Mollusc (Mollusca)	<i>Mimachlamys asperrima</i>	Larvae	2	NOEC (Development)	33	18	5	Krassoï et al. (1997)
–							<b>5</b>	<b>VALUE USED IN SSD</b>
Mollusc (Mollusca)	<i>Mytilus edulis</i>	Eggs/Larvae	2	EC50 (Development)	34	17	175	Martin et al. (1981)
–							<b>35<sup>b</sup></b>	<b>VALUE USED IN SSD</b>
Mollusc (Mollusca)	<i>Mytilus galloprovincialis</i>	Embryo	2	EC50 (Development)	34	20	182 <sup>e</sup>	Williams and Hall (1999)
–							<b>36<sup>b</sup></b>	<b>VALUE USED IN SSD</b>
Mollusc (Mollusca)	<i>Mytilus trossulus</i>	Embryo	2	EC20 (Development)	NR	20	64	Nadella et al. (2009)
–							<b>64</b>	<b>VALUE USED IN SSD</b>
Mollusc (Mollusca)	<i>Saccostrea glomerata</i>	Larvae	14	LC50 (Mortality)	34	20	10 700	Butterfield (1987)
–							<b>2 080<sup>b</sup></b>	<b>VALUE USED IN SSD</b>

NR = not reported.

**a** Values were chronic LOEC values that were converted to chronic NOEC/EC10 values by dividing by 2.5 (Warne et al. 2018).

**b** Values were chronic LC/EC50 values that were converted to chronic NOEC/EC10 values by dividing by 5 (Warne et al. 2018).

**c** Value represents a geometric mean of three NOEC values (1 730, 2 030, 5 500 µg/L).

**d** The LC10 value was derived by Maycock et al. (2012) based on the data reported by Ahsanullah and Williams (1991) using Toxicity Relationship Analysis Program (TRAP) from the USEPA National Health and Environmental Effects Research Laboratory (NHEERL). See Maycock et al. (2012) for further details.

**e** Value represents a geometric mean of 27 EC50 values (140, 140, 140, 150, 150, 150, 150, 160, 160, 160, 160, 170, 190, 190, 190, 190, 200, 200, 210, 210, 210, 220, 220, 230, 230, 230, 240 µg/L).

## Appendix C: Chronic toxicity data, New Zealand and Australian species excluded from default guideline value derivation

**Table C 1 Chronic toxicity data excluded from default guideline value derivation, zinc in marine water**

Taxonomic group	Species	Life stage	Exposure duration (d)	Toxicity measure (test endpoint)	Salinity (ppt)	Temperature (°C)	Reported toxicity value (µg/L)	Final toxicity value (µg/L)	Reason for exclusion	Reference
Cnidarian (Coral)	<i>Acropora tenuis</i>	Gametes	0.229	LOEC (Fertilisation)	NR	NR	10	4 <sup>a</sup>	No measurement of zinc	Reichelt-Brushett and Harrison (2005)
Echinoderm	<i>Heliocidaris erythrogramma</i>	Larvae	6	NOEC (Development)	35.5	20	13	13	No measurement of zinc	King (1999)
Mollusc	<i>Haliotis rubra</i>	Embryo	2	EC10 (Development)	NR	20	20	20 <sup>b</sup>	No measurement of zinc	Gorski and Nugegoda (2006)
Diatom	<i>Chaetoceros compressum</i>	Exponential growth	3	EC19 (Population growth rate)	NR	17	20	20 <sup>b</sup>	No measurement of zinc	Fisher and Frood (1980)
Echinoderm	<i>Tripneustes gratilla</i>	Gametes	0.25	NOEC (Development)	31	28	25	25	No measurement of zinc	Edullantes and Galapate (2014)
Green alga	<i>Ulva intestinalis</i>	Germling	21	NEC (Mortality)	33	19.5	30	30	No measurement of zinc	Girling et al. (2015)
Echinoderm	<i>Centrostephanus rodgersii</i>	Sperm	0.055	NOEC (Fertilisation)	35.5	20	40	40	No measurement of zinc	King (1999)
Echinoderm	<i>Heliocidaris tuberculata</i>	Gametes	3	NOEC (Development)	34	18	55	55	No measurement of zinc	Doyle et al. (2003)

Toxicant default guideline values for aquatic ecosystem protection: Zinc in marine water

Taxonomic group	Species	Life stage	Exposure duration (d)	Toxicity measure (test endpoint)	Salinity (ppt)	Temperature (°C)	Reported toxicity value (µg/L)	Final toxicity value (µg/L)	Reason for exclusion	Reference
Diatom	<i>Skeletonema costatum</i>	Exponential growth	3	EC27 (Population growth rate)	NR	17	60	60 <sup>b</sup>	No measurement of zinc	Fisher and Frood (1980)
Echinoderm	<i>Centrostephanus rodgersii</i>	Larvae	2.8	NOEC (Development)	35.5	20	109	109	No measurement of zinc	King (1999)
Crustacean	<i>Macrophthalmus erato</i>	Zoocytes	4–11	NOEC (Development)	25	27	139	139	No measurement of zinc	Kannupandi et al. (2001)
Annelid	<i>Capitella capitata</i>	Adult	28	LC50 (Mortality)	NR	NR	1 250	250 <sup>c</sup>	No measurement of zinc, study pre-1980	Reish et al. (1976)
Annelid	<i>Ctenodrilus serratus</i>	NR	96	LC50 (Mortality)	32	20	1 750	350 <sup>c</sup>	No measurement of zinc, study pre-1980	Reish et al. (1977)
Annelid	<i>Capitella capitata</i>	NR	28	LC50 (Mortality)	32	10–20	2 400	480 <sup>c</sup>	No measurement of zinc, study pre-1980	Reish et al. (1977)
Crustacean	<i>Tenagomysis novaezealandiae</i>	Juvenile	7	NOEC (Growth)	34	20	1 000	1 000	No measurement of zinc	Nipper and Williams (1997)
Brown alga	<i>Hormosira banksia</i>	Gamete	3	EC50 (Growth)	35	18	19 000	3 800 <sup>c</sup>	No measurement of zinc	Myers et al. (2006)
Brown alga	<i>Eklonia radiata</i>	Gamete	2	NOEC (Reproduction)	34	20	6 350	6 350	No measurement of zinc	Bidwell et al. (1998)

NR = not reported.

**a** Value converted to a negligible effect (NOEC/EC10) concentration by dividing the reported LOEC by the default conversion factor of 2.5 (Warne et al. 2018).

**b** The data have been included in the derivation of a zinc PNEC for the United Kingdom (Maycock et al. 2012) as the protocol allows data with nominal concentrations to be used in PNEC derivation.

**c** Value converted to a negligible effect (NOEC/EC10) concentration by dividing the reported EC/LC50 by the default conversion factor of 5 (Warne et al. 2018)..

## Appendix D: Guideline value derivation based on preferred toxicity estimates only

Chronic toxicity data representing only ‘no or low effect’ data (based on Warne et al. 2018) are summarised in Table D 1. The species sensitivity distribution (SSD) based on these data is shown in Figure D 1. The fit of the Burr III model to the data was poor. Based on (i) the use of only these chronic data, (ii) the number of species (8 species), and (iii) the poor fit of the SSD, the resulting guideline values would have moderate reliability. Therefore, additional data were sought and included in the default guideline value (DGV) derivation, to result in a higher reliability set of DGVs (see Section 4).

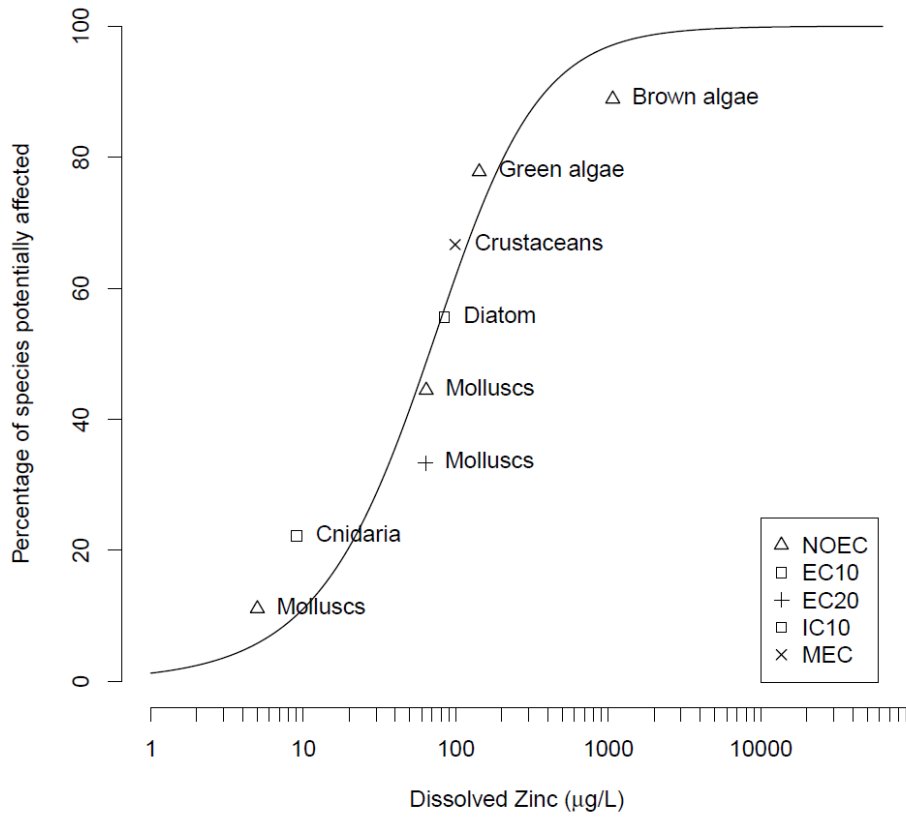
**Table D 1 Summary, preferred chronic toxicity data values, zinc in marine water**

Taxonomic group (phylum)	Species	Life stage	Exposure duration (d)	Toxicity measure (test endpoint)	Toxicity value (µg/L)
Diatom (Ochrophyta)	<i>Ceratoneis closterium</i>	Log phase	3	IC10 (Population)	84
Green alga (Chlorophyta)	<i>Ulva fasciata</i>	Zoospores	4	NOEC (Growth/Reproduction)	143
Brown alga (Ochrophyta)	<i>Macrocystis pyrifera</i>	Zoospores	16	NOEC (Reproduction)	1 070
Anemone (Cnidaria)	<i>Aiptasia pulchella</i>	Adult	28	EC10 (Reproduction)	9
Crustacean (Arthropoda)	<i>Allorchestes compressa</i>	Juveniles	28	MEC <sup>a</sup> (Mortality)	99
Mollusc (Mollusca)	<i>Haliotis diversicolor</i>	NR	28	NOEC (Growth)	64
	<i>Mimachlamys asperrima</i>	Larvae	2	NOEC (Development)	5
	<i>Mytilus trossulus</i>	Embryos	2	EC20 (Development)	64

NR = not reported.

<sup>a</sup> MEC: Minimum effect concentration. See Ahsanullah and Williams (1991) for details.





**Figure D 1 Species sensitivity distribution, preferred chronic toxicity estimates only, zinc in marine water**

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